SALT EFFECT ON THE ACTIVITY COEFFICIENT OF SOME POLAR NON-ELECTROLYTES

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CERTIFICATE

This is to certify that this thesis bound herewith is an authentic record of the research work carried out by the author under my supervision in partial fulfilment of the requirements of the Degree of Doctor of Philosophy of the Cochin University of Science & Technology and that no part thereof has been presented before for any other degree.

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Supervising Teacher

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INTRODUCTION

Addition of molecules and ions to a solvent gives rise to subtle changes in the solvent-solvent interactions. This also affects the solute-solute correlations. Therefore a better insight into the molecular interactions in solution can only be understood if we have a reliable model for the solvent structure. As the present study is confined to aqueous solutions, attention is drawn only to the structural aspects of water. Though no real conclusion about the structure of water has been made so far, recent developments[1-3] do, however, seem to portend real progress toward a comprehensive model of water structure. Such a model should account for all the properties of water, and of aqueous solutions of both ionic and nonionic solutes.

1. Structure of water

Water is unique among solvents in the sense that many of its properties are anomalous. For example, the maximum of density and certain associated properties, the unusually large heat capacity of water etc. are some of them. These properties of water are believed to be due to a fairly high degree of 'structuredness or icelikeness' in water. Attempts were then made to account for the gradual disappearance of this property as the temperature or pressure is increased. Different models have been proposed for water structure.

The models that have been proposed were classified in terms of the following fundamental question: 'what would happen to ice when it melts'. Chronologically speaking the first suggestion was made by Rontgen[4] from his X-ray studies. After hydrogen bond had been identified[5] in water some of the properties of water have been successfully explained but qualitatively. The concept of hydrogen bonding in water however, revealed that water has a great deal of structure. A very valuable compendium[6] on all aspects of water structure is now available.

Bernal and Fowler[7] proposed the 'uniformist' hypothesis. The approach is based on the consideration of what happens when ice suffers melting. They emphasized the tetrahedral nature of hydrogen bonding in water and considered that melting of ice is due to the bonding, and not breaking, of hydrogen bonds. Thus every molecule of water in the liquid state is viewed as being surrounded by neighbours in distorted positions and orientations, and the average degree of bond bending is the parameter which is sensitive to temperature and pressure. The significance of the term 'uniformist' is thus clear. However, some of the spectroscopic data[8] do not lend support to rationalize this model.

Frank and Wen[9] suggested a 'flickering-cluster' model for water structure. According to this model, hydrogen bond formation in liquid water is essentially a cooperative phenomenon. That is, when one bond forms many will tend to form and vice-versa. Thus there will be fully bonded, partially bonded and free water molecules in liquid water which are said to consist of a 'mixture' of several species. Since the density of free water molecules should be larger than those of hydrogen bonded species, the former is denoted by the symbol $(H_2O)_d$, and the latter $(H_2O)_b$. At any given temperature and pressure, there is an equilibrium between the two forms. A rise in temperature would shift the equilibrium in favour of $(H_2O)_d$, the free water molecule. The hydrogen bonded species are more stable under normal conditions of temperature and pressure. The fact that a large proportion of the water molecules are hydrogen bonded together in an open low density arrangement, '$(H_2O)_b$' has been confirmed by physico-chemical studies such as X-ray scattering[10], spectral studies[11-13], dielectric relaxation[14], measurement of self-diffusion coefficient[15], neutron scattering[16], and ultrasonic absorption.[17] The results of these studies were quite often controversial particularly spectroscopic studies. This model was modified[18] further, but still have not met with universal acceptance.

Whatever be the shortcomings of this model, it is very useful in some respects. For example, the large heat capacity of water can be attributed to the need to 'melt' part of $(H_2O)_b$. Another advantage lies in the fact that salts can be classified as structure-promoters or structure-breakers according to the effect of the salt on the 'structuredness' of water.

Another way by which the density could increase when ice melts was pointed out by Samoilov.[19] The capacity of the individual molecules that could be 'shaken loose' from their positions in the lattice and take up positions in the cavities which the lattice encloses is considered here. Samoilov's ideas are therefore viewed as the prototype of the 'interstitial' model.[20] The temperature and pressure sensitive parameter is taken as the fraction of the interstitial sites which are occupied. The model implies that no long-range order is present in liquid water. In this respect, this model draws a close parallelism with the 'continuous' model.[21] The model suffers some draw-backs such as (i) the structure of the interstitial guests is not specified and (ii) the difficulty in accommodating solute with a larger molar volume as a guest in the interstitial void. These criticisms have been partially overcome by Mikhailov[22] but not fully successful.

All of the above models and its modifications have been subjected to serious criticism of one kind or another. None can satisfactorily answer the question: 'what must water be like?' This is consistent with the fact that most of the models were introduced for special and limited purpose. For example the model suggested by Hall[23] shows how the anomalous acoustic absorption of water must be accounted.

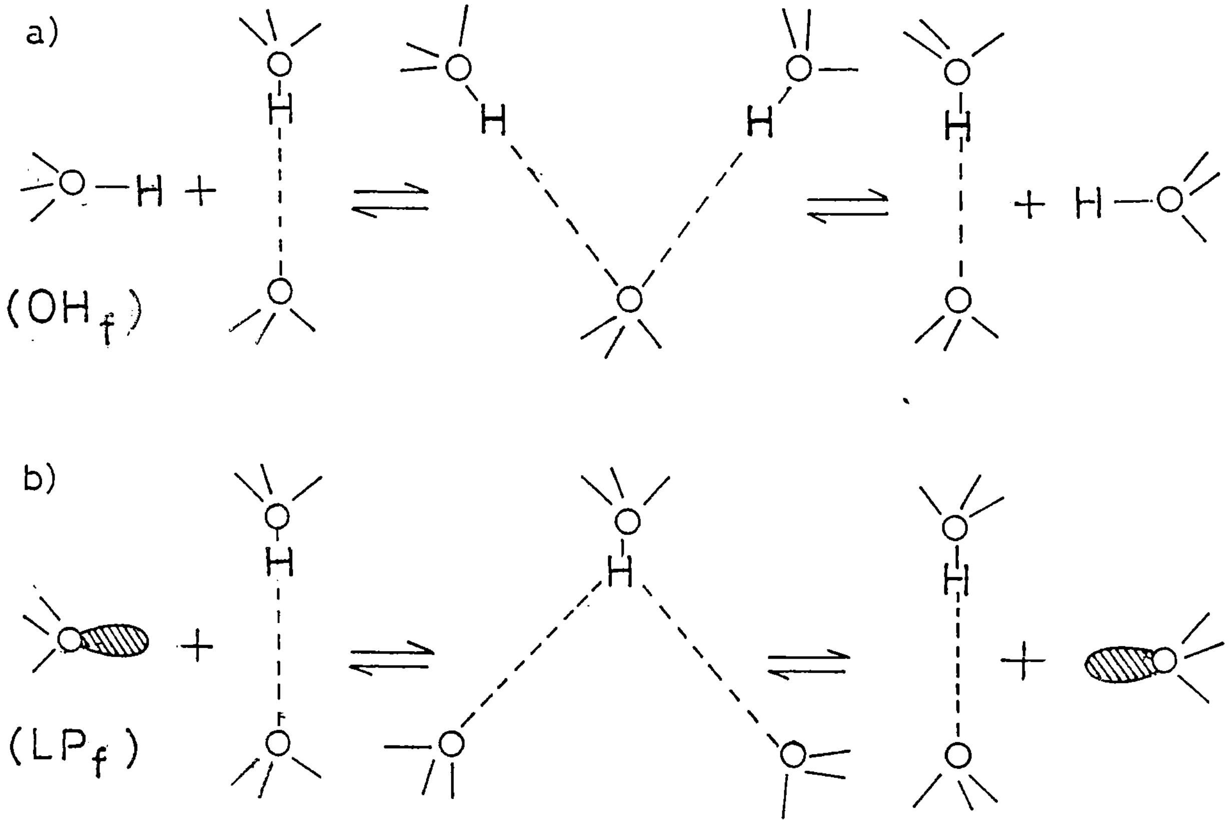

Fig.1 Exchange processes involving bifurcated hydrogen bonds when the three dimensional network of water molecules break.

In a recent review on water structure and reactivity, Symons[24] expressed the following concept on water structure. Water consists of a three dimensional network of hydrogen bonded molecules with near tetrahedral bonding. This network is assumed to consist of tetrahedral units fortuitously linked together, with four, five, six and seven ring systems that are distinguishable. In view of the thermal motions of the molecules, hydrogen bonds are subject to constant strain. Thus they bend, stretch, and occasionally break. When they break, the 'ends' move away and become uncorrelated. Two possibilities are envisaged as shown in Fig. 1. In (a) two hydroxyl groups share one lone pair, and in (b) two lone pairs share a hydroxyl group. OH_f signifies not a monomeric water molecule but a non-bonded hydroxyl group, forming part of molecules still forming three hydrogen bonds. LP_f refers to non-bonded lone-pairs. It follows that in pure water, the number of OH_f should be equal to that of LP_f. This view has been supported by infrared overtone measurements at ambient temperatures.

2. Aqueous solution of electrolytes

It is generally agreed that a salt dissolves in water because the 'hydration energy' of the ions overcomes the electrostatic forces of ions in the crystal. Since the water molecules involved in the hydration process must be subject to the strong electrical field of the ion, it is quite rational to conclude that the dissolution process affect the structure of water. To understand the structural changes involved in aqueous electrolyte solutions when an electrolyte is introduced into water, the following essential features are to be considered: (i) The ion with its electrical field constitute an electrostricted layer of water molecules in the inner zone which we call the first co-ordination sphere. The inner sphere water molecules will have their positive ends pointing outwards from hydrated cations. Their hydrogen atoms will be somewhat more positive than in bulk water, and hence more strongly tending towards hydrogen bonding. For hydrated anions the situation should be the opposite one. (b) Beyond the first co-ordination sphere, the ion has still an orienting influence on the water molecules. The ion tends to orient the water molecules through ion-dipole interactions and further through ion-multipole interactions. (c) The bulk water then orient the water molecules in conformity with the tetrahedral geometry favourable for the three dimensional hydrogen-bonded network. If the ion contains non-polar parts, they may shield the region near the ion from disruption of its structure by the thermal motion of 'free' water molecules. Thus the tetrahedral structure in this region is enhanced.

These three effects compete with each other in the orientation of the water molecules beyond the first hydration shell. The factors which determine the strength of these effects include the charge of the ion, its size and shape, its being mono- or polyatomic and its possible content of nonpolar portions. The outcome of the above three competing effects will cause a certain region around the ion to consist of disoriented water molecules and is called a 'thawed' region.

For small multivalent ions, effect (ii) will predominate to cause a net structuring of water around the first hydration shell. This net structuring of water is typical for Mg^{2+} ion but less obvious for Na^+ ion. Destruction of the water structure takes place in Cs^+ ion or Br^- ion. Certain ions fit into the structure of water without affecting it one way or other; eg., NH_4^+.

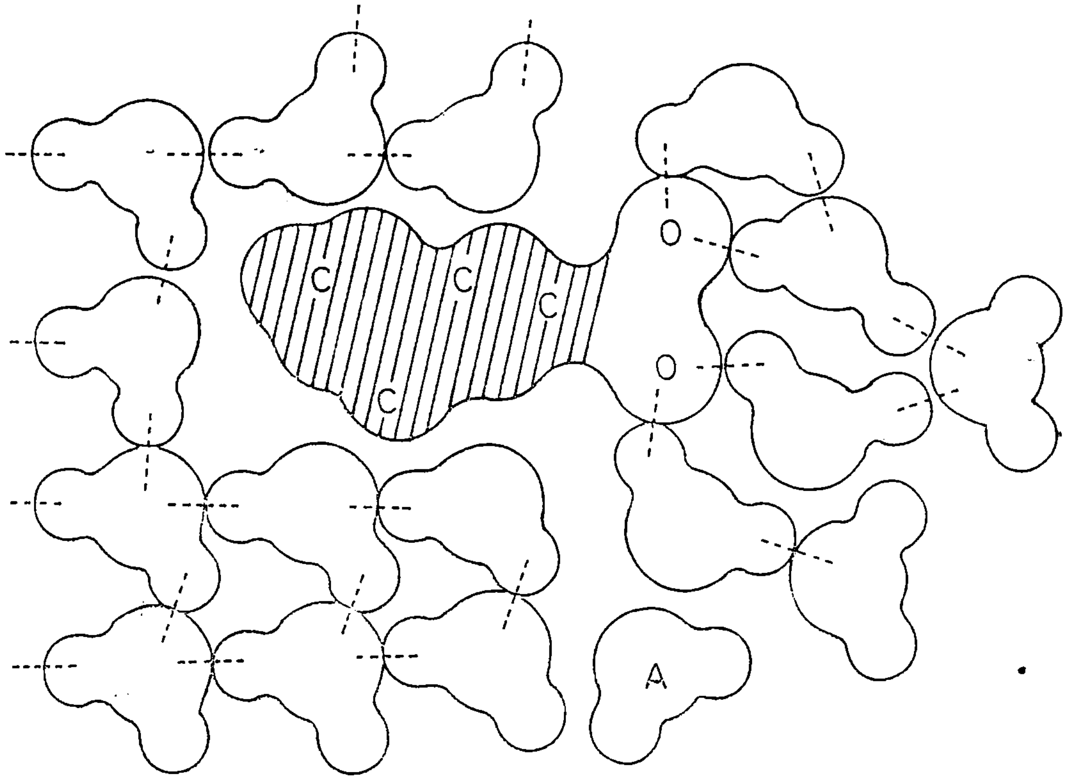

Fig:2 Butanoate ion showing different degrees of structuredness in water.

In tetraalkylammonium ions the structure-enhancing effect of the inert alkyl chains may gain the upper hand if they are long enough. Thus $(CH_3)_4N^+$ is considered as structure-breaker, $(C_2H_5)_4N^+$ as indifferent and $(C_nH_{2n+1})N_4^+$ with $n \geqslant 3$ as structure-maker. Carboxylate ions, nonsysmmetrical alkylammonium ions and similar ions have different regions around their different parts. Charge-dipole interactions and ion-water hydrogen bonds near the polar part form one kind of structure, the structure enhancing effect near the non-polar part forms a different kind. A non-structured regions results in between: eg., butanoate ion.

The water-structure affecting properties of the ions can be measured quantitatively by making use of various parameters such as entropy of hydration[25], change in the activation energy for water exchange[26] or on the basis of viscosity of water.[27] Thus negative entropy of hydration, positive free energy of activation for water exchange and ions which enhance the viscosity in dilute solutions are structure-makers. However these thermodynamic parameters reveal only the macroscopic aspects of hydration.

3. Aqueous solution of non-electrolytes

Generally the solubility of nonelectrolytes in water is very low. The presence of polar groups in the nonelectrolyte increases solubility. It is a widely accepted principle that the solubility depends on the relative magnitudes of solute-solute and solute-solvent interactions.[28] If the solute-solute interaction exceeds solute-solvent interactions the solubility is low and vice-versa. Since the present work is related only to polar solutes the discussion is limited to the behaviour of polar solutes in aqueous solutions.

4. Aqueous solution of polar nonelectrolytes

The study of polar molecules in aqueous solution is more complex because of the possibility of various types of interactions between the solute and water. It has been generally stated that the solubility is due to hydration interactions (through hydrogen bonding) between water and solute. The common functional groups which are capable of interacting with water by virtue of their proton donating or accepting properties are summarised in table 1.

Table 1

Proton donor and acceptor potentials of functional groups in organic molecules

Functional group	Exchangable protons	Proton acceptor sites
-O-	0	2
-OH	1	2
$>C=O$	0	2
$-NH_2$	2	2
$>NH$	1	1
$\geqslant N$	0	1
$-CONH_2$	2	1
-COOH	1	4

The behaviour of aqueous solution of a polar solute is determined by several features of the solute molecule.[30] They are: (i) the number of hydrogen bonding sites in relation to the size of the nonpolar residue, (ii) the degree of unsaturation or aromaticity of the hydrocarbon residue and (iii) the relative positions of polar groups. On this basis the polar solutes can be classified into two groups: (1) The solutions of monofunctional solutes and exhibiting large negative entropies, pronounced heat capacity and concentration dependence of all physical properties in the very dilute solution range. Furthermore, as the ratio of polar to nonpolar groups is increased the solution behaviour changes to a different pattern. The main factor determining the solution behaviour of monofunctional solutes is the size of the apolar alkyl group rather than the hydrogen-bonding groups.

In the second category of polyfunctional hydrophilic solutes, the specific interactions between polar groups and water molecules is more important. Here, the thermodynamic properties are highly sensitive to minor stereochemical differences in the solute molecules. Moreover, no evidence of 'solute clustering' has been found in such systems.

5. Activity coefficient of non-electrolytes in aqueous salt solutions

When a solute molecule or ion is transferred from one particular environment to another, there is a corresponding free energy change. The ideal free energy change for such a transfer is defined by -RTlnc, where c is the concentration of the solute in moles per litre. In real systems, however, there is deviation from ideal behaviour. For such cases the non-ideal free energy change is defined by the expression, RTlnf, where f is the activity coefficient. Thus the problem of explaining salt effects is essentially the problem of calculating ΔG, the non-ideal free energy change for transferring a solute molecule from pure water to the salt solution. Since at a given temperature, the chemical potential of a solute is the same in all saturated solutions we have

$$\Delta G = RT\ln f \tag{1}$$

aside from a factor involved in the conversion from practical to rational units.

The solubilities are directly related to activity coefficient measurements. Provided the appropriate standard state is chosen so that at equilibrium the activity in all phases is equal, then the solubility relationships can be expressed by

$$f_o s_o = fs \tag{2}$$

$$\frac{f}{f_o} = \frac{s_o}{s} \tag{3}$$

where s_o and s are the solubilities of a given species in two phases at equilibrium. For a sufficiently dilute solution, the activity coefficient f_o is assumed unity. In the case of nonelectrolyte solutes, it is a rational assumption in view of low solubility.

The addition of a salt to a solution of non-electrolyte in water may cause an increase or decrease in the solubility of the latter. The associated phenomenon is termed salting-in and salting-out respectively. For a given solute-electrolyte pair at constant temperature and pressure there exists an empirical relationship[31]

$$\log \frac{s_o}{s} = K_s C_s \tag{4}$$

where K_s is the Setschenow constant and C_s is the concentration of the salt in moles per dm^{-3} in the aqueous phase. But applying eqn.(3) into eqn.(4) results

$$\log f = \log \frac{s_o}{s} = K_s C_s \qquad (5)$$

where f is the activity coefficient of the solute in aqueous salt solution.

Setschenow equation has been tested many times[32] and has found wide applications for assessing the effects of different salts on the activity coefficient behaviour of nonelectrolyte systems. Different theories have been proposed to predict K_s, the salt-interaction parameters and to account for the observed salt effects on the solubility behaviour of nonelectrolytes in aqueous solutions.

6.a Hydration theory[33]

During the latter half of the ninenteenth century, a study of the solubility of carbon dioxide in water and in salt solutions led Setschenow to the conclusion that the gas was always less soluble in the presence of salts than in pure water. He put forward the hypothesis that 'salt solutions are compounds of the salt and water. On this basis we could regard the solution as if only the solvent, water, were the absorbing medium for the gas, while the salt combines with water and weakens its absorbing power'. Rothmund and others described the salting-out action of electrolytes is due to the preferential hydration of the salt decreasing the availability of the solvent for the solute. This extremely plausible view failed to explain the salting-in phenomenon. Moreover, the dependence of the hydration numbers of the ions on the nature of the salting pattern could not be accounted. Though it lacked theoretical support, it represented the first step to point out that local solvent structure would play a significant role.

6.b Electrostatic theories[34]

Debye and McAulay relate salt effect to the influence of the nonelectrolyte on the dielectric constant of water. Here the work necessary to desolvate the ions in a pure solvent of dielectric constant D_o and to recharge them in a solution of dielectric constant D containing the nonelectrolyte was calculated. They assumed that the nonideality was due to electrostatic interactions involving ionic charges. A close examination of the observed K_s values and those calculated by this theory reveals its inadequacy in absolutism. The failure of the theory has been attributed to (i) the assumption of solvent as a continuous dielectric medium and (ii) the non-inclusion of other possible interactions, especially when salting in occurs by large ions.

6.c Dispersion theory[35]

When a solute is added to a solvent, there are two types of forces operating. The first is a short-range electrostatic force and the second a non-electrostatic dispersion force. The net salt effect is the cumulative effect of these two forces. Bockris has shown that large ions of high polarizability interact more strongly with nonelectrolyte molecules than with the small water molecules and therefore salting-in is observed. However the low salting-out generally observed for lithium and hydrogen ions could not be accounted satisfactorily.

6.d Internal pressure theory[36]

Tamman and Gibson[37] pointed out that when an electrolyte is dissolved in water, the water behaves as if it were under an additional pressure. It decreases the volume of the solution owing to the compression of the water itself. This concept has been used by Long and McDevit to predict salt effects on the activity coefficient behaviour of nonelectrolytes.

The internal pressure theory predicts that salt effects can be explained in terms of the electrostriction of solvent by electrolytes. That is, the internal pressure of a salt solution is proportional to the extent of electrostriction, E, of the solvent, and is determined by

$$E = V_s - \bar{V}_s^o$$

Positive values of E cause salting-out and negative values produce salting-in. Thus the salting-out of a nonpolar solute may be regarded as simply 'the squeezing out' caused by electrostriction and increased average strength of the mutual interaction of the solvent molecules in the presence of salt.

Deno and Berkheimer[38] have correlated the solubility for a large number of solutes where dipolar and specific bonding interactions are minimal by the equation,

$$RT\ln f = V \Delta P_e \qquad (6)$$

where V is the molecular volume of the solute molecule in cc mole^{-1} and ΔP_e is the difference in internal pressures of the solvent systems. Equation (6) was derived on the basis that the observed free energy change when a solute molecule is transferred from one liquid phase to another was due to the difference in volume expansion energies of the solute in each solvent. The concept of volume expansion energies led Long and McDevit to derive the following expression for K_s,

$$K_s = \frac{\bar{V}_i^o(V_s - \bar{V}_s^o)}{2.3RT\,\beta_o} \qquad (7)$$

where $\bar{V}_i^o$ is the partial molal volume of the solute, V_s the intrinsic volume of the salt in solution, $\bar{V}_s^o$ the partial molal volume of the salt and β_o the compressibility of water.

Although $\bar{V}_s^o$ data are available for most salts, one of the difficulties in applying the internal pressure equation to salt effects has been the evaluation of V_s, the intrinsic volume of the salt in solution. However, Mukerjee[39] has shown that solvent electrostriction data for a large number of salts can be correlated with the compressibility data of Gibson.[40] In cases which involve large organic ions, such as the alkyl ammonium ions, Mukerjee's treatment is inapplicable. Using the parachor of these ions to evaluate V_s, however, provides reasonable data.

The McDevit-Long equation has been successful in predicting the correct trend in salt effect. However, with aluminium sulphate the observed K_s value was very much less than the predicted value for benzene. Due to the compact size and high charge, $Al_2(SO_4)_3$ should be expected to have a very high salting-out parameter. The deviation may be due to strong electrostatic interaction between Al^{3+} ion and benzene producing an abnormally high solubility. Moreover, the radius of the hydrated aluminium ion will be larger than the Al^{3+} ion itself resulting less electrostriction, and the value of K_s would be lowered. This effect and the possible intervention of the electrostatic contribution tend to lower the value of the calculated K_s, bringing closer agreement with the experimental value.

The internal pressure theory has been modified[41] further so as to apply it to polar nonelectrolyte solutes.

As was pointed out earlier, polar molecules interact directly with solvent, and hydrogen bonding interactions are specially important in aqueous systems. These energies have been found to be characteristic for various functional groups. The magnitude of this effect, however, depends upon the relative intensities of the solute-solvent interactions with respect to the internal pressure term. Equation (6) has been modified to account for such interaction leading to

$$RT\ln f = V \Delta P_e + \Delta F_H \qquad (8)$$

The ΔF_H term represents the change in specific bonding energy when a molecule is transferred from one solvent to another. Deno and others[42] has shown that ΔF_H has a characteristic value for different functional groups and is additive. The energies calculated by the above equation contain an additional entropy factor. So it seems reasonable that ΔF_H and ΔS terms are compensatory. As the hydrogen bond becomes stronger producing large enthalpies solvent orientation causes an increased entropy term also. This makes ΔF_H relatively invariant with the strength of the hydrogen bond produced.

Considering hydrogen-bonded solutes and differentiating eqn.(8) with respect to salt concentration, eqn.(9) results

$$RT\,\frac{d\ln f}{dC_s} = V\,\frac{d\,\Delta P_e}{dC_s} + \frac{d\,\Delta F_H}{dC_s} = K_s \qquad (9)$$

This equation predicts that the Setschenow parameter for hydrogen bonded solutes depends upon the rate of change of ΔF_H with salt concentration as well as the internal pressure change. If $\frac{d\,\Delta F_H}{dC_s}$ is very nearly zero, the values of K_s for polar solutes should be independent of the functional groups prone to hydrogen bonding.

For acidic and basic solutes, Long and Bergen[43] have shown that variation in ΔF_H with salt concentration is more pronounced. However, their studies also implied that the internal pressure factor is responsible for a large part of the activity coefficient changes.

6.e Scaled Particle theory[44]

The scaled particle theory of Reiss et al. and its recent modifications consisted of the following salient features. Firstly, no assumption about the structure of liquid water is made in this theory. Secondly, it figures the necessity of creating a cavity of proper size in the solvent to accommodate the solute species and the energy of such process is calculated. According to this theory, the third step is the transfer process, that is the transfer of the solute molecule into the solvent cavity created for it and is identified this factor as one of interaction with the solvent.

Using scaled particle theory, Pierotti[7] derived an expression for K_s. It consisted of three terms which are additive. They are K_α (the expression for the free energy for cavity formation); K_β (the expression for the free energy for the transfer of the solute to the cavity), and K_γ called the number density, a factor relating to the concentration of the species in the solution. Furthermore, the expression derived for K_α, K_β and K_γ are all in terms of parameters characteristic of the nonelectrolyte solute and the ions of the electrolytes and are easily available. The equation is

$$K_S = K_\alpha + K_\beta + K_\gamma$$

$$= 2.15 \times 10^{20} (\sigma_3^3 + \sigma_4^3) - 2.47 \times 10^{-4} \phi_0 +$$

$$\sigma_1 \left[6.45\times10^{20}\left(\sigma_3^2+\sigma_4^2\right) + 1.314\times10^{28}\left(\sigma_3^3+\sigma_4^3\right) - 4.23\times10^{4}\,\phi_0\right]$$

$$+\ \sigma_1^2 \left[6.45\times10^{20}\left(\sigma_3+\sigma_4\right) + 4.01\times10^{28}\left(\sigma_3^2+\sigma_4^2\right) + 1.32\times10^{36}\left(\sigma_3^3+\sigma_4^3\right) - 4.17\times10^{12}\,\phi_0\right]$$

$$-\ 1.85\times10^{14}\left(\frac{\epsilon_1}{K}\right)^{1/2}\left[\alpha_3^{3/4} Z_3^{1/4}\,\frac{\left(\sigma_1+\sigma_3\right)^3}{\sigma_3^3} + \alpha_4^{3/4} Z_4^{1/4}\,\frac{\left(\sigma_1+\sigma_4\right)^3}{\sigma_4^3}\right]$$

$$+\ 6.26\times10^{17}\,\phi_0\left(\frac{\epsilon_1}{K}\right)\left(\sigma_1+\sigma_2\right)^3 + 4.00\times10^{-2}\,\frac{\phi_0\,\alpha_1}{\left(\sigma_1+\sigma_2\right)^3}$$

$$+\ 0.016 - 4.34\times10^{-4}\,\phi_0 \quad ------ \quad (10)$$

where ϕ_0 = the apparent molal volume of the salt at infinite dilution; σ_3 and σ_4 are the diameters and α_3 and α_4 are the polarizabilities of the cation and anion respectively, σ_1 = the diameter, $\frac{\epsilon_1}{K}$ = the energy parameter, α_1 = the polarizability of the nonelectrolyte molecule; and σ_2 = σ_{H_2O} = 2.75A. Recently[45,46,47] expressions for evaluating the parameter needed to calculate K_s are also developed.

The sign of K_s depends on the relative magnitude of $K\alpha$, $K\beta$ and $K\gamma$. Unless ϕ_o is very large $K\gamma$ can be neglected. K_α is always positive. The free energy of cavity formation becomes more positive with the increase in electrolyte concentration. Thus cavity formation is more difficult in aqueous solution of alkali halides than in water itself. K_β is always negative. That is to say the transfer of the solute to the cavity is more easier in salt solution than in pure water. This is because the solute experiences a net attraction when water molecules in the surrounding cavity are replaced by alkali halide ions. Scaled particle theory predicts less salting-out as the sizes and polarizabilities of the cation and anion increase and for large nonelectrolytes with strong intermolecular forces.

Recently[48-51], scaled particle theory has been used to predict K_s for both polar and nonpolar solutes in aqueous salt solutions. It has been found that for nonpolar solutes the scaled particle theory leads to correct

K_s whereas for large solute molecules agreement with experiment is rather poor. The disagreement between, the observed and predicted values of K_s may be due to the uncertainties in evaluating the parameters, particularly the σ and ϵ/K. At this juncture, attention is recalled towards the high sensitivity of K_s to these parameters.

Though there are certain limitations, the scaled particle theory is much more satisfactory in principle because it allows for both solute-ion interaction and solvent-ion interaction. Furthermore, the idea that solubility of a nonelectrolyte in water depends on the energy required to create a cavity and the free energy of the transfer of the solute from the pure state to solvent is highly rational. The only difficulty in computing K_s using scaled particle theory lies in the evaluation of a number of molecular parameters.

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Chapter II

STATEMENT OF THE PROBLEM OF RESEARCH

1. Review of the work

Studies of salt effect on activity coefficient can provide considerable information of theoretical importance to the complex interactions of ions and neutral molecules and also to the unique nature of water as a solvent. The problem also has practical applications such as understanding the mechanism of reactions, in the separation of nonelectrolytes from water solutions by salting-out processes, in hydrometallurgy, in organic synthesis and in biological systems.

Investigations in this field led to the accumulation of a large body of data for a variety of solid, liquid, and gaseous nonelectrolytes. We have classified the available data on salt effects under the categories of nonpolar and polar nonelectrolytes.

a. Nonpolar nonelectrolytes

Salt effect studies on nonpolar nonelectrolytes were done extensively because these systems offer minimal complications arising from solute-solute and solute-solvent interactions. Furthermore, it gives a good reference point for the polar nonelectrolytes. It was assumed that the major role of a nonpolar solute is simply to occupy volume and thereby modify the ion-solvent interactions characteristic of a particular electrolyte.

The effect of different electrolytes on the activity coefficient for a number of nonpolar species such as hydrogen[1], oxygen[2], benzene[3], polynuclear aromatic hydrocarbons[4], alkyl benzenes[5] and nitrous oxide[6] were reported. Although the latter compound is not strictly nonpolar, this is included in this group since its structure and dipole moment indicate that its polarity is very low. It has been observed that in all cases the Setchenow empirical relationship was valid giving straight lines for the plot of log f versus c_s where f is the activity coefficient of the solute at the salt concentration c_s. It is also noted that the linearity of the plots actually holds upto high concentrations of the salt. Since the solubilities of these solutes are very small, it is rational to conclude that the self-interaction term is negligible.

The most striking features of the data for the nonpolar molecules are the considerably different effects of various salts on a given nonelectrolyte and the very similar salt order for the various nonelectrolytes. Thus the order of salting out for the various salts is essentially the same for such different species as hydrogen, nitrous oxide and benzene. The fact that specificities enter even with these nonpolar molecules and are so consistent, strongly suggests that they follow from the properties of the electrolyte solutions themselves rather than from specific interactions with the nonelectrolytes.

Salt effects on the solubilities of helium and argon have been given by Akerloff and others:[7] observed orders of the salting parameters differed significantly in detail from those for other nonpolar solutes. However, these measurements were all made with quite large concentrations of electrolyte and there is thus some uncertainty as to whether the calculated salt parameters are the same as the limiting values at low salt concentration. Furthermore, the result for the salting-out of argon by sodium chloride differs considerably from the value given by Eucken and Hertzberg.[8]

The data for a given nonpolar solute reveal that the concentrations of the ions to the values for the salts are generally additive within experimental accuracy. Thus the difference in K_s for chloride and bromide salts is virtually independent of the cation. Similarly, the difference for sodium and potassium salts is independent of the anion. The obvious conclusion is that the effect of a given salt is simply the sum of the effects of the constituent ions.

In general, the degree of salting in of nonpolar solutes increases with ionic size. There are however, several notable exceptions. One such is lithium ion, which invariably salts in much more than the larger sodium ion. Two other cations which give large salting-out effects in relation to their size are ammonium ion and hydrogen ion.

b. Polar nonelectrolytes

For polar nonelectrolytes one would expect the salt effect to consist of contributions from two factors:

i) a salting-out contribution roughly proportional to the volume of the nonelectrolyte and ii) an increased salting-in proportional to the dipole moment of the molecule and to the specific interaction such as hydrogen-bonding through the polar groups present in the solute.

To illustrate the influence of dipole moment on salt effect a comparison of the salt effects for carbon dioxide[6] and sulphur dioxide[9] are considered. These molecules are similar in size, the major difference being that the linear carbon dioxide has a dipole moment close to zero, whereas that for the bent sulphur dioxide, it is 1.7 D. It has been observed that while sulphur dioxide is salted-in, carbon dioxide is salted-out by the same electrolytes. Though the polarity of the molecule changed the overall magnitude of the salting-out it was made without greatly affecting the variations from one salt to another. In another work to show the effect of varying polarity Gross[10] studied salt effects on acetone and hydrogen cyanide and found that majority of the salts salted-out acetone whereas hydrogen cyanide is salted-in. An interesting example of extensive salting-in for a large, polar nonelectrolyte is provided with triammine trinitro cobalt (III).[11,12] In this case even sodium sulphate causes marked salting-in. Somewhat analogous results are shown by amino acids[13] in solutions which have particularly high dipole moments. It is difficult from the data[14] in Table 2 to establish a relation between the polarity of the nonelectrolyte and the salting-out effect of the given electrolyte. Although the percentage salting-out is greatest for substances which possess no dipolemoment it is also high with ethyl iodide (μ = 1.7 D) and low with chlorobenzene (1.56 D). The view that no clear parallelism can be observed to relate the observed salt effect with dipole moment is supported by the following observations: (a) Nitrobenzene and benzene, though differ greatly in their polar properties, have the same salting-out constant. (b) The effect of substituted ammonium chlorides on the solubilities of quinone and hydroquinone[15] in water showed that with hydroquinone the salts caused high salting-in and the salting-in parameter changes with change in size of the cation. In contrast, quinone is salted-out by all these salts, and the salting-out parameter is small and unchanged.

Neuberg[16] noted that many nonelectrolytes, mostly polar, are salted-in with large anions such as sodium benzoate and sodium p-toluene sulphonate. It has been found

Table 2

Dipole moment and salting-out parameters

Compound	Dipole moment	Salting-out parameter K_s
p-Nitroaniline	6.5	0.049
p-Nitrophenol	5	0.050
Nitrobenzene	4	0.166
Salicylic acid	2.6	0.126
Benzoic acid	1.7	0.144
Phenol	1.6	0.133
Aniline	1.5	0.130
p-Phenylenediamine	1.5	0.018
Benzene	0	0.166

that these salts are able to bring into solution substances of various classes which are insoluble in water which include hydrocarbons, alkaloids, ketones and aldehydes, proteins, fats etc. and called this phenomenon 'hydrotropism'. The studies further revealed that hydrotropic salts are specific in their action. Sulphonates bring proteins and alkaloids into solution, but not essential oils, higher alcohols or ketones.

Booth and Everson[17] studied the effect of sodium o-, m- and p- xylene sulphonates on the aqueous solubility of acetophenone, aniline, benzaldehyde, o-cresol, cyclohexanone and diethyl ether. They found that all the three salts increase the solubility of these substances to the same extent. Their work also led to the conclusion that hydrotropic salts which increase the solubility of polar solutes behave altogether differently towards some non-electrolytes. Thus the solubility of benzene, carbon tetrachloride, cotton seed oil and n-hexane is decreased in solutions of these salts, whereas that of benzoic acid, o-cresol, and cyclohexane is greatly increased.

A study of the salting-in effects of a homologus series of salts is given by Durand[18] who measured the solubility of benzene in solutions of the sodium salts of straight chain carboxylic acids from C_3 to C_{11}. The amount of salting-in increases regularly with increasing ionic size for these salts, a result which suggests that there may be a continuous transition from ordinary salt effects to the complex phenomenon of 'solubilization'. This aspect of solubilization is discussed in detail in a review by Kelvens.[19]

When the specific effects of salts on polar nonelectrolytes are considered more closely it is found that the variations in salt effect fall into two distinct groups: (i) Nonelectrolytes that have a definite basic character showing increased sensitivity to changes in the anion of the salt and (ii) those nonelectrolytes which include weak acids show relatively greater sensitivity for changes in the cation. Finally, there is an intermediate group where the salt order is similar to that for nonpolar nonelectrolytes.

c. Basic nonelectrolytes

The work[20] on the effect of salt on the activity coefficient of three typical basic nonelectrolytes, ammonia, trimethylamine and aniline led to the following conclusions:

(1) with the weaker base, aniline, the cation order is much closer to that for nonpolar solutes, (2) however aniline, like other basic nonelectrolytes also shows greater sensitivity to changes in the anion. (3) basic nonelectrolytes, relative to nonpolar solutes are more salted-in by lithium ion, but are more salted-out by sulphate and hydroxide ions. (4) Among basic nonelectrolytes of similar size, the stronger base shows much more sensitivity in cation order.

d. Acidic nonelectrolytes

More extensive data[21] are available on acidic nonelectrolytes. It has been found that the observed salt effects on undissociated phthalic, benzoic and succinic acids are quite similar but differ considerably from those for the basic solutes. For all of these acids the cation order for alkali metal ions parallels ion size. That is as the cation size increases, these acidic solutes showed a tendency to salt-in. Similar is the result with a variety of acidic nonelectrolytes ranging from aromatic to aliphatic acids.[22]

A further study on phthalic acid, benzoic acid and phenol with different acid strength but of similar size revealed that the observed K_s valsues for a given salt for benzoic acid and phenol are similar and phthalic acid showed less salting-out. Another contrasting observation is that for lithium chloride the K_s values increase considerably from phenol to benzoic acid to phthalic acid and the latter actually gives the highest K_s value. This occurs despite the fact that the latter possesses highest polarity expecting more salting-in.

e. Intermediate nonelectrolytes

Considerable data on the salt effect on the solubility of neutral polar nonelectrolytes have been accumulated.[23,24,25] For example the data on acetone (dipole moment 2.74), diacetone alcohol and γ-butyro lactone (dipole moment 4.2) show salt orders similar in nature but considerable difference in the salting-out parameter. The results show that the magnitude of the salting-out is by no means simply determined by the dipole moment; in fact, the number and nature of the polar substituents is much more significant.

Present work

Recent work[26] on nitrobenzoic acids revealed that these acidic solutes behave differently from other acidic nonelectrolytes in three respects. Firstly, all electrolytes salted-in nitrobenzoic acids in the entire range of concentration studied. Secondly, though the acids showed a tendency to salt-in as the size of the anion increases there are exceptions to this generalization. In fact, KF and K_2SO_4 showed more salting-in than other electrolytes and this behaviour could not be accounted in terms of 'normal salt effect'. Thirdly, in none of the cases, the Setschenow equation has been found valid. Parallel results were obtained from the studies on some of the acid terephthalic esters.[27]

The salient differences in the behaviour of these esters with those of the acid phthalic esters were rationalized on the assumption that in the phthalate esters, intramolecular hydrogen-bonding was effectively competitive with intermolecular hydrogen bonding between water molecules and with the carboxyl group and the ester group. In the acid terephthalate esters, intermolecular hydrogen bonding is the only possibility. Since the carboxyl group requires a lone pair of electron (LP_f in Symon's terminology), and the ester group (OH_f), any change in the availability of water molecules for hydrogen bonding will have a substantial effect on solubility.

The above observations led us to investigate the problem in detail by choosing a series of monosubstituted benzoic acids. For this purpose we studied methyl-, fluoro-, chloro-, bromo-, iodo-, hydroxy-, and aminobenzoic acids as the polar nonelectrolyte solutes. The activity coefficient of these solutes were determined in the presence of potassium fluoride, potassium chloride, potassium bromide, potassium iodide, potassium thiocyanate, potassium nitrate, potassium sulphate, magnesium sulphate, tetramethylammonium chloride and sodium formate from solubility measurements. Since the K_s (Setschenow parameter) offers a means to compare the salt effect on different systems, this parameter has been determined from a plot of log f versus c_s, the molar concentration of the electrolyte for those systems which obey the Setschenow equation.

It is a known fact that thermodynamics provides a powerful tool for the study of the interactions between solutes and water in aqueous solution. Recently$^{28-31}$ much attention has been paid in this direction. So the thermodynamic parameters of the transfer of the solute from water to salt solution were computed from the activity coefficient measurements at different temperatures of 20°C, 25°C, 35°C and 40°C. The details of the computation of these parameters were given in Chapter IV of the thesis.

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Chapter III

RESULTS AND DISCUSSION

Introduction

Earlier work[1,2,3] of salt effect on the activity coefficient of nonpolar solutes in aqueous solution can be summarized as follows:

(i) In the overwhelming majority of cases, salting-out phenomenon is observed.

(ii) As the size of the ion (cation or anion) increases, the salting-out is decreased with a tendency to cause salting-in.

(iii) The smaller an ion having a given charge, ie., where there is high charge localization on an ion, the greater is its salting-out action.

(iv) In all cases, the systems obey the Setschenow equation at all concentrations of the electrolytes studied. Here, we have to note two factors. One is that the solutes are nonpolar nonelectrolytes so that the solute-solvent interaction is either nil or a bare minimum. The second factor is that the solubility of all the nonpolar solutes in water is low which is a necessary condition for the Setschenow equation to be followed.

But, this is not the case when the effect of added electrolytes on the activity coefficient of polar solutes are considered. The presence of polar group on the solute enhances its hydrophilicity and hence the solubility also. When the solubility of the solute becomes appreciable the limiting Setschenow equation may break down as is observed in the case of nitrobenzoic acids.[4] However, there are other reasons also for the failure of the Setschenow equation in the above case.

Bharati Das and Ratna Ghosh[5,6] studied the salt effect on monosubstituted phenols in water using the electrolytes NaCl, Na_2SO_4, $NaClO_4$ and KSCN at different temperatures. They found that the Setschenow equation was obeyed in all salts and the Setschenow parameter decreases in the order $Na_2SO_4 > NaCl > NaClO_4 > KSCN$. They rationalized these observations on the basis of the relative influence of the ion on water structure. An examination of the value of K_s reported[7,8,9] for different salts on a number of polar solutes revealed the following points: (i) The salt effects on polar solutes are highly specific, (ii) The number and nature of polar groups on the solutes would also play a significant role in the K_s values. For example, while benzoic, phthalic and succinic acids are salted out by a number of electrolytes, nitrobenzoic acids were salted-in by the same electrolytes, and (iii) None of the theories could quantitatively correlate the observed K_s values for different salts as with nonpolar solutes.

As stated above the difference in behaviour of added salts on the activity coefficient of benzoic, phthalic and succinic acids on one hand and nitrobenzoic acids on the other hand have prompted us to investigate the problem in depth by selecting monosubstituted benzoic acids as the substrates. The problem then can be separated into two: (a) what parameters affect the activity coefficient of a solute by the addition of an electrolyte, (ii) in what way the determination of thermodynamic parameters of transfer of solute from water to salt solutions be helpful in understanding the observed salt effect. Since there is no satisfactory theory to account for the activity coefficient of aqueous solution of polar solutes as a function of the ionic strength of the solution, the first problem is more acute than the second. Furthermore, additional assumptions are required especially with acidic and basic nonelectrolytes. In the case of scaled particle theory (SPT), prediction of K_s depends on the precise choice of molecular parameters (σ) and pair-potential parameters ($\in$/K) for the solute in question. A slight variation for the above parameters cause wide discrepancy from the observed value of K_s. Thus the authors were left with no other alternative but to explain the observed salt effect qualitatively on the basis of localized hydrolysis model.[10]

a) Solubility studies

i) Choice of substrates:

When a comparison is made of the salt effects on the activity coefficient of benzoic acid[11] and phthalic acid[12] on one hand and nitrobenzoic acids [4] on the other hand, one is struck by the contrasting behaviour shown by these solutes. The reported Setschenow parameters for these three cases in respect of KCl, KBr and KI are given in Table 3.

Table 3

Setschenow parameters for the salt effect on the activity coefficient of benzoic, phthalic and nitrobenzoic acids for KCl, KBr and KI

Salt	Benzoic acid	o-phthalic acid	o-nitrobenzoic acid
KCl	+0.144	+0.093	-0.06
KBr	+0.109	+0.073	-0.06
KI	+0.049	+0.041	-0.26

Two observations can be made: (i) The K_s values for the acids decrease as the size of the anion increases; that is to say, a tendency towards salting-in. (ii) The values of K_s are all negative for o-nitrobenzoic acid, while it is positive for o-phthalic acid. In the case of m- and p-nitrobenzoic acids also, the values reported for K_s for these electrolytes are negative. We do not know in any detail what parameters cause this "specificity" of the salt effect. But we can accept this much: if one assumes that a salt can alter the "structuredness" of liquid water, then two types of specific salt effects can be recognized; one which depends on the action of the salt on water structure and the other, comprising of other factors about which our knowledge is far from complete. Thus, by assuming the validity of the localized hydrolysis model one can understand that the H-bonding interactions which occur through the proton of the carboxyl group of the acidic nonelectrolyte and water molecules are greatly affected by the orientation of the water molecules in the hydration sphere of the ion. Another point also needs attention in this connection: that is if there are two hydrogen bonding sites as in phthalic acids and nitrobenzoic acids, the hydrogen bonding capacity of the two sites are not independent and will affect the salting-phenomenon. This point will be discussed in detail later.

We have earlier stated that the determination of thermodynamic parameters of transfer of solute from water to salt solution was also done in this work. The idea behind this determination is this: The dissolution of hydrocarbon in water is thermodynamically unfavourable (ie ΔG is positive). This result is due to a dominant negative entropy term, enthalpy being negative.[13] An explanation which has secured widespread acceptance is based on the proposal by Frank and Evans[14] that the presence of the apolar solute molecule causes an increase in the order of the water surrounding the solute.[15] It should, however, be pointed out that alternative explanations are possible. For example, Frank and Franks[16], suggest that the propane molecule acts as a water structure-breaker and explain the dominant negative entropy term due to a fraction of the solute molecules going into an entirely different kind of dissolved state where the neighbouring solvent molecules cannot relax away from them. Whatever be the correct explanation, the fact remains that the process of dissolution of an apolar solute molecule in water is dominated by a negative entropy term.

The position in regard to polar nonelectrolytes which contain only one functional group, eg., the aliphatic alcohols, is surprisingly similar, in particular, the dominant term is still be the negative entropy of solution.[17] The apolar region of the alcohol molecule is apparently affecting the solvent water in a manner similar to an apolar solute. We got similar results with benzoic acids and methylbenzoic acids. So, if one increases the size and shape of the 'apolar' region in a systematic fashion, solubility data should provide some insight into the nature of the interaction of this region and the water molecules. Furthermore, the thermodynamic parameters are also helpful to corroborate the findings in the K_s values of different solutes for different salts.

ii) Data from solubility studies

It is already stated that when a solute molecule or ion is transferred from one particular environment to another, then that process is accompanied by a corresponding free energy change. For real systems where there is deviation from ideal behaviour the non-ideal free energy change is obtained from activity coefficient measurements. Thus the problem of explaining salt effect is essentially the problem of calculating ΔG, the non-ideal free energy change for transferring a solute molecule from pure water to the salt solution. Though several methods are available for this purpose, it seems that the solubility measurements are sufficient in the evaluation of ΔG. But there is one condition: the solute is sparingly soluble so that the solution is dilute. The solute used in the present study are sparingly soluble and the spectrophotometric determination of the concentration of the solutes in the presence and absence of electrolytes is of high precision. From the results of the solubility measurements in water in the absence and presence of various added electrolytes at different temperatures, one can compute the free energy of transfer, the enthalpy and entropy of transfer of the solute to the salt solution. However, in this connection one point deserves our attention. The enthalpy of solution must be obtained from solubility data over a temperature range and then applying the Vant't Hoff equation. Because of the thermodynamic relationship

$$\Delta G = \Delta H - T \Delta S$$

a relatively small error in ΔH will have a disproportionately large effect because of the temperature factor. Again, the validity of the Van't Hoff's equation rests on the assumption that the heat capacity of solution is constant over the temperature interval at which measurements of solubility are made. In many cases this assumption may be valid, but one can never be sure that this is the case always. There are also other limitations. The best method for the evaluation of the thermodynamic parameters is the calorimetric method. We could not make use of this method because of the non-availability of a calorimeter. Because of these limitations of the method, the values so obtained have been used only as an adjunct to the main arguments based on activity coefficients at a single temperature.

A. Effect of salts on the activity coefficient of the solutes in aqueous solutions

The activity coefficient measurements of solutes were done for an electrolyte at different concentrations (mol dm^{-3}) at 20°C, 25°C, 35°C and 40°C. For the purpose of comparison, the activity coefficient data for all of the solutes for a given electrolyte are assembled together. The observed K_s values for the three isomeric acids were grouped together in a table followed by the plots of log f versus c_s, the electrolyte concentration for the convenience of the discussion of the results.

Discussion

For the convenience of the discussion of the above results the salts showing almost similar effects on all the different solutes studied are grouped together and discussed the results separately. The discussion of results is therefore divided into four parts: (i) sodium formate and potassium fluoride, (ii) potassium chloride, potassium bromide, potassium iodide, potassium nitrate and potassium thiocyanate, (iii) tetramethylammonium chloride and (iv) potassium sulphate and magnesium sulphate.

At this point we think that before proceeding to consider the results, a brief discussion of the nature of the forces responsible for the dissolution process in water is necessary. In an aqueous electrolyte solution there are only three types of interaction; viz: water-water, water-ion and ion-ion. But in the aqueous electrolyte solution containing a nonelectrolyte solute, there are five main types of interactions which are solute-solute, solute-water, ion-solute, ion-ion and water-water interactions. Generally speaking, when the solute-water interaction exceeds that of solute-solute, the solute gets dissolved in water.

However, here we have to note that this process is influenced by ion-water interactions ultimately leading to the classification of ions as structure-makers and structure-breakers.[18,19], The above view is purely qualitative rather than quantitative but nonethless provides a better tool for understanding the problem.

The best rational approach from the theoretical point of consideration is the scaled particle theory. As outlined in Chapter I of the thesis, the SPT consists of two sequential steps for the dissolution process: (i) the creation of a cavity of suitable size to accommodate the solute in the solvent and (ii) the transfer of the solute to the cavity. An increase in the molar volume of the solute and of intermolecular forces of attraction in the solvent should increase the energy required for cavity formation. This can be illustrated by the known fact that the solubility of straight chain alkanes become small as the size of the alkyl group is increased. The second point is exemplified by the observation that alkanes are readily soluble in benzene, but not in water. The transfer of the solute molecule to the solvent will depend on the energies of interaction between the two. The forces which are generally considered, are the electrostatic interaction, dispersion forces, hydrophobic interaction and hydrogen bonding.[20] In so far as the solute is concerned, the first factor will be affected by its dipole moment and possibility on polarizability. The dispersion forces[21] operate only at very short intermolecular distances and further are nonsaturative. The hydrophobic effect becomes important when the normal type of solvation of a solute by water is energetically less favourable than when the solute molecules form aggregates in such a way that solute-water interaction is minimised.[22] The nature of hydrogen bonding is of very importance in our problem to merit discussion. Since quantification of the relative importance of these factors in determining solute-water interactions is not possible in the present state of our knowledge, we have to rely on our intuition to settle the question under consideration on the basis of the above factors.

i) Effect of potassium fluoride and sodium formate

Potassium fluoride and sodium formate salted-in all the nonelectrolyte solutes extensively. The Setschenow equation was not obeyed with these electrolytes over the entire range of concentration studied (Tables 4 and 5).

Table 4

Effect of sodium formate on the activity coefficient of mono-substituted benzoic acids in aqueous solutions at 35°C

1. 2-nitrobenzoic acid

Solubility of 2-nitrobenzoic acid in water at 35°C

(10^2 mol dm^{-3}) = 4.145

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.2980	—	Setschenow equation is not obeyed. This is due to the fact that the degree of salting-in at high concentrations of the electrolyte is less than would be required for fitting in the Setschenow equation
0.10	-0.4508		
0.15	-0.5572		
0.20	-0.6397		
0.25	-0.7065		
0.30	-0.7612		
0.35	-0.7910		

2. 3-nitrobenzoic acid

Solubility of 3-nitrobenzoic acid in water at 35°C

(10^2 mol dm^{-3}) = 2.708

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.3335	—	Setschenow equation is not obeyed
0.10	-0.4565		
0.15	-0.5407		
0.20	-0.6078		
0.25	-0.6520		
0.30	-0.6936		
0.35	-0.7146		

3. 4-nitrobenzoic acid

Solubility of 4-nitrobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.689

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.907		
0.10	-0.999		
0.15	-1.068	—	Setschenow equation is not obeyed.
0.20	-1.147		
0.25	-1.190		
0.30	-1.229		
0.35	-1.257		

4. 2-methylbenzoic acid

Solubility of 2-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 11.896

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.3088		
0.10	-0.3635		
0.15	-0.4158	—	Setschenow equation is not obeyed.
0.20	-0.4608		
0.25	-0.4890		
0.30	-0.5110		
0.35	-0.5388		

5. 3-methylbenzoic acid

Solubility of 3-methylbenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 11.341

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.2888		
0.10	-0.3427		
0.15	-0.3982	—	Setschenow equation is not obeyed.
0.20	-0.4369		
0.25	-0.4725		
0.30	-0.4980		
0.35	-0.5195		

6. 4-methylbenzoic acid

Solubility of 4-methylbenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 3.421

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.4417		
0.10	-0.5005		
0.15	-0.5751	—	Setschenow equation is not obeyed.
0.20	-0.5961		
0.25	-0.6354		
0.30	-0.6671		
0.35	-0.6932		

7. 2-fluorobenzoic acid

Solubility of 2-fluorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 7.368

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1530		
0.10	-0.2588		
0.15	-0.3419	—	Setschenow equation is not obeyed.
0.20	-0.3857		
0.25	-0.4190		
0.30	-0.4490		
0.35	-0.4622		

8. 3-fluorobenzoic acid

Solubility of 3-fluorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.401

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.2945		
0.10	-0.3635		
0.15	-0.4424	—	Setschenow equation is not obeyed.
0.20	-0.4830		
0.25	-0.5110		
0.30	-0.5440		
0.35	-0.5815		

9. 4-fluorobenzoic acid

Solubility of 4-fluorobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 7.292

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.4118		
0.10	-0.4649		
0.15	-0.5252	—	Setschenow equation is not obeyed.
0.20	-0.5773		
0.25	-0.6460		
0.30	-0.6994		
0.35	-0.8174		

10. 2-chlorobenzoic acid

Solubility of 2-chlorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 1.360

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.5378		
0.10	-0.7101		
0.15	-0.7516	—	Setschenow equation is not obeyed.
0.20	-0.8118		
0.25	-0.8581		
0.30	-0.8983		
0.35	-0.9324		

11. 3-chlorobenzoic acid

Solubility of 3-chlorobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 3.273

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.5909		
0.10	-0.7082		
0.15	-0.7790	—	Setschenow equation is not obeyed.
0.20	-0.8304		
0.25	-0.8710		
0.30	-0.9154		
0.35	-0.9516		

12. 4-chlorobenzoic acid

Solubility of 4-chlorobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 5.071

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.954		
0.10	-1.026		
0.15	-1.084	—	Setschenow equation is not obeyed.
0.20	-1.138		
0.25	-1.185		
0.30	-1.229		
0.35	-1.272		

13. 3-bromobenzoic acid

Solubility of 3-bromobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.757

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.756		
0.10	-0.863		
0.15	-0.943		Setschenow equation
0.20	-0.990	—	is not obeyed.
0.25	-1.024		
0.30	-1.053		
0.35	-1.081		

14. 4-bromobenzoic acid

Solubility of 4-bromobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 2.335

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-1.201		
0.10	-1.239		
0.15	-1.270		Setschenow equation
0.20	-1.313	—	is not obeyed.
0.25	-1.358		
0.30	-1.403		
0.35	-1.441		

15. 2-iodobenzoic acid

Solubility of 2-iodobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 2.446

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.797		
0.10	-0.891		
0.15	-1.015	—	Setschenow equation is not obeyed.
0.20	-1.110		
0.25	-1.195		
0.30	-1.256		
0.35	-1.292		

16. 3-iodobenzoic acid

Solubility of 3-iodobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 4.363

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.998		
0.10	-1.073		
0.15	-1.130	—	Setschenow equation is not obeyed.
0.20	-1.184		
0.25	-1.226		
0.30	-1.264		
0.35	-1.294		

17. 2-hydroxybenzoic acid

Solubility of 2-hydroxybenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.805

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.4819	—	Setschenow equation is not obeyed.
0.10	-0.6227		
0.15	-0.6901		
0.20	-0.7599		
0.25	-0.8155		
0.30	-0.8537		
0.35	-0.8961		

18. 4-hydroxybenzoic acid

Solubility of 4-hydroxybenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 7.181

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1048	—	Setschenow equation is not obeyed.
0.10	-0.1462		
0.15	-0.1805		
0.20	-0.2069		
0.25	-0.2175		
0.30	-0.2401		
0.35	-0.2596		

19. 2-aminobenzoic acid

Solubility of 2-aminobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 5.352

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0870		
0.10	-0.1145		
0.15	-0.1334	—	Setschenow equation is not obeyed.
0.20	-0.1645		
0.25	-0.1827		
0.30	-0.1936		
0.35	-0.2055		

20. 4-aminobenzoic acid

Solubility of 4-aminobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 5.498

HCOONa conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0625		
0.10	-0.0943		
0.15	-0.1190	—	Setschenow equation is not obeyed.
0.20	-0.1361		
0.25	-0.1500		
0.30	-0.1618		
0.35	-0.1714		

Table 5

Effect of potassium fluoride on the activity coefficient of monosubstituted benzoic acids in aqueous solutions at 35°C

1. 2-nitrobenzoic acid

Solubility of 2-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 4.145

KF conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.2247	—	Setschenow equation is not obeyed.
0.10	-0.3354		
0.15	-0.4258		
0.20	-0.5091		
0.25	-0.5706		
0.30	-0.6486		
0.35	-0.6909		

2. 3-nitrobenzoic acid

Solubility of 3-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.708

KF conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.3021	—	Setschenow equation is not obeyed.
0.10	-0.3726		
0.15	-0.4575		
0.20	-0.5144		
0.25	-0.5722		
0.30	-0.5766		
0.35	-0.5473		

3. 4-nitrobenzoic acid

Solubility of 4-nitrobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.689

KF conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.811	—	Setschenow equation is not obeyed.
0.10	-0.888		
0.15	-1.018		
0.20	-1.109		
0.25	-1.170		
0.30	-1.215		
0.35	-1.243		

4. 2-methylbenzoic acid

Solubility of 2-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 11.896

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.2666	—	Setschenow equation is not obeyed.
0.10	-0.3305		
0.15	-0.3902		
0.20	-0.4373		
0.25	-0.4794		
0.30	-0.5200		
0.35	-0.5578		

5. 3-methylbenzoic acid

Solubility of 3-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 11.341

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.2626	—	Setschenow equation is not obeyed.
0.10	-0.3368		
0.15	-0.3744		
0.20	-0.4273		
0.25	-0.4748		
0.30	-0.5133		
0.35	-0.5584		

6. 4-methylbenzoic acid

Solubility of 4-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 3.421

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.5021	—	Setschenow equation is not obeyed.
0.10	-0.5200		
0.15	-0.6051		
0.20	-0.6582		
0.25	-0.7187		
0.30	-0.7502		
0.35	-0.7809		

7. 2-fluorobenzoic acid

Solubility of 2-fluorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 7.368

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1197		
0.10	-0.1888		
0.15	-0.2519	—	Setschenow equation is not obeyed.
0.20	-0.2931		
0.25	-0.3335		
0.30	-0.3712		
0.35	-0.3944		

8. 3-fluorobenzoic acid

Solubility of 3-fluorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.401

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.2205		
0.10	-0.3089		
0.15	-0.4254	—	Setschenow equation is not obeyed.
0.20	-0.4901		
0.25	-0.5265		
0.30	-0.5577		
0.35	-0.5863		

9. 4-fluorobenzoic acid

Solubility of 4-fluorobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 7.292

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.3277		
0.10	-0.3882		
0.15	-0.4920	—	Setschenow equation is not obeyed.
0.20	-0.5679		
0.25	-0.6343		
0.30	-0.6812		
0.35	-0.7900		

10. 2-chlorobenzoic acid

Solubility of 2-chlorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 1.360

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.4189		
0.10	-0.5686		
0.15	-0.6503	—	Setschenow equation is not obeyed.
0.20	-0.7249		
0.25	-0.7848		
0.30	-0.8261		
0.35	-0.8768		

11. 3-chlorobenzoic acid

Solubility of 3-chlorobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 3.273

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.5506		
0.10	-0.6352		
0.15	-0.7447	—	Setschenow equation is not obeyed.
0.20	-0.8021		
0.25	-0.8707		
0.30	-0.9299		
0.35	-0.9754		

12. 4-chlorobenzoic acid

Solubility of 4-chlorobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 5.071

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.991		
0.10	-1.117		
0.15	-1.226		
0.20	-1.337	—	Setschenow equation is not obeyed.
0.25	-1.422		
0.30	-1.487		
0.35	-1.539		

13. 3-bromobenzoic acid

Solubility of 3-bromobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.757

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.696		
0.10	-0.801		
0.15	-0.924	—	Setschenow equation is not obeyed.
0.20	-0.980		
0.25	-1.006		
0.30	-1.051		
0.35	-1.082		

14. 4-bromobenzoic acid

Solubility of 4-bromobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 2.335

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-1.185		
0.10	-1.276		
0.15	-1.402	—	Setschenow equation is not obeyed.
0.20	-1.494		
0.25	-1.551		
0.30	-1.585		
0.35	-1.631		

15. 2-iodobenzoic acid

Solubility of 2-iodobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 2.446

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.764		
0.10	-0.857		
0.15	-0.977	—	Setschenow equation is not obeyed.
0.20	-1.080		
0.25	-1.129		
0.30	-1.163		
0.35	-1.184		

16. 3-iodobenzoic acid

Solubility of 3-iodobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 4.363

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.745		
0.10	-0.970		
0.15	-1.069	—	Setschenow equation is not obeyed.
0.20	-1.141		
0.25	-1.209		
0.30	-1.259		
0.35	-1.314		

17. 2-hydroxybenzoic acid

Solubility of 2-hydroxybenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.805

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.3444	—	Setschenow equation is not obeyed.
0.10	-0.4893		
0.15	-0.6131		
0.20	-0.6730		
0.25	-0.7242		
0.30	-0.7766		
0.35	-0.8394		

18. 4-hydroxybenzoic acid

Solubility of 4-hydroxybenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 7.181

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0807	—	Setschenow equation is not obeyed.
0.10	-0.1134		
0.15	-0.1527		
0.20	-0.1887		
0.25	-0.2101		
0.30	-0.2322		
0.35	-0.2504		

19. 2-aminobenzoic acid

Solubility of 2-aminobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 5.352

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0811		
0.10	-0.1129		
0.15	-0.1318	—	Setschenow equation is not obeyed.
0.20	-0.1588		
0.25	-0.1841		
0.30	-0.2171		
0.35	-0.2599		

20. 4-aminobenzoic acid

Solubility of 4-aminobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 5.498

KF conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0540		
0.10	-0.0824		
0.15	-0.1383	—	Setschenow equation is not obeyed.
0.20	-0.1610		
0.25	-0.1790		
0.30	-0.2036		
0.35	-0.2141		

The interpretation of these results assumes that potassium fluoride and sodium formate do not exhibit a "pure salt effect". Had this been the case, we would have expected the salt to show a greater salting-out. This is because both fluoride ion and formate ion are very powerful structure-makers.[23] The failure of Setschenow's empirical relationship has been accounted in the case of nitrobenzoic acids when the electrolyte is KF. It is suggested that the Setschenow equation can be applied at low concentrations of the solute. In KF solution, the solubilities of 2-, 3 and 4- nitrobenzoic acids are appreciably high enough to show considerable deviation in activity from concentration. It is also suggested that the two sites for hydrogen bonding cannot make independent contributions to the solubility because as the hydrogen bonding occurs at one site, the change in its electronegativity will be transmitted to the other site of hydrogen bonding. As the [salt] is increased there will be change in the capacity for hydrogen-bonding of these two sites and this would result in the failure of Setschenow equation.

The data on fluoro- and hydroxybenzoic acids can be explained on the same lines. Even if we argue that the above proposal holds good with HCOONa for nitro-, fluoro-, and hydroxybenzoic acids, then what would be the case with solutes such as methyl-, chloro-, bromo-, iodo-, and aminobenzoic acids with only one hydrogen bonding site, ie., the carboxyl group. We are of the view that the failure of the Setschenow equation could not be accounted for by this suggestion. On the other hand if we recognize the fluoride and formate ions with its highly localized charge acting as a base then some sort of acid-base interaction can be suggested as below:

$$\mathrm{R\text{-}\emptyset\text{-}COOH...F^{-}} \text{ and } \mathrm{R\text{-}\emptyset\text{-}COOH...\bar{O}OC\text{-}H}$$

(1) (2)

If the fact be so, the breakdown of the Setschenow equation with KF and HCOONa wosuld be due to the increased solubility of the solutes arising from the interaction of the electron cloud of the ion with the proton of the carboxyl group of the benzoic acids. When there are two hydrogen bonding sites as in nitro-, fluoro- and hydroxybenzoic acids the hydrogen bonding interaction of the other group would be affected by the carboxyl proton-anion interaction. For example, in 4-nitrobenzoic acids the anion-carboxyl proton interaction increases the electron density at the nitro group. This is a consequence of inductive and mesomeric effect also. The nitro group thus enhances the hydrogen bonding capacity through LP_f (using the terminology of Symons) of the water molecule.

Fluoride and formate ions are considered to be powerful structure-makers. The structure-making ability decreases in the order $HCO\bar{O} > \bar{F}$. In such a situation, the desolvation of the ion to make it bonded with the proton of the carboxyl group requires high energy. Since the transfer of the solute to salt solution is spontaneous, the process will be accompanied by a negative free energy. But free energy can be negative because of the different combinations of the enthalpy and the entropy since,

$$\Delta G = \Delta H - T \Delta S$$

The details of the thermodynamics of the transfer process will be discussed later.

ii) Effect of potassium chloride, potassium bromide, potassium iodide, potassium nitrate and potassium thiocyanate

With the above electrolytes, the findings are as follows: Excepting the nitro-, bromo- and iodobenzoic acids, the Setschenow equation was obeyed. For all nitrobenzoic acids, salting-in is observed and the K_s values are all negative. However, the region of validity varied with the salt and the solute. With all other acids the activity coefficient increases with the electrolyte concentration. Thus thé K_s values for these electrolytes are generally positive for methyl-, fluoro-, chloro-, hydroxy-, and amino-benzoic acids. Such diverse results spread over a number of solutes, if discussed as one entity, would not help us to make a conclusion regarding the effect of these salts. We therefore plan to discuss the effect of the above electrolytes on the solubility of three isomeric benzoic acids as one group.

When we consider the relative magnitudes of the salt effects in terms of the K_s values, we have to keep in mind the following reservations. Though in many cases, a positive value of the Setschenow parameter implies salting-out and a negative value, salting-in, this need not necessarily be the case always. Two possibilities can be distinguished. Consider a system having a positive value for the Setschenow parameter. This may arise because there is salting-out at all concentrations or because there is salting-in at low concentrations which changes to salting-out with increase in salt concentration. Thus the only requirement for a positive value for the parameter is that the activity coefficient of the substrate should increase with the increase in salt concentration. For majority of the cases studied, the second possibility is true.

Before the discussion of the results, we feel that it is better to have a glimpse on the results of the work done on similar solutes. It should be noted that with benzoic acid[24], phthalic acid[12], salicylic acid[7], succinic acid[25], and a number of aliphatic acids[26], the Setschenow equation is obeyed. All the above findings were rationalized on the basis of the localized hydrolysis model and on the classification of ions as structure promoters and structure breakers.

Firstly, consider the case of nitrobenzoic acids. All electrolytes salted-in all the three nitrobenzoic acids. The K_s values and the concentration range of each of the electrolyte upto which the Setschenow equation was valid were reported in Tables 6 to 10.

Table 6

Effect of potassium chloride on the activity coefficient of monosubstituted benzoic acids in aqueous solutions at 35°C

1. 2-nitrobenzoic acid

Solubility of 2-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 4.145

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01901	-0.12±0.003	Setschenow equation was obeyed from 0.05 mol dm^{-3} to 0.2 mol dm^{-3} of the electrolyte
0.10	-0.02600		
0.15	-0.03174		
0.20	-0.03735		
0.25	-0.04482		
0.30	-0.03863		
0.35	-0.03047		

2. 3-nitrobenzoic acid

Solubility of 3-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.708

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01637	-0.19±0.009	Setschenow equation was valid upto 0.2 mol dm^{-3} of the electrolyte
0.10	-0.02989		
0.15	-0.03732		
0.20	-0.04563		
0.25	-0.03835		
0.30	-0.02614		
0.35	-0.01155		

3. 4-nitrobenzoic acid

Solubility of 4-nitrobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.689

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01336		
0.10	-0.03029		Setschenow equation
0.15	-0.04560	-0.28±0.009	was valid upto
0.20	-0.06084		0.2 mol dm^{-3}
0.25	-0.07209		
0.30	-0.08200		
0.35	-0.06772		

4. 2-methylbenzoic acid

Solubility of 2-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 11.896

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.00658		
0.10	0.01061		
0.15	0.01891		Setschenow equation
0.20	0.03113	0.23±0.009	was obeyed upto
0.25	0.04484		0.35 mol dm^{-3} of
0.30	0.05895		the salt.
0.35	0.07078		

5. 3-methylbenzoic acid

Solubility of 3-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 11.341

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.02284		
0.10	0.03012		
0.15	0.03632		Setschenow equation was valid upto 0.35 mol dm^{-3} of KCl.
0.20	0.04135	0.16±0.004	
0.25	0.04771		
0.30	0.05287		
0.35	0.06347		

6. 4-methylbenzoic acid

Solubility of 4-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 3.421

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00303		
0.10	0.00114		Setschenow equation was valid upto 0.35 mol dm^{-3} of the electrolyte.
0.15	0.00820		
0.20	0.01815	0.21±0.009	
0.25	0.03009		
0.30	0.04518		
0.35	0.05819		

7. 2-fluorobenzoic acid

Solubility of 2-fluorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 7.368

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.01842		
0.10	0.02530		Setschenow equation
0.15	0.03369	0.16±0.004	was obeyed upto
0.20	0.03940		0.35 mol dm^{-3} of
0.25	0.04512		KCl.
0.30	0.04952		
0.35	0.05537		

8. 3-fluorobenzoic acid

Solubility of 3-fluorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.401

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.00272		
0.10	0.01378		Setschenow equation
0.15	0.02570		was obeyed upto
0.20	0.03306	0.18±0.004	0.35 mol dm^{-3} of
0.25	0.04054		the salt.
0.30	0.04856		
0.35	0.05693		

9. 4-fluorobenzoic acid

Solubility of 4-fluorobenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 7.292

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.00654		
0.10	0.01968		Setschenow equation
0.15	0.02602	0.28±0.008	was valid upto
0.20	0.03354		0.35 mol dm^{-3}
0.25	0.04383		
0.30	0.05436		
0.35	0.06787		

10. 2-chlorobenzoic acid

Solubility of 2-chlorobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 1.360

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00602		
0.10	0.00		Setschenow equation
0.15	0.01001	0.14±0.005	was valid upto
0.20	0.01893		0.35 mol dm^{-3}
0.25	0.02429		
0.30	0.02905		
0.35	0.03455		

11. 3-chlorobenzoic acid

Solubility of 3-chlorobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 3.273

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00775	0.13±0.002	Setschenow equation was valid upto 0.35 mol dm^{-3} of the electrolyte.
0.10	-0.00317		
0.15	0.00507		
0.20	0.01211		
0.25	0.01705		
0.30	0.02442		
0.35	0.03221		

12. 4-chlorobenzoic acid

Solubility of 4-chlorobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 5.071

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00873	-0.098±0.005	The Setschenow equation was valid upto 0.15 mol dm^{-3} of the salt. KCl in fact produces salting-out as the concentration is increased.
0.10	-0.01374		
0.15	-0.01861		
0.20	-0.01366		
0.25	-0.00747		
0.30	0.00647		
0.35	0.01552		

13. 3-bromobenzoic acid

Solubility of 3-bromobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.757

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.05123		
0.10	-0.05821	—	Setschenow equation is not obeyed.
0.15	-0.06486		
0.20	-0.06015		
0.25	-0.05517		
0.30	-0.04947		
0.35	-0.04213		

14. 4-bromobenzoic acid

Solubility of 4-bromobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 2.335

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.02965		
0.10	-0.04097		
0.15	-0.04468	—	Setschenow equation is not obeyed.
0.20	-0.04835		
0.25	-0.05200		
0.30	-0.05887		
0.35	-0.05381		

15. 2-iodobenzoic acid

Solubility of 2-iodobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 2.446

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01535	—	Setschenow equation is not obeyed.
0.10	-0.02131		
0.15	-0.02535		
0.20	-0.02968		
0.25	-0.03479		
0.30	-0.03984		
0.35	-0.04707		

16. 3-iodobenzoic acid

Solubility of 3-iodobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 4.363

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01764	—	Setschenow equation is not obeyed.
0.10	-0.02701		
0.15	-0.03006		
0.20	-0.02649		
0.25	-0.01443		
0.30	-0.00583		
0.35	0.00992		

17. 2-hydroxybenzoic acid

Solubility of 2-hydroxybenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.805

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00262	11±0.003	Setschenow equation was valid upto 0.35 mol dm^{-3} of the salt.
0.10	0.00108		
0.15	0.00513		
0.20	0.01034		
0.25	0.01689		
0.30	0.02240		
0.35	0.02913		

18. 4-hydroxybenzoic acid

Solubility of 4-hydroxybenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 7.181

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.00236	0.14±0.002	Setschenow equation obeyed upto 0.35 mol dm^{-3} of KCl.
0.10	0.00701		
0.15	0.01539		
0.20	0.02113		
0.25	0.02972		
0.30	0.03680		
0.35	0.04354		

19. 2-aminobenzoic acid

Solubility of 2-aminobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 5.352

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00291		Setschenow equation was valid upto 0.35 mol dm^{-3} of the electrolyte.
0.10	0.00		
0.15	0.00358	0.07±0.004	
0.20	0.00843		
0.25	0.02257		
0.30	0.03823		
0.35	0.05808		

20. 4-aminobenzoic acid

Solubility of 4-aminobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 5.498

KCl conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.00468		Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the salt.
0.10	0.01104		
0.15	0.01576	0.10±0.002	
0.20	0.01947		
0.25	0.02428		
0.30	0.03068		
0.35	0.03622		

Table 7

Effect of potassium bromide on the activity coefficient of monosubstituted benzoic acids in aqueous solutions at 35°C

1. 2-nitrobenzoic acid

Solubility of 2-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 4.145

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.03006	—	Setschenow equation is not obeyed.
0.10	-0.03771		
0.15	-0.04114		
0.20	-0.04482		
0.25	-0.04891		
0.30	-0.05133		
0.35	-0.05502		

2. 3-nitrobenzoic acid

Solubility of 3-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.708

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.02326	-0.26±0.009	Setschenow equation was valid upto 0.15 mol dm^{-3} of KBr.
0.10	-0.03746		
0.15	-0.04936		
0.20	-0.05776		
0.25	-0.04764		
0.30	-0.03748		
0.35	-0.02719		

3. 4-nitrobenzoic acid

Solubility of 4-nitrobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.689

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.02303		Setschenow equation
0.10	-0.03719		was obeyed upto
0.15	-0.05927	-0.36±0.009	0.2 mol of the
0.20	-0.07513		salt.
0.25	-0.08981		
0.30	-0.09293		
0.35	-0.09603		

4. 2-methylbenzoic acid

Solubility of 2-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 11.896

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00025		Setschenow equation
0.10	0.00799		was obeyed upto
0.15	0.01701	0.21±0.004	0.35 mol dm^{-3} of
0.20	0.02801		the electrolyte.
0.25	0.03997		
0.30	0.05239		
0.35	0.06084		

5. 3-methylbenzoic acid

Solubility of 3-methylbenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 11.341

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.01734	0.14±0.003	Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the salt.
0.10	0.02437		
0.15	0.03202		
0.20	0.03712		
0.25	0.04690		
0.30	0.05188		
0.35	0.06254		

6. 4-methylbenzoic acid

Solubility of 4-methylbenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 3.421

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.02443	0.19±0.008	Setschenow equation was valid upto 0.35 mol dm^{-3} of the salt.
0.10	-0.01620		
0.15	-0.00966		
0.20	0.00859		
0.25	0.01564		
0.30	0.02254		
0.35	0.02941		

7. 2-fluorobenzoic acid

Solubility of 2-fluorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 7.368

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.01068	0.14±0.009	Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the electrolyte.
0.10	0.02197		
0.15	0.03236		
0.20	0.03972		
0.25	0.04557		
0.30	0.04925		
0.35	0.05390		

8. 3-fluorobenzoic acid

Solubility of 3-fluorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.401

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00342	0.16±0.002	Setschenow equation was obeyed upto 0.35 mol dm^{-3} of KBr.
0.10	0.00564		
0.15	0.01584		
0.20	0.02360		
0.25	0.03209		
0.30	0.04074		
0.35	0.05242		

9. 4-fluorobenzoic acid

Solubility of 4-fluorobenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 7.292

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00626	0.23±0.004	Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the electrolyte.
0.10	0.00563		
0.15	0.02067		
0.20	0.03846		
0.25	0.05436		
0.30	0.06433		
0.35	0.07305		

10. 2-chlorobenzoic acid

Solubility of 2-chlorobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 1.360

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01568	0.14±0.009	Setschenow equation was valid upto 0.35 mol dm^{-3}.
0.10	-0.00947		
0.15	0.00384		
0.20	0.01362		
0.25	0.01793		
0.30	0.02127		
0.35	0.02633		

11. 3-chlorobenzoic acid

Solubility of 3-chlorobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 3.273

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.02413	-0.11±0.007	Setschenow equation was valid only upto 0.1 mol dm^{-3} of KBr. The salting in decreases with an increase in the salt concentration.
0.10	-0.03061		
0.15	-0.03516		
0.20	-0.03954		
0.25	-0.03357		
0.30	-0.02638		
0.35	-0.02136		

12. 4-chlorobenzoic acid

Solubility of 4-chlorobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 5.071

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0547	—	Setschenow equation is not obeyed.
0.10	-0.0739		
0.15	-0.0948		
0.20	-0.1130		
0.25	-0.1239		
0.30	-0.1328		
0.35	-0.1404		

13. 3-bromobenzoic acid

Solubility of 3-bromobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.757

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0878	—	Setschenow equation is not obeyed.
0.10	-0.0920		
0.15	-0.0964		
0.20	-0.1002		
0.25	-0.1039		
0.30	-0.1132		
0.35	-0.1209		

14. 4-bromobenzoic acid

Solubility of 4-bromobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 2.335

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1261	—	Setschenow equation is not obeyed.
0.10	-0.1611		
0.15	-0.1870		
0.20	-0.1966		
0.25	-0.2087		
0.30	-0.2191		
0.35			

15. 2-iodobenzoic acid

Solubility of 2-iodobenzoic acid in water at 35°C
$(10^3 \text{ mol dm}^{-3}) = 2.446$

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.02198	—	Setschenow equation is not obeyed.
0.10	-0.03397		
0.15	-0.03854		
0.20	-0.04499		
0.25	-0.05151		
0.30	-0.05746		
0.35	-0.06471		

16. 3-iodobenzoic acid

Solubility of 3-iodobenzoic acid in water at 35°C
$(10^4 \text{ mol dm}^{-3}) = 4.363$

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0429	—	Setschenow equation is not valid
0.10	-0.0563		
0.15	-0.0736		
0.20	-0.0871		
0.25	-0.1027		
0.30	-0.1168		
0.35	-0.1289		

17. 2-hydroxybenzoic acid

Solubility of 2-hydroxybenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.805

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01236	0.097±0.002	Setschenow equation was valid upto 0.35 mol dm^{-3} of the salt.
0.10	-0.00843		
0.15	-0.00354		
0.20	0.00279		
0.25	0.00670		
0.30	0.01209		
0.35	0.01593		

18. 4-hydroxybenzoic acid

Solubility of 4-hydroxybenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 7.181

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.00054	0.11±0.007	Setschenow equation was obeyed upto 0.35 mol dm^{-3} of KBr.
0.10	0.00401		
0.15	0.01196		
0.20	0.02151		
0.25	0.02649		
0.30	0.02920		
0.35	0.03193		

19. 2-aminobenzoic acid

Solubility of 2-aminobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 5.352

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00379	-0.11±0.006	Setschenow equation was obeyed upto 0.15 mol dm^{-3} of the electrolyte.
0.10	-0.00851		
0.15	-0.01476		
0.20	-0.00529		
0.25	0.00744		
0.30	0.01276		
0.35	0.01705		

20. 4-aminobenzoic acid

Solubility of 4-aminobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 5.498

KBr conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.00174	0.09±0.002	Setschenow equation was valid upto 0.35 mol dm^{-3} of the salt.
0.10	0.00500		
0.15	0.00997		
0.20	0.01454		
0.25	0.01955		
0.30	0.02412		
0.35	0.02814		

Table 8

Effect of potassium iodide on the activity coefficient of monosubstituted benzoic acids in aqueous solutions at 35°C

1. 2-nitrobenzoic acid

Solubility of 2-nitrobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 4.145

KI conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.03620	—	Setschenow equation is not obeyed.
0.10	-0.04001		
0.15	-0.04803		
0.20	-0.05985		
0.25	-0.06411		
0.30	-0.06932		
0.35	-0.08904		

2. 3-nitrobenzoic acid

Solubility of 3-nitrobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 2.708

KI conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.02975	—	Setschenow equation is not obeyed.
0.10	-0.04229		
0.15	-0.04965		
0.20	-0.05773		
0.25	-0.06731		
0.30	-0.07426		
0.35	-0.08441		

3. 4-nitrobenzoic acid

Solubility of 4-nitrobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.689

KI conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0295	—	Setschenow equation is not obeyed.
0.10	-0.0488		
0.15	-0.0737		
0.20	-0.0900		
0.25	-0.1028		
0.30	-0.1086		
0.35	-0.1251		

4. 2-methylbenzoic acid

Solubility of 2-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 11.896

KI conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01302	0.19±0.008	Setschenow equation was obeyed upto 0.35 mol dm^{-3} of KI.
0.10	-0.00641		
0.15	-0.00359		
0.20	0.00803		
0.25	0.01675		
0.30	0.03337		
0.35	0.04525		

5. 3-methylbenzoic acid

Solubility of 3-methylbenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 11.341

KI conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01888		Setschenow equation was valid upto 0.35 mol dm^{-3} of the salt.
0.10	-0.00995		
0.15	-0.00634	0.13±0.007	
0.20	-0.00198		
0.25	0.00469		
0.30	0.01528		
0.35	0.02527		

6. 2-fluorobenzoic acid

Solubility of 2-fluorobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 7.368

KI conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.00503		Setschenow equation was valid upto 0.35 mol dm^{-3} of KBr.
0.10	0.00953		
0.15	0.01673	0.12±0.003	
0.20	0.02199		
0.25	0.02840		
0.30	0.05560		
0.35	0.04271		

7. 3-fluorobenzoic acid

Solubility of 3-fluorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.401

KI conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01001	0.07±0.002	Setschenow equation was valid upto 0.35 mol dm^{-3} of the salt.
0.10	-0.00360		
0.15	-0.00090		
0.20	0.00217		
0.25	0.00656		
0.30	0.00858		
0.35	0.01285		

8. 4-fluorobenzoic acid

Solubility of 4-fluorobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 7.292

KI conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00626	0.19±0.006	Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the electrolyte.
0.10	0.00563		
0.15	0.02067		
0.20	0.03846		
0.25	0.05436		
0.30	0.06433		
0.35	0.07305		

9. 2-hydroxybenzoic acid

Solubility of 2-hydroxybenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 2.805

KI conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01693		Setschenow equation
0.10	-0.01131		was valid upto
0.15	-0.00584	0.08±0.003	0.35 mol dm^{-3} of
0.20	0.00584		the salt.
0.25	0.00576		
0.30	0.01066		
0.35	0.01528		

10. 2-aminobenzoic acid

Solubility of 2-aminobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 5.352

KI conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00923		Setschenow equation
0.10	-0.01303		was obeyed upto
0.15	-0.01609	-0.07±0.003	0.35 mol dm^{-3} of
0.20	-0.01177		the electrolyte.
0.25	0.00530		
0.30	0.01276		
0.35	0.01814		

11. 4-aminobenzoic acid

Solubility of 4-aminobenzoic acid in water at 35°C

(10^2 mol dm^{-3}) = 5.498

KI conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00397	0.06±0.004	Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the electrolyte.
0.10	-0.00102		
0.15	0.00		
0.20	0.00348		
0.25	0.00773		
0.30	0.01161		
0.35	0.01609		

Table 9

Effect of potassium thiocyanate on the activity coefficient of monosubstituted benzoic acids in aqueous solutions at 35°C

1. 2-nitrobenzoic acid

Solubility of 2-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 4.145

KSCN conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.03820	—	Setschenow equation is not obeyed.
0.10	-0.04711		
0.15	-0.05373		
0.20	-0.06035		
0.25	-0.06802		
0.30	-0.07504		
0.35	-0.08231		

2. 3-nitrobenzoic acid

Solubility of 3-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.708

KSCN conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.03643	—	Setschenow equation is not obeyed.
0.10	-0.04750		
0.15	-0.05562		
0.20	-0.06538		
0.25	-0.07480		
0.30	-0.08665		
0.35	-0.09652		

3. 4-nitrobenzoic acid

Solubility of 4-nitrobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.689

KSCN conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0357	—	Setschenow equation is not obeyed.
0.10	-0.0597		
0.15	-0.0864		
0.20	-0.0956		
0.25	-0.1106		
0.30	-0.1164		
0.35	-0.1348		

4. 2-fluorobenzoic acid

Solubility of 2-fluorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 7.368

KSCN conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.00189	0.11±0.005	Setschenow equation was obeyed upto 0.35 mol dm^{-3} of KSCN.
0.10	0.00483		
0.15	0.01233		
0.20	0.02027		
0.25	0.02718		
0.30	0.03134		
0.35	0.03702		

5. 3-fluorobenzoic acid

Solubility of 3-fluorobenzoic acid in water at 35°C

(10^2 mol dm^{-3}) = 2.401

KSCN conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01072	0.07±0.002	Setschenow equation was valid upto 0.35 mol dm^{-3} of the electrolyte.
0.10	-0.00575		
0.15	-0.00108		
0.20	0.00199		
0.25	0.00472		
0.30	0.00784		
0.35	0.01192		

Table 10

Effect of potassium nitrate on the activity coefficient of monosubstituted benzoic acids in aqueous solutions at 35°C

1. 2-nitrobenzoic acid

Solubility of 2-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 4.145

KNO_3 conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00920	—	Setschenow equation is not obeyed.
0.10	-0.02652		
0.15	-0.04731		
0.20	-0.05704		
0.25	-0.06133		
0.30	-0.06657		
0.35	-0.07161		

2. 3-nitrobenzoic acid

Solubility of 3-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.708

KNO_3 conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01960	-0.21±0.009	Setschenow equation was valid only upto 0.2 mol dm^{-3} of the electrolyte.
0.10	-0.03198		
0.15	-0.04302		
0.20	-0.05022		
0.25	-0.06095		
0.30	-0.07060		
0.35	-0.08083		

3. 4-nitrobenzoic acid

Solubility of 4-nitrobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.689

KNO_3 conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.02352	—	Setschenow equation is not obeyed.
0.10	-0.03931		
0.15	-0.05985		
0.20	-0.07858		
0.25	-0.08855		
0.30	-0.09911		
0.35	-0.11082		

4. 2-methylbenzoic acid

Solubility of 2-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 11.896

KNO_3 conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00838	0.17±0.009	Setschenow equation was valid upto 0.35 mol dm^{-3} of the electrolyte.
0.10	-0.00102		
0.15	0.00469		
0.20	0.00944		
0.25	0.02044		
0.30	0.03247		
0.35	0.04480		

5. 3-methylbenzoic acid

Solubility of 3-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 11.341

KNO_3 conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.04271		Setschenow equation
0.10	-0.03174		was obeyed upto
0.15	-0.02881	0.17±0.009	0.35 mol dm^{-3} of KNO_3.
0.20	-0.02507		
0.25	-0.01093		
0.30	0.00019		
0.35	0.00983		

6. 2-fluorobenzoic acid

Solubility of 2-fluorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 7.368

KNO_3 conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.01165		Setschenow equation
0.10	0.01842		was obeyed upto
0.15	0.02951		0.35 mol dm^{-3} of the
0.20	0.03650	0.15±0.004	electrolyte.
0.25	0.04368		
0.30	0.04952		
0.35	0.05537		

7. 3-fluorobenzoic acid

Solubility of 3-fluorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.401

KNO_3 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.008774		Setschenow equation
0.10	-0.004678		was obeyed upto
0.15	-0.001264		0.35 mol dm^{-3} of the
0.20	0.002176	0.07±0.0008	salt.
0.25	0.005644		
0.30	0.008586		
0.35	0.012852		

8. 4-fluorobenzoic acid

Solubility of 4-fluorobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 7.292

KNO_3 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	0.00654		Setschenow equation
0.10	0.01968		was valid upto
0.15	0.02602		0.35 mol dm^{-3} of the
0.20	0.03354	0.21±0.006	electrolyte.
0.25	0.04383		
0.30	0.05436		
0.35	0.06787		

9. 2-hydroxybenzoic acid

Solubility of 2-hydroxybenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 2.805

KNO_3 conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.02584		Setschenow equation
0.10	-0.02277		was valid upto
0.15	-0.02056		0.35 mol dm^{-3} of the
0.20	-0.01789	0.056±0.001	salt.
0.25	-0.01536		
0.30	-0.01161		
0.35	-0.008585		

10. 2-aminobenzoic acid

Solubility of 2-aminobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 5.352

KNO_3 conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.002931		Setschenow equation
0.10	0.01001		is not obeyed.
0.15	0.02807		
0.20	0.03602		
0.25	0.04516		
0.30	0.05219		
0.35	0.05688		

11. 4-aminobenzoic acid

Solubility of 4-aminobenzoic acid in water at 35°C

(10^2 mol dm^{-3}) = 5.498

KNO_3 conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00102		Setschenow equation
0.10	0.00		was obeyed upto con-
0.15	0.00253	0.07±0.003	tration of
0.20	0.00636		0.35 mol dm^{-3} KNO_3.
0.25	0.01055		
0.30	0.01478		
0.35	0.01938		

The values of the Setschenow parameters for all the three isomeric nitrobenzoic acids with all of the above electrolytes are closely similar. While solutes like benzoic acid, phthalic acid and succinic acid are salted out, the nitroacids are salted-in by the same electrolytes. The difference in behaviour can be accounted for on the basis of the difference in the hydrogen bonding abilities of the solutes. In nitrobenzoic acids there are two independent sites for hydrogen bonding with water molecules. The structure breaking action[27] of the ions of the salts would liberate water molecules which in turn would enter into hydrogen-bond interaction with the carboxyl and the nitro groups. According to the localized hydrolysis model the orientation of water molecules by the anions of the electrolytes would favour increased solubility by hydrogen-bonding with the carboxyl group. The structure-breaking action would decrease in the order $SCN^- > I^- > Br^- > NO_3^- > Cl^-$.[23] This would favour increased solubility in the same order. The relative values of the salting-in parameter support the argument.

Another point which deserves our attention is this: In 3-nitrobenzoic acid the mesomeric effect due to nitro group is absent. Therefore the nitro group and the carboxyl proton may make independent contributions to the hydrogen bonding. But this is not the case with 2-nitrobenzoic acid and 4-nitrobenzoic acid. Here the hydrogen bonding is what we call a 'co-operative' process and always depend on the electronegativity considerations of the two hydrogen bonding sites in the solutes.

In 2-nitrobenzoic acid, the main effect will be inductive rather than resonance effect. This is because of steric inhibition phenomenon. Due to this inductive effect, a comparison of the pk_a of the three nitro acids reveal that 2-nitrobenzoic acid is very much strong than the other two. This should enhance the capacity of the carboxyl groups to form hydrogen bonds. But the possibility of intramolecular hydrogen bonding in 2-nitrobenzoic acid definitely reduce the intermolecular hydrogen bonding with water molecules. The fact that the extent of salting-in of the 2-isomer is much less than that of the 4-isomer supports the above view.

The effect of added salts such as KCl, KBr, KI, KNO_3 on the activity coefficient of methyl-, amino- and hydroxybenzoic acids is now considered. This is because the behaviour of the above solutes were almost the same. For example, KCl, KBr, KI and KNO_3 salted-out these solutes. Furthermore, the Setschenow equation was obeyed in all cases over the entire concentration (0.05 - 0.35 mol dm^{-3}) of the electrolyte; (for K_s values see Tables 6 to 10). It was found that the value of the Setschenow parameter decreases as the ion size increases, but the variation is very nominal. With 4-methyl- and 4-hydroxybenzoic acids experiments could not be done in KI and KNO_3 because both of the electrolytes absorb strongly in the absorption region of these solutes. Though fluorobenzoic acids also showed similar results, the discussion on these solutes would be done together with other halobenzoic acids.

In methylbenzoic acids the presence of a larger apolar group than that of nitrobenzoic acids can lead to intermolecular hydrophobic interactions which in turn causes increased 'structuredness' of the surrounding water molecules. Though there are no satisfactory experimental methods available at present to understand the range and the magnitude of the hydrophobic interactions[28], the increased solute aggregation and the surrounding 'solvent' ordering were confirmed from the studies on hydrocarbons and aliphatic primary alcohols.[29] Whether this sort of hydrophobic association alone would be the reason for the salting-out of these solutes is debatable on the ground that the electrolyte tetramethylammonium chloride produced salting-in phenomenon with all solutes. Lack of theoretical and experimental methods to understand the nature of hydrophobic interaction prompted us to find alternative explanations for the observed salt effect on these solutes.

The pivotal idea in relating the observed variations in the effects of different salts is based on the electrostriction produced by the electrolyte on the water molecules. Here we assume that the role of the solute is simply to occupy volume and thus to modify the ion-water interactions in this simple fashion. When an electrolyte is added to an aqueous solution of nonelectrolyte, the increase in internal pressure resulting from ion-water interaction compresses the water molecules and 'squeeze the solutes out'. Thus, the effect of electrolytes on the activity coefficient of solutes is determined by the extent to which the water structure is compacted or loosened. This in turn depends on the relative size of ion and water molecule and the charge on the ion. Small ions of high charge will make the water structure more rigid and will increase the cohesive energy density. The entry of solute molecule into the solution is thus obstructed and produce salting-out by the ions of these electrolytes. On the other hand large ions having the same charge, will loosen the water structure, diminish its internal pressure, and thereby favour the passage of molecules of nonelectrolyte into the solution: ie., they will salt-in. Further, the water molecules with their electric dipoles are considered to be partially oriented with respect to the dipoles of the dissolved electrolyte and to be less free to induce dipoles in the molecules of the solute. Hence such water molecules will contribute less effectively to the carboxylic acid dissolution through hydrogen bonding. As the concentration of the electrolyte is increased, the number of water molecules that are 'tied-up', in the orientation zone increased and the solubility of the carboxylic acids is correspondingly decreased.

The effect of added KCl, KBr, KI, KSCN and KNO_3 would be thus, in short is decided by the charge:size ratio. This ratio is in the order $C\bar{l} > B\bar{r} > N\bar{O}_3 > \bar{I} > SC\bar{N}$. We expect therefore from the above sequence that salting-out parameter also should decrease in the same order as we move from chloride ion to thiocyanate ion and which is the observed phenomenon for methyl-, hydroxy- and aminobenzoic acids.

Alternatively, if we think to explain the effect of these salts on the basis of the classification of electrolytes as 'structure-breakers' and 'structure-promoters' then again we reach the same conclusion, that is to say as the structure-breaking action of the ions of the electrolytes increases in the order $SC\bar{N} > \bar{I} > B\bar{r} > N\bar{O}_3 > C\bar{l}$, the same salting-in pattern will also be observed as has happened in our case.

It is observed that generally the para isomer is more salted-out than the other two isomeric acids in a series. For example, the parahydroxy benzoic acid is salted-out more than the ortho isomer. It may be due to the solute aggregation through some sort of solute-solute interaction mechanism which may be more predominant in the para isomer. We are of the view that the solute-solute association through hydrophobic association while prevalent in the para methyl- and aminobenzoic acids such is not possible in the ortho compounds because of the steric inhibition in them. The high solubility of 4-hydroxybenzoic acid than 2-hydroxybenzoic acid in the absence of electrolytes indicates a strong intermolecular hydrogen bonding interaction with water molecules. Intermolecular hydrogen bonding is also possible between the solute species; the presence of which has been confirmed by infra-red spectral studies. When the electrolytes are added, ion-water interaction exceeds solute-water interaction. This makes the solute molecules to hydrogen bond intermolecularly among themselves increasing the molar volume and results salting-out in the presence of electrolytes. This type of aggregation of the solutes if exists, increases the molar volume of the solute and therefore makes it more difficult to be introduced in the 'hole' created in the solvent.

With halobenzoic acids, the effect due to the electrolytes KCl, KBr, KI, KSCN and KNO_3 are as follows: (i) All the three fluorobenzoic acids are salted-out by the above electrolytes, (ii) The Setschenow equation was valid in all cases and in the whole concentration range studied (0.05 mol dm^{-3} to 0.35 mol dm^{-3}), (iii) The trend in the observed K_s values, in general, showed less salting-out as the size of the anion increases. Thus, the size of the anion increases in the order $C\bar{l} < B\bar{r} < \bar{I} < SC\bar{N}$ showing the same order towards salting-in. (iv) With chloro-, bromo- and iodobenzoic acids, salt effect is studied only for KCl and KBr. Here bromo-, and iodobenzoic acids are salted-in and do not obey the Setschenow equation. Among chlorobenzoic acids except 2-chlorobenzoic acids the validity of the Setschenow equation is limited to low concentration of KCl and KBr. Here also tendency towards salting-in is observed with the increase in size of the anion and also with the increase in the molar volume of the solute.

In the case of fluoro- and chlorobenzoic acids the salting-out phenomenon by these electrolytes can be compared with the similar observation among hydroxybenzoic acids. We explained the salting-out of hydroxybenzoic acids by the electrostriction produced by the addition of the electrolyte into the aqueous solution of the solute forcing the latter to come out of the solution. The same explanation is valid here also.

As we have seen an alternative explanation for the salt effect is that they depend partly on the interaction of the ions with the structure of water. Here the K_s values are positive for 'order-producing' ions and negative for disorder-causing solutes. In this sense salting-in occurs when an ion causes a loosening-up of the water-structure and all the above electrolytes are classified as structure-breakers elsewhere. Therefore we are expecting salting-in by these ions contrary to our observation. We are of the view that a single theory of salt effects will not permit explanation of the different sorts of behaviour shown by the solutes. For example while we explained the salting-in of nitrobenzoic acids by $\overline{\mathrm{Cl}}$, $\overline{\mathrm{Br}}$, $\overline{\mathrm{I}}$, $\mathrm{SC\overline{N}}$ and $\mathrm{N\overline{O}_3}$ ion on the basis of structure making/breaking action of these ions, the same explanation could not be applied to fluoro- and chlorobenzoic acids.

With chlorobenzoic acids initial salting-in to salting-out is observed. With bromo- and iodobenzoic acid complete salting-in with tendency to salt-out at still higher concentrations. In essential, as we go from fluorobenzoic acids to iodobenzoic acids, a regular gradation in salting action can be observed: ie., salting-out for fluoro, initial salting-in to salting-out for chloro- and salting-in for bromo- and iodobenzoic acids. Here we suggest that this difference may be due to the difference in the nature of fluoro-, chloro-, bromo- and iodo groups. As the size of these groups increase from fluoro to iodo the polarizability also will increase in the same order affecting the acidity of the carboxyl proton. We admit that the polarity of these groups are also different so that the net result will be resultant of these two factors. Support to this argument comes from the observation that K_s decreases with the increasing polarity of solutes like benzaldehyde, nitrobenzene etc.[30] The acidity of carboxyl proton in iodobenzoic acids is much more than that in fluorobenzoic acids. In other words, we expect salting-in for bromo- and iodobenzoic acids similar to the case of nitrobenzoic acids.

iii) Effect of tetramethylammonium chloride

With tetyramethylammonium chloride, the results are the following: (i) All solutes are salted-in by tetramethylammonium chloride, (ii) The Setschenow equation was obeyed for all solutes except nitro-, bromo- and iodobenzoic acids. With 3-chloro- and 4-chlorobenzoic acid the region of validity of the above equation varied; with other solutes, Setschenow equation was obeyed in the entire range of the

Table 11

Effect of tetramethylammonium chloride on the activity coefficient of monosubstituted benzoic acids in aqueous solutions at 35°C

1. 2-nitrobenzoic acid

Solubility of 2-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 4.145

$(CH_3)_4NCl$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.04255	—	Setschenow equation is not obeyed.
0.10	-0.05434		
0.15	-0.06711		
0.20	-0.07670		
0.25	-0.08901		
0.30	-0.09952		
0.35	-0.11012		

2. 3-nitrobenzoic acid

Solubility of 3-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.708

$(CH_3)_4NCl$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.02824	—	Setschenow equation is not obeyed.
0.10	-0.04273		
0.15	-0.04608		
0.20	-0.05051		
0.25	-0.05675		
0.30	-0.06178		
0.35	-0.06909		

3. 4-nitrobenzoic acid

Solubility of 4-nitrobenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 1.689

$(CH_3)_4NCl$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.02010	—	Setschenow equation is not obeyed.
0.10	-0.03482		
0.15	-0.05340		
0.20	-0.06062		
0.25	-0.07035		
0.30	-0.07686		
0.35	-0.08687		

4. 2-methylbenzoic acid

Solubility of 2-methylbenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 11.896

$(CH_3)_4NCl$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00302	-0.14±0.007	Setschenow equation was valid upto 0.35 mol dm^{-3} of the salt.
0.10	-0.01042		
0.15	-0.02116		
0.20	-0.03052		
0.25	-0.03599		
0.30	-0.04028		
0.35	-0.04422		

5. 3-methylbenzoic acid

Solubility of 3-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 11.341

$(CH_3)_4NCl$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00373		Setschenow equation
0.10	-0.00657		was obeyed upto
0.15	-0.01550	-0.13±0.003	0.35 mol dm^{-3} of the
0.20	-0.02213		electrolyte.
0.25	-0.02864		
0.30	-0.03613		
0.35	-0.04240		

6. 4-methylbenzoic acid

Solubility of 4-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 3.421

$(CH_3)_4NCl$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00504		Setschenow equation
0.10	-0.00867		was valid upto
0.15	-0.01460		0.35 mol dm^{-3} of the
0.20	-0.02082	-0.13±0.004	salt.
0.25	-0.02790		
0.30	-0.03510		
0.35	-0.04288		

7. 2-fluorobenzoic acid

Solubility of 2-fluorobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 7.368

$(CH_3)_4NCl$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00898		Setschenow equation was
0.10	-0.02094		obeyed upto
0.15	-0.02380		0.35 mol dm^{-3} of
0.20	-0.02846	-0.09±0.006	$(CH_3)_4NCl$.
0.25	-0.03055		
0.30	-0.03569		
0.35	-0.03979		

8. 3-fluorobenzoic acid

Solubility of 3-fluorobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 2.401

$(CH_3)_4NCl$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01458		Setschenow equation
0.10	-0.01963		was obeyed
0.15	-0.02529		upto 0.35 mol dm^{-3} of
0.20	-0.03240	-0.12±0.002	the salt.
0.25	-0.03846		
0.30	-0.04563		
0.35	-0.05033		

9. 4-fluorobenzoic acid

Solubility of 4-fluorobenzoic acid in water at 35°C

(10^3 mol dm^{-3}) = 7.292

$(CH_3)_4NCl$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00591	-0.08±0.002	Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the electrolyte.
0.10	-0.00954		
0.15	-0.01314		
0.20	-0.01774		
0.25	-0.02183		
0.30	-0.02612		
0.35	-0.03235		

10. 2-chlorobenzoic acid

Solubility of 2-chlorobenzoic acid in water at 35°C

(10^2 mol dm^{-3}) = 1.360

$(CH_3)_4NCl$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00507	-0.13±0.002	Setschenow equation was obeyed over the entire range of concentration of $(CH_3)_4NCl$.
0.10	-0.01383		
0.15	-0.01966		
0.20	-0.02693		
0.25	-0.03141		
0.30	-0.03877		
0.35	-0.04659		

11. 3-chlorobenzoic acid

Solubility of 3-chlorobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 3.273

$(CH_3)_4NCl$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01564		Setschenow equation
0.10	-0.03258		was valid upto
0.15	-0.04340		0.35 mol dm^{-3} of
0.20	-0.05325	-0.20±0.007	the electrolyte.
0.25	-0.06243		
0.30	-0.07119		
0.35	-0.07945		

12. 4-chlorobenzoic acid

Solubility of 4-chlorobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 5.071

$(CH_3)_4NCl$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01951		Setschenow equation
0.10	-0.03990		was valid upto
0.15	-0.05811	-0.32±0.009	0.35 mol dm^{-3} of the
0.20	-0.07680		electrolyte.
0.25	-0.09044		
0.30	-0.10483		
0.35	-0.11672		

13. 3-bromobenzoic acid

Solubility of 3-bromobenzoic acid in water at 35°C
$(10^3$ mol dm$^{-3})$ = 1.757

$(CH_3)_4NCl$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0749		Setschenow equation is not obeyed.
0.10	-0.0866	—	
0.15	-0.0956		
0.20	-0.1024		
0.25	-0.1091		
0.30	-0.1147		
0.35	-0.1211		

14. 4-bromobenzoic acid

Solubility of 4-bromobenzoic acid in water at 35°C
$(10_4$ mol dm$^{-3})$ = 2.335

$(CH_3)_4NCl$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0445		Setschenow equation is not obeyed.
0.10	-0.0648	—	
0.15	-0.0857		
0.20	-0.1042		
0.25	-0.1249		
0.30	-0.1432		
0.35	-0.1595		

15. 2-iodobenzoic acid

Solubility of 2-iodobenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 2.446

$(CH_3)_4NCl$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.06882	—	Setschenow equation is not obeyed.
0.10	-0.07856		
0.15	-0.08736		
0.20	-0.09755		
0.25	-0.10791		
0.30	-0.11942		
0.35	-0.13353		

16. 3-iodobenzoic acid

Solubility of 3-iodobenzoic acid in water at 35°C (10^4 mol dm^{-3}) = 4.363

$(CH_3)_4NCl$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.02729	—	Setschenow equation is not obeyed.
0.10	-0.04091		
0.15	-0.05130		
0.20	-0.06411		
0.25	-0.07680		
0.30	-0.08735		
0.35	-0.11183		

17. 2-hydroxybenzoic acid

Solubility of 2-hydroxybenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.805

$(CH_3)_4NCl$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00675		Setschenow equation
0.10	-0.01641		was valid upto
0.15	-0.02875	-0.2±0.007	0.35 mol dm^{-3} of
0.20	-0.04357		the salt.
0.25	-0.05148		
0.30	-0.05952		
0.35	-0.06608		

18. 4-hydroxybenzoic acid

Solubility of 4-hydroxybenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 7.181

$(CH_3)_4NCl$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00048		Setschenow equation
0.10	-0.00199		was obeyed upto
0.15	-0.01490	-0.22±0.009	0.35 mol dm^{-3} of
0.20	-0.03160		$(CH_3)_4NCl$.
0.25	-0.04177		
0.30	-0.05128		
0.35	-0.05969		

19. 2-aminobenzoic acid

Solubility of 2-aminobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 5.352

$(CH_3)_4NCl$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00411		Setschenow equation
0.10	-0.01843		was valid upto
0.15	-0.03123	-0.27±0.005	0.35 mol dm^{-3} of
0.20	-0.04278		the salt.
0.25	-0.05122		
0.30	-0.05951		
0.35	-0.07027		

20. 4-aminobenzoic acid

Solubility of 4-aminobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 5.498

$(CH_3)_4NCl$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01521		Setschenow equation
0.10	-0.01969		was obeyed upto
0.15	-0.02494	-0.19±0.001	0.35 mol dm^{-3} of
0.20	-0.03365		the electrolyte.
0.25	-0.04555		
0.30	-0.05948		
0.35	-0.07278		

concentration. (iii) It has been observed that salting-in increases as the concentration of tetramethylammonium chloride increases.

It was observed that while KCl salted-out all the solutes except a very few, $(CH_3)_4NCl$ salted-in all of them. Thus it is not irrational to assume that the difference in behaviour of these two electrolytes arises from the difference in the effects of their cationic parts. Bockris *et al.*[24] attributed the salting-in of benzene by larger ions such as tetraalkylammonium ions to dispersion forces between ions and neutral solute and solvent molecules. Long-McDevit theory also predicts salting-in of the non-electrolytes by this electrolyte as the quantity $v_s-\bar{v}_s^o$ in the equation

$$K_s = \frac{(v_s-\bar{v}_s^o)\bar{v}_i^o}{2.3\,RT\beta_o}$$

is negative. On the basis of localised hydrolysis model, tetramethylammonium cation is considered to be a structure-breaker[31], resulting salting-in phenomenon. Thus whatever be the model all of them predicts salting-in by tetramethylammonium ion. However, it is to be noted that none of these theories succeeded in predicting the absolute value of the salting coefficient for this electrolyte with different solutes.

It has been observbed that while the solubility of nonelectrolytes in water is generally reduced by the common inorganic salts, the tetraalkylammonium ions may have an opposite effect.[32,33] In general, a salt can affect the solubility of a solute by three mechanisms: (i) a change in the proportion of $(H_2O)_d$, (ii) the effect of the cation and the anion on the stability of the solute through electrostatic interaction as described by the localized hydrolysis model and (iii) the electrostatic field of the cation and the anion on the surrounding molecules. A comparison between KCl and $(CH_3)_4NCl$ with respect to the above effects will reveal that in any case $(CH_3)_4N$ cation produces more salting-in than K^+ ion. For example, in the present case, the first factor should increase solubility by increasing the proportion of $(H_2O)_d$ through the structure-breaking action of both the K^+ and $(CH_3)_4N^+$ cations, the second factor should increase solubility because the repulsive interaction between the potassium ion and the cationic charge on the carboxylic hydrogen should be greater than that between the tetraalkylammonium ion and the carboxylic proton. The third factor should also serve to increase solubility because the electrostatic field of the potassium ion is greater than that of the organic cation so that the water molecules will be under greater constraint in the former case. The results then can be accommodated by assuming that the dominant factor is the effect on the cohesive energy density of these cations. The potassium ion will increase this quantity while the tetraalkylammonium ion will have little effect. This itself was the conclusion reached by Long and McDevit while explaining the salt effects on benzene.

iv) Effect of potassium and magnesium sulphate

The findings with potassium and magnesium sulphate are as follows: (i) with all the three nitrobenzoic acids, salting-in is observed and the Setschenow equation is not valid, (ii) with methylbenzoic acids, fluorobenzoic acids, aminobenzoic acids and 4-hydroxybenzoic acid, salting-out is found. Here the Setschenow equation is valid upto 0.35 mol dm^{-3} of the electrolyte. (iii) Chloro-, bromo-, and iodobenzoic acids are salted-in by these electrolytes, and the Setschenow equation is not obeyed. (iv) 2-hydroxy-

Table 12

Effect of potassium sulphate on the activity coefficient of monosubstituted benzoic acids in aqueous solutions at 35°C

1. 2-nitrobenzoic acid

Solubility of 2-nitrobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 4.145

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1155	—	Setschenow equation is not obeyed.
0.10	-0.1362		
0.15	-0.1787		
0.20	-0.2080		
0.25	-0.2342		
0.30	-0.2542		
0.35	-0.2678		

2. 3-nitrobenzoic acid

Solubility of 3-nitrobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 2.708

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.04490	—	Setschenow equation is not obeyed.
0.10	-0.05491		
0.15	-0.06552		
0.20	-0.07073		
0.25	-0.07331		
0.30	-0.06386		
0.35	-0.05843		

3. 4-nitrobenzoic acid

Solubility of 4-nitrobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.689

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1498	—	Setschenow equation is not obeyed.
0.10	-0.1865		
0.15	-0.1961		
0.20	-0.2118		
0.25	-0.2189		
0.30	-0.2272		
0.35	-0.2392		

4. 2-methylbenzoic acid

Solubility of 2-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 11.896

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00911	0.18±0.009	Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the electrolyte.
0.10	-0.00300		
0.15	0.01308		
0.20	0.02471		
0.25	0.03109		
0.30	0.04117		
0.35	0.04768		

5. 3-methylbenzoic acid

Solubility of 3-methylbenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 11.341

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00999		Setschenow equation
0.10	-0.00320		was valid upto
0.15	0.01074		0.35 mol dm^{-3} of the
0.20	0.02151	0.25±0.009	salt.
0.25	0.03247		
0.30	0.04767		
0.35	0.06605		

6. 4-methylbenzoic acid

Solubility of 4-methylbenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 3.421

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01387		Setschenow equation
0.10	-0.00717		was valid over the
0.15	0.00293	0.17±0.003	whole concentration
0.20	0.01341		of K_2SO_4.
0.25	0.02014		
0.30	0.02792		
0.35	0.03598		

7. 2-fluorobenzoic acid

Solubility of 2-fluorobenzoic acid in water at 35°C
(10^2 and dm^{-3}) = 7.368

K_2SO_4 conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00182	0.15±0.008	Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the electrolyte.
0.10	0.00671		
0.15	0.01128		
0.20	0.01578		
0.25	0.02497		
0.30	0.03568		
0.35	0.04715		

8. 3-fluorobenzoic acid

Solubility of 3-fluorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.401

K_2SO_4 conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.04968	0.18±0.007	Setschenow equation was obeyed upto concentration of the salt.
0.10	-0.03341		
0.15	-0.02683		
0.20	-0.01598		
0.25	-0.00877		
0.30	-0.00162		
0.35	0.00784		

9. 4-fluorobenzoic acid

Solubility of 4-fluorobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 7.292

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.03686	0.16±0.004	Setschenow equation was valid upto 0.35 mol dm^{-3} of K_2SO_4.
0.10	-0.03175		
0.15	-0.02438		
0.20	-0.01216		
0.25	-0.00925		
0.30	0.00344		
0.35	0.01079		

10. 2-chlorobenzoic acid

Solubility of 2-chlorobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 1.360

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0878	—	Setschenow equation is not obeyed.
0.10	-0.0998		
0.15	-0.1117		
0.20	-0.1156		
0.25	-0.1198		
0.30	-0.1251		
0.35	-0.1277		

11. 3-chlorobenzoic acid

Solubility of 3-chlorobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 3.273

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0911	—	Setschenow equation is not obeyed.
0.10	-0.1005		
0.15	-0.1075		
0.20	-0.1123		
0.25	-0.1177		
0.30	-0.1227		
0.35	-0.1268		

12. 4-chlorobenzoic acid

Solubility of 4-chlorobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 5.071

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1557	—	Setschenow equation is not obeyed.
0.10	-0.1799		
0.15	-0.2148		
0.20	-0.2274		
0.25	-0.2362		
0.30	-0.2456		
0.35	-0.2539		

13. 3-bromobenzoic acid

Solubility of 3-bromobenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 1.757

K_2SO_4 conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1558	—	Setschenow equation is not obeyed.
0.10	-0.1725		
0.15	-0.1867		
0.20	-0.1939		
0.25	-0.1939		
0.30	-0.1939		
0.35	-0.1930		

14. 4-bromobenzoic acid

Solubility of 4-bromobenzoic acid in water at 35°C (10^4 mol dm^{-3}) = 2.335

K_2SO_4 conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.2451	—	Setschenow equation is not obeyed.
0.10	-0.2756		
0.15	-0.3004		
0.20	-0.3278		
0.25	-0.3635		
0.30	-0.3834		
0.35	-0.4027		

15. 2-iodobenzoic acid

Solubility of 2-iodobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 2.446

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.2613	—	Setschenow equation is not obeyed.
0.10	-0.2783		
0.15	-0.2903		
0.20	-0.3022		
0.25	-0.3078		
0.30	-0.3112		
0.35	-0.3149		

16. 3-iodobenzoic acid

Solubility of 3-iodobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 4.363

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1758	—	Setschenow equation is not obeyed.
0.10	-0.1876		
0.15	-0.2221		
0.20	-0.2471		
0.25	-0.2635		
0.30	-0.2787		
0.35	-0.2917		

17. 2-hydroxybenzoic acid

Solubility of 2-hydroxybenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 2.805

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0947	—	Setschenow equation is not obeyed.
0.10	-0.1036		
0.15	-0.1079		
0.20	-0.1160		
0.25	-0.1239		
0.30	-0.1298		
0.35	-0.1375		

18. 4-hydroxybenzoic acid

Solubility of 4-hydroxybenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 7.181

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00150	0.11±0.002	Setschenow equation was valid upto 0.35 mol dm^{-3} of the electrolyte.
0.10	0.00609		
0.15	0.01155		
0.20	0.01595		
0.25	0.02170		
0.30	0.02649		
0.35	0.03408		

19. 2-aminobenzoic acid

Solubility of 2-aminobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 5.352

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	0.00317	0.13±0.007	Setschenow equation was valid upto 0.35 mol dm^{-3} of K_2SO_4.
0.10	0.01059		
0.15	0.01603		
0.20	0.02435		
0.25	0.03260		
0.30	0.0.045		
0.35	0.05577		

20. 4-aminobenzoic acid

Solubility of 4-aminobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 5.498

K_2SO_4 conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00141	0.20±0.002	Setschenow equation was valid upto 0.35 mol dm^{-3} of the electrolyte.
0.10	0.00756		
0.15	0.01650		
0.20	0.02663		
0.25	0.03838		
0.30	0.04771		
0.35	0.05797		

Table 13

Effect of magnesium sulphate on the activity coefficient of monosubstituted benzoic acids in aqueous solutions at 35°C

1. 2-nitrobenzoic acid

Solubility of 2-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 4.145

$MgSO_4$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0900	—	Setschenow equation is not obeyed.
0.10	-0.1122		
0.15	-0.1287		
0.20	-0.1245		
0.25	-0.1218		
0.30	-0.1186		
0.35	-0.1138		

2. 3-nitrobenzoic acid

Solubility of 3-nitrobenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.708

$MgSO_4$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.02614	—	Setschenow equation is not obeyed.
0.10	-0.03658		
0.15	-0.04534		
0.20	-0.05037		
0.25	-0.03990		
0.30	-0.02926		
0.35	-0.02187		

3. 4-nitrobenzoic acid

Solubility of 4-nitrobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.689

$MgSO_4$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1372		Setschenow equation is not obeyed.
0.10	-0.1635	—	
0.15	-0.1798		
0.20	-0.1914		
0.25	-0.2087		
0.30	-0.2185		
0.35	-0.2268		

4. 2-methylbenzoic acid

Solubility of 2-methylbenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 11.896

$MgSO_4$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	0.01865		Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the electrolyte.
0.10	0.02405		
0.15	0.03496		
0.20	0.04602	0.19±0.006	
0.25	0.05828		
0.30	0.06578		
0.35	0.07159		

5. <u>3-methylbenzoic acid</u>

Solubility of 3-methylbenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 11.341

$MgSO_4$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	0.00450		Setschenow equation was obeyed upto 0.35 mol dm^{-3} of $MgSO_4$
0.10	0.01377		
0.15	0.02458		
0.20	0.03566	0.25±0.009	
0.25	0.00		
0.30	0.06405		
0.35	0.08171		

6. <u>4-methylbenzoic acid</u>

Solubility of 4-methylbenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 3.421

$MgSO_4$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	0.00820		Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the salt.
0.10	0.01630		
0.15	0.02562	0.19±0.002	
0.20	0.03653		
0.25	0.04462		
0.30	0.05458		
0.35	0.06404		

7. 2-fluorobenzoic acid

Solubility of 2-fluorobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 7.368

$MgSO_4$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	0.02101		Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the electrolyte.
0.10	0.02863		
0.15	0.03516		
0.20	0.04121	0.13±0.002	
0.25	0.04912		
0.30	0.05403		
0.35	0.05900		

8. 3-fluorobenzoic acid

Solubility of 3-fluorobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 2.401

$MgSO_4$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00216		Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the electrolyte.
0.10	0.00840		
0.15	0.01678		
0.20	0.02475	0.17±0.002	
0.25	0.03384		
0.30	0.04373		
0.35	0.05079		

9. 4-fluorobenzoic acid

Solubility of 4-fluorobenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 7.292

$MgSO_4$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.01848		Setschenow equation was valid upto 0.35 mol dm^{-3} of the electrolyte.
0.10	-0.00562		
0.15	0.00611	0.3±0.006	
0.20	0.02186		
0.25	0.03716		
0.30	0.05308		
0.35	0.07179		

10. 2-chlorobenzoic acid

Solubility of 2-chlorobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 1.360

$MgSO_4$ conc. (mol dm^{-3})	log f	K_s	Remarks
0.05	-0.05763	—	Setschenow equation is not obeyed.
0.10	-0.07080		
0.15	-0.07891		
0.20	-0.08578		
0.25	-0.09203		
0.30	-0.09358		
0.35	-0.09512		

11. 3-chlorobenzoic acid

Solubility of 3-chlorobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 3.273

$MgSO_4$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.05711	—	Setschenow equation is not obeyed.
0.10	-0.06415		
0.15	-0.07399		
0.20	-0.07989		
0.25	-0.08494		
0.30	-0.09068		
0.35	-0.09656		

12. 4-chlorobenzoic acid

Solubility of 4-chlorobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 5.071

$MgSO_4$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1234	—	Setschenow equation is not obeyed.
0.10	-0.1431		
0.15	-0.1863		
0.20	-0.1941		
0.25	-0.2026		
0.30	-0.2092		
0.35	-0.2192		

13. 3-bromobenzoic acid

Solubility of 3-bromobenzoic acid in water at 35°C
(10^3 mol dm^{-3}) = 1.757

$MgSO_4$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1383	—	Setschenow equation is not obeyed.
0.10	-0.1442		
0.15	-0.1504		
0.20	-0.1561		
0.25	-0.1604		
0.30	-0.1554		
0.35	-0.1504		

14. 4-bromobenzoic acid

Solubility of 4-bromobenzoic acid in water at 35°C
(10^4 mol dm^{-3}) = 2.335

$MgSO_4$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1753	—	Setschenow equation is not obeyed.
0.10	-0.1965		
0.15	-0.2329		
0.20	-0.2554		
0.25	-0.2733		
0.30	-0.2837		
0.35	-0.2916		

15. 2-iodobenzoic acid

Solubility of 2-iodobenzoic acid in water at 35°C (10^3 mol dm^{-3}) = 2.446

$MgSO_4$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.2245	—	Setschenow equation is not obeyed.
0.10	-0.2297		
0.15	-0.2463		
0.20	-0.2537		
0.25	-0.2614		
0.30	-0.2685		
0.35	-0.2760		

16. 3-iodobenzoic acid

Solubility of 3-iodobenzoic acid in water at 35°C (10^4 mol dm^{-3}) = 4.363

$MgSO_4$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.1337	—	Setschenow equation is not obeyed.
0.10	-0.1562		
0.15	-0.1760		
0.20	-0.1856		
0.25	-0.1943		
0.30	-0.1992		
0.35	-0.2049		

17. 2-hydroxybenzoic acid

Solubility of 2-hydroxybenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 2.805

$MgSO_4$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.0642	—	Setschenow equation is not obeyed.
0.10	-0.0793		
0.15	-0.0836		
0.20	-0.0926		
0.25	-0.1152		
0.30	-0.1087		
0.35	-0.1116		

18. 4-hydroxybenzoic acid

Solubility of 4-hydroxybenzoic acid in water at 35°C
(10^2 mol dm^{-3}) = 7.181

$MgSO_4$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.00559	0.26±0.003	Setschenow equation was valid upto 0.35 mol dm^{-3} of the salt.
0.10	0.01489		
0.15	0.02920		
0.20	0.04454		
0.25	0.05760		
0.30	0.07107		
0.35	0.08372		

19. 2-aminobenzoic acid

Solubility of 2-aminobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 5.352

$MgSO_4$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	0.00317	0.22±0.005	Setschenow equation was valid upto 0.35 mol dm^{-3} of $MgSO_4$
0.10	0.01385		
0.15	0.02342		
0.20	0.03602		
0.25	0.04863		
0.30	0.06538		
0.35	0.07521		

20. 4-aminobenzoic acid

Solubility of 4-aminobenzoic acid in water at 35°C (10^2 mol dm^{-3}) = 5.498

$MgSO_4$ conc.(mol dm^{-3})	log f	K_s	Remarks
0.05	-0.00228	0.2±0.003	Setschenow equation was obeyed upto 0.35 mol dm^{-3} of the electrolyte.
0.10	0.00564		
0.15	0.01462		
0.20	0.02470		
0.25	0.03511		
0.30	0.04604		
0.35	0.05698		

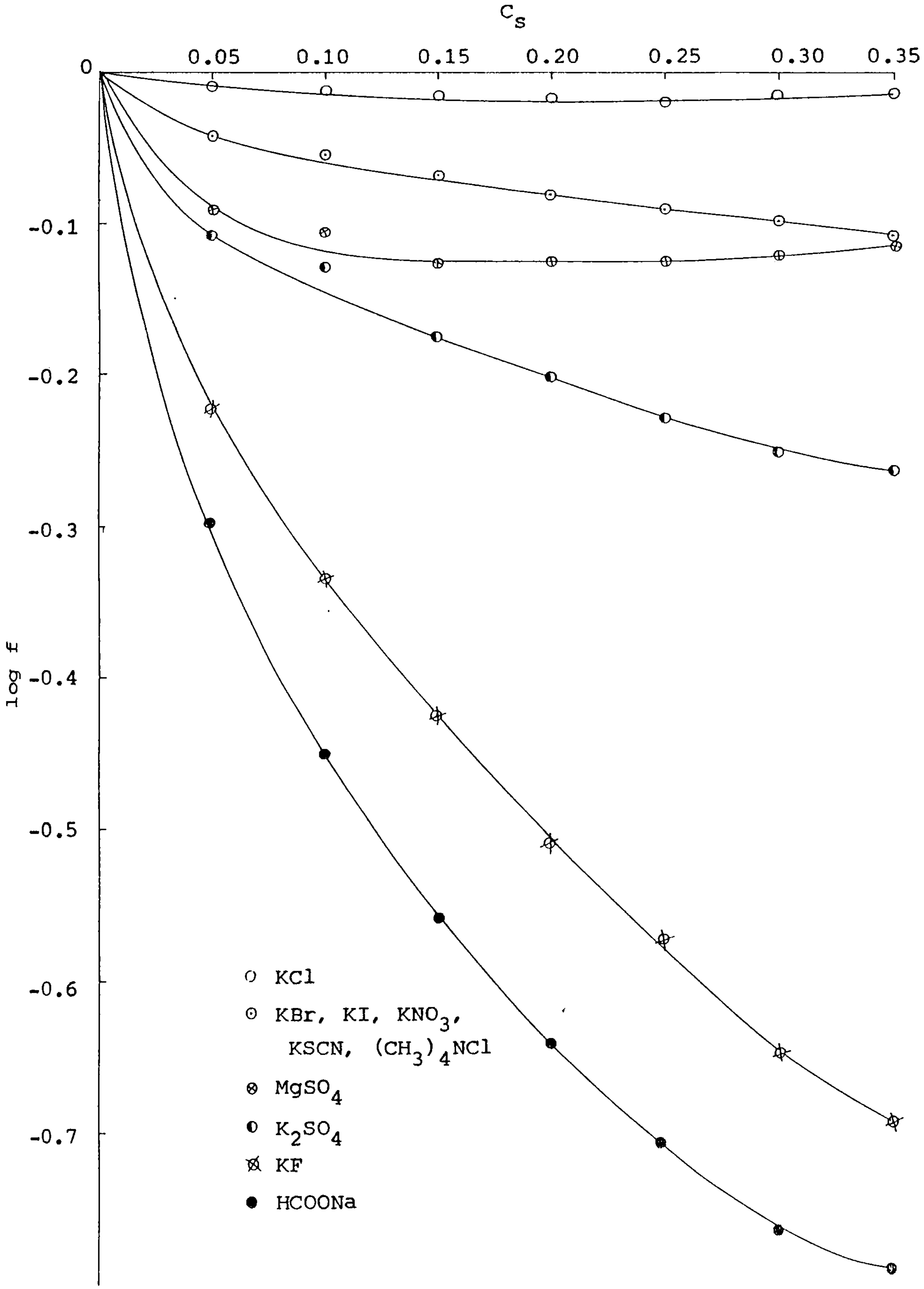


Fig.3 Effect of salts on the activity coefficient of 2-nitrobenzoic acid.

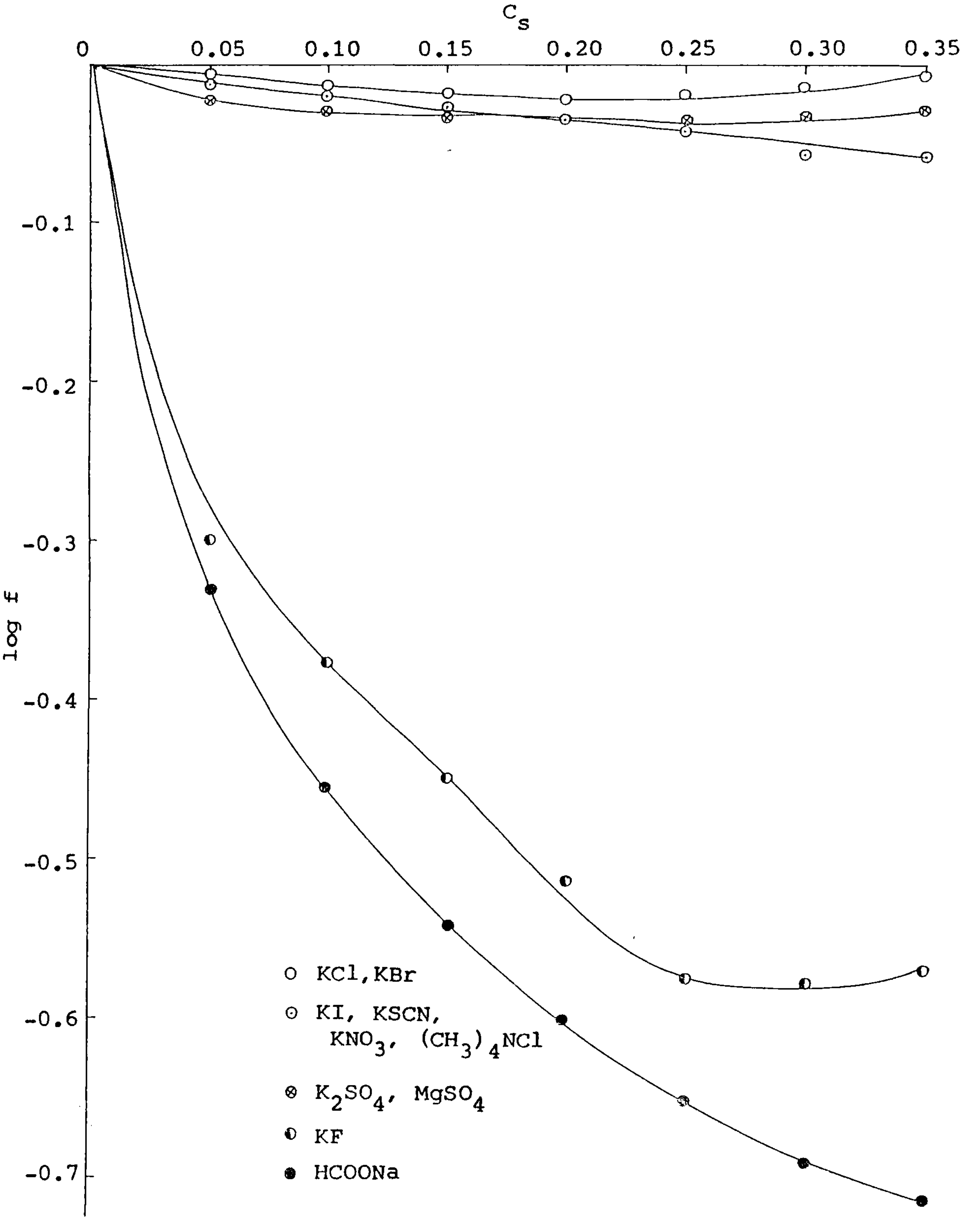


Fig.4 Effect of salts on the activity coefficient of 3-nitrobenzoic acid.

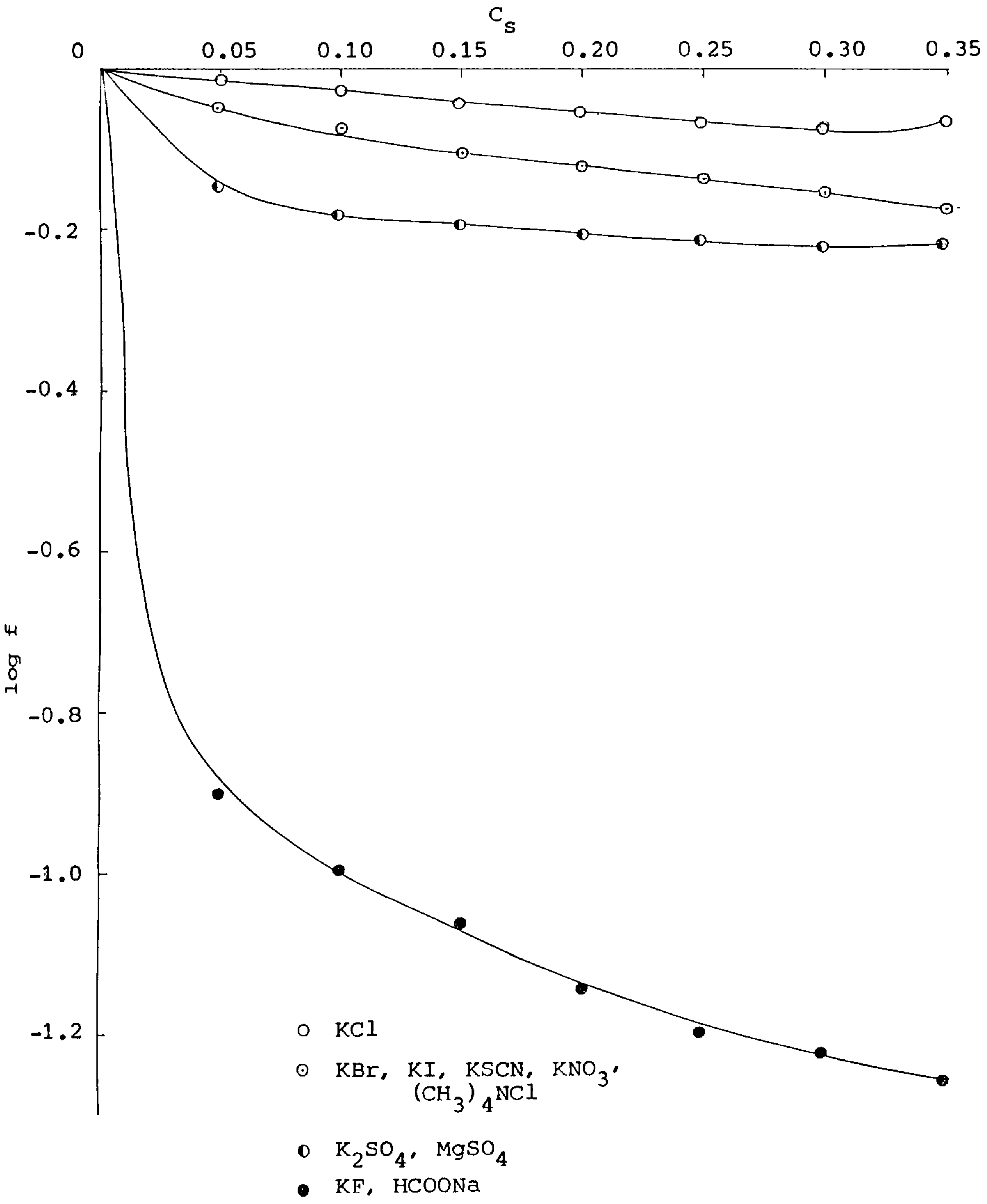


Fig.5 Effect of salts on the activity coefficient of 4-nitrobenzoic acid.

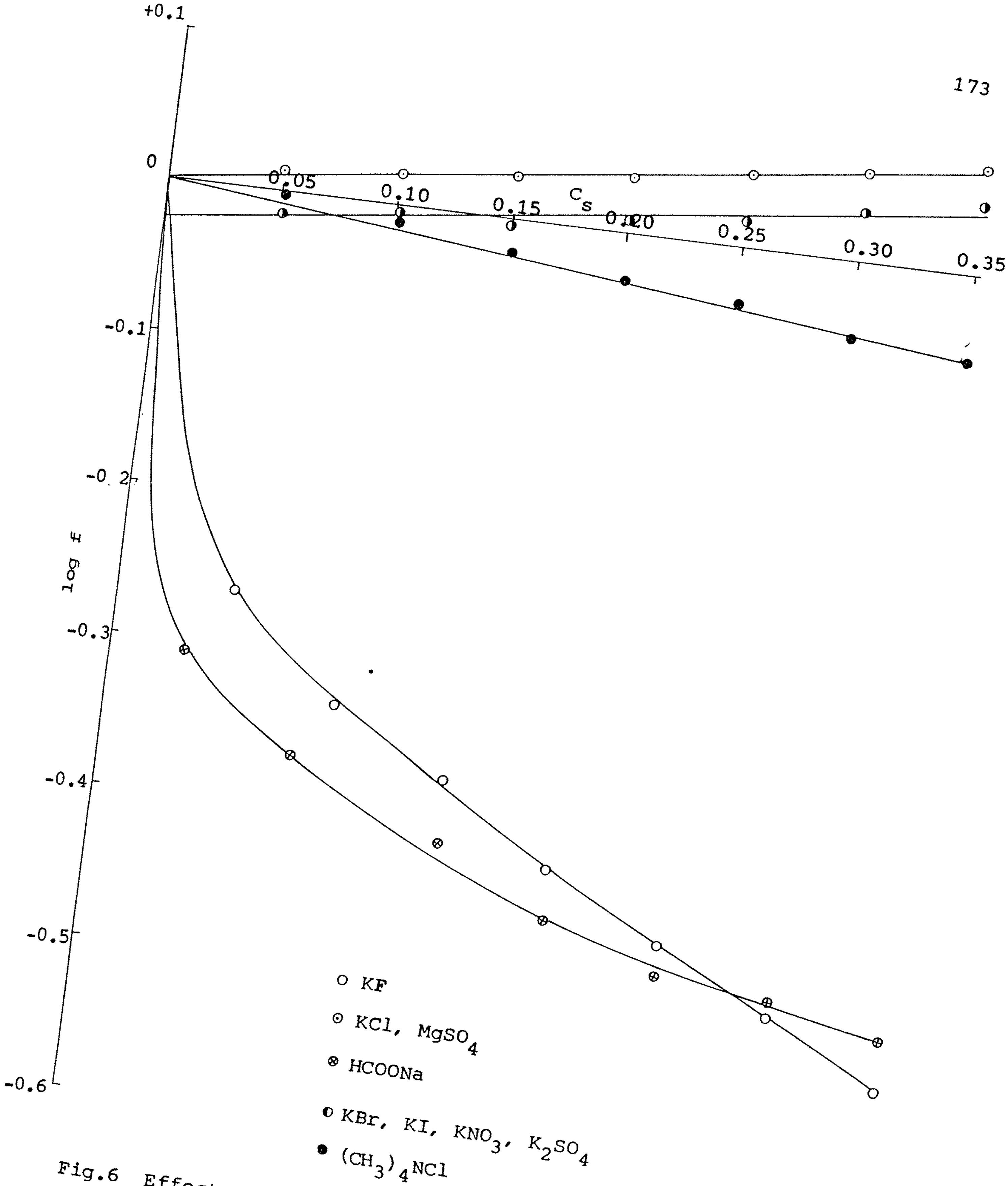


Fig.6 Effect of salts on the activity coefficient of 2-methylbenzoic acid.

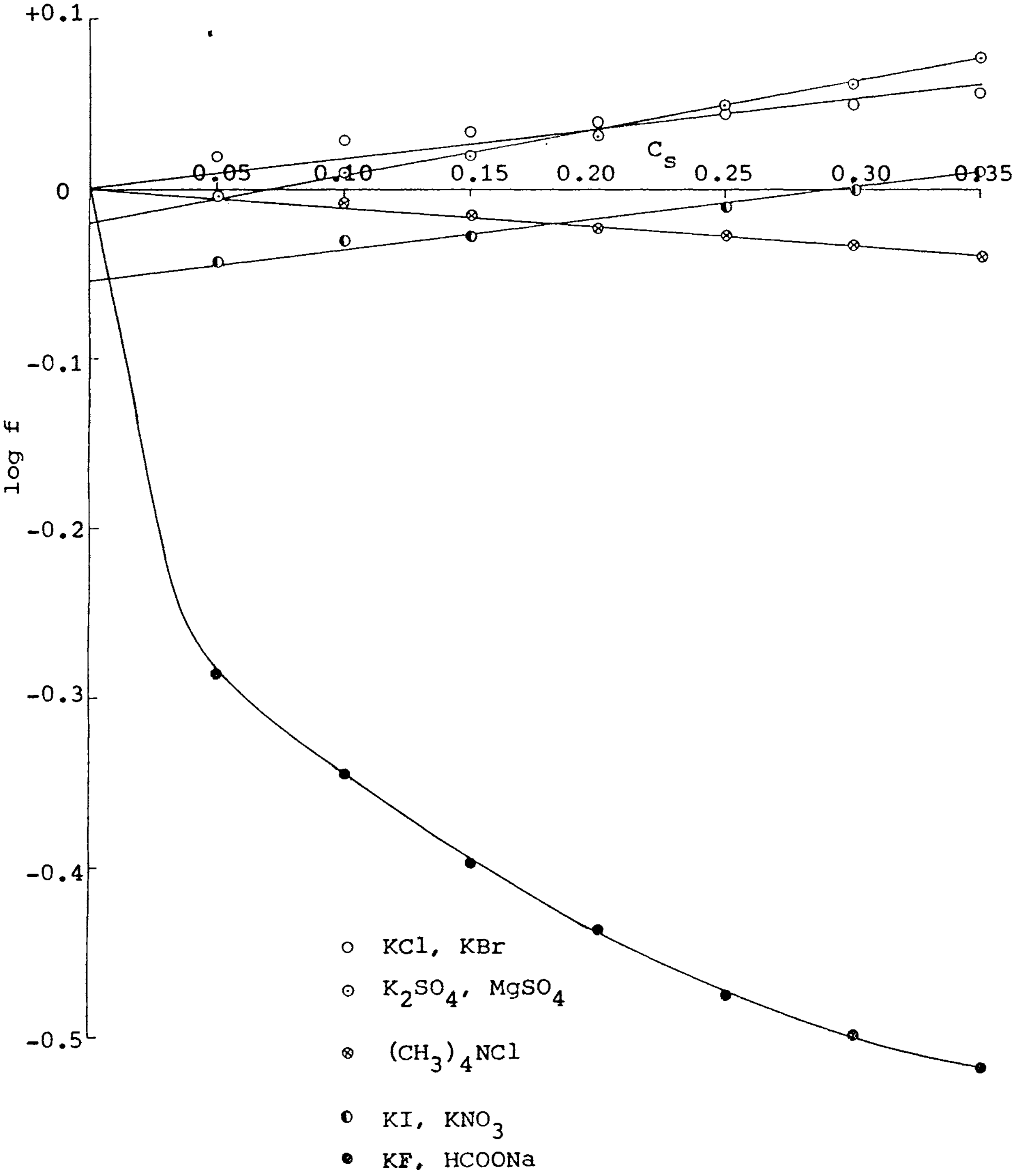


Fig.7 Effect of salts on the activity coefficient of 3-methylbenzoic acid.

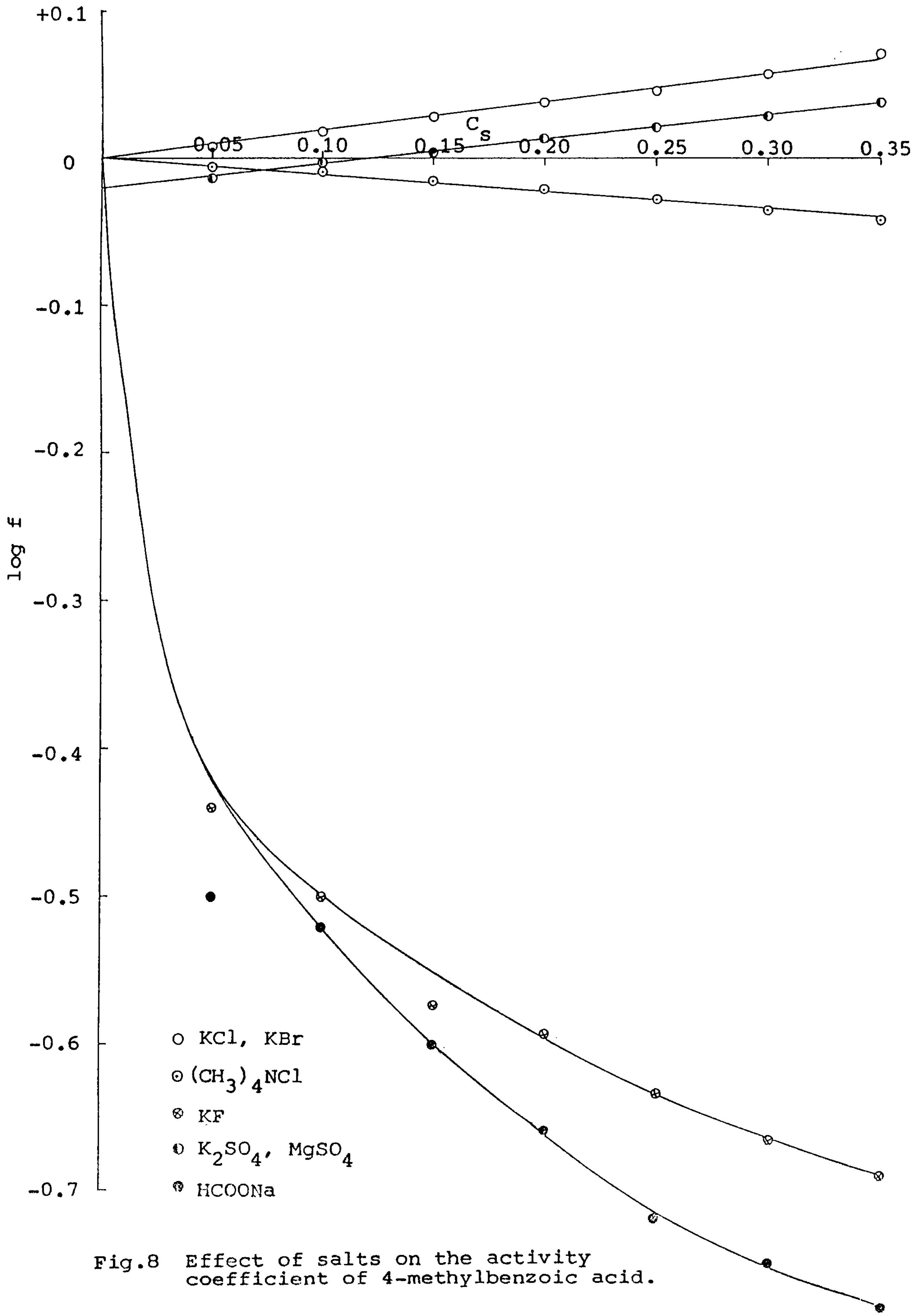


Fig.8 Effect of salts on the activity coefficient of 4-methylbenzoic acid.

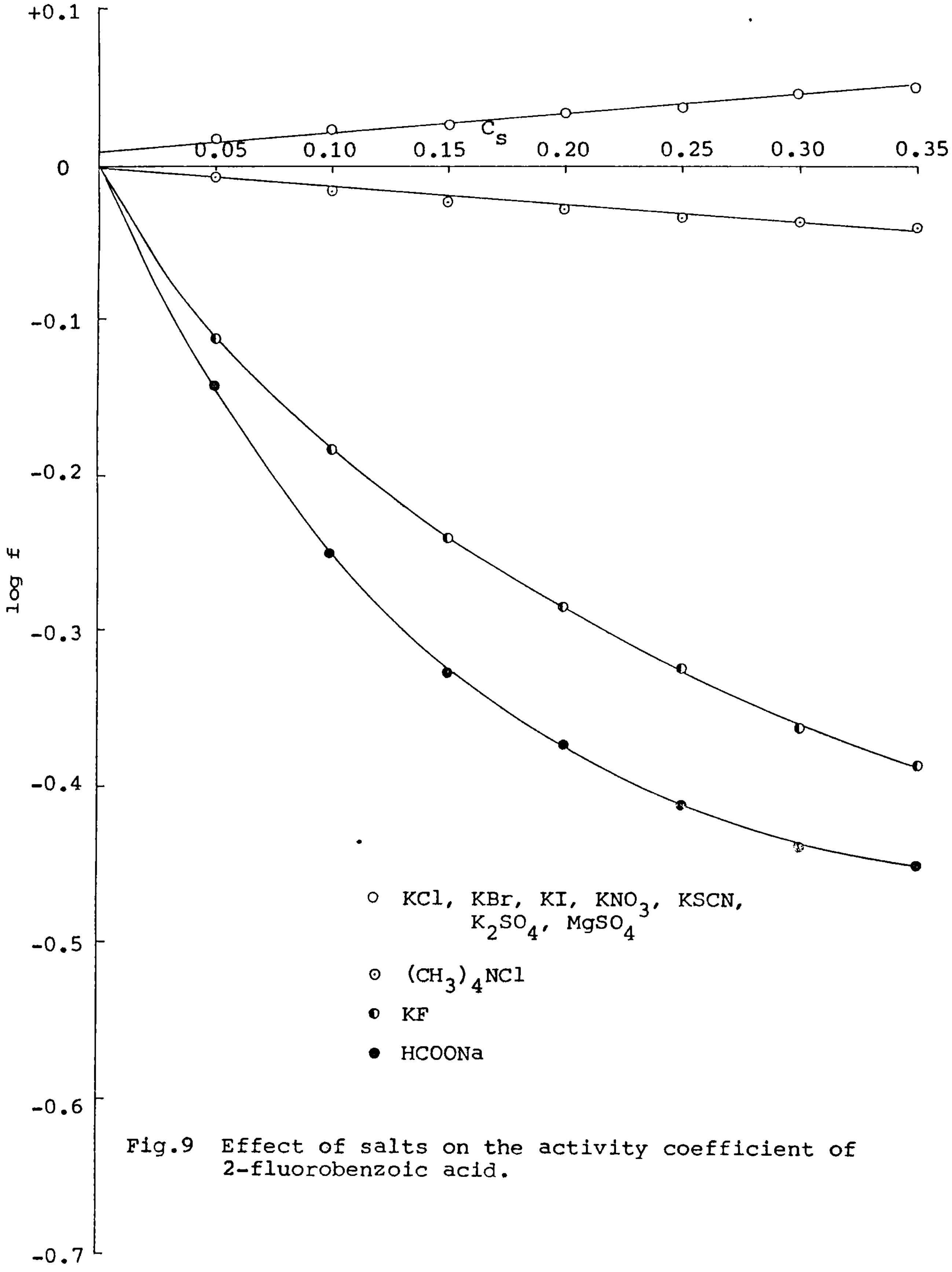


Fig.9 Effect of salts on the activity coefficient of 2-fluorobenzoic acid.

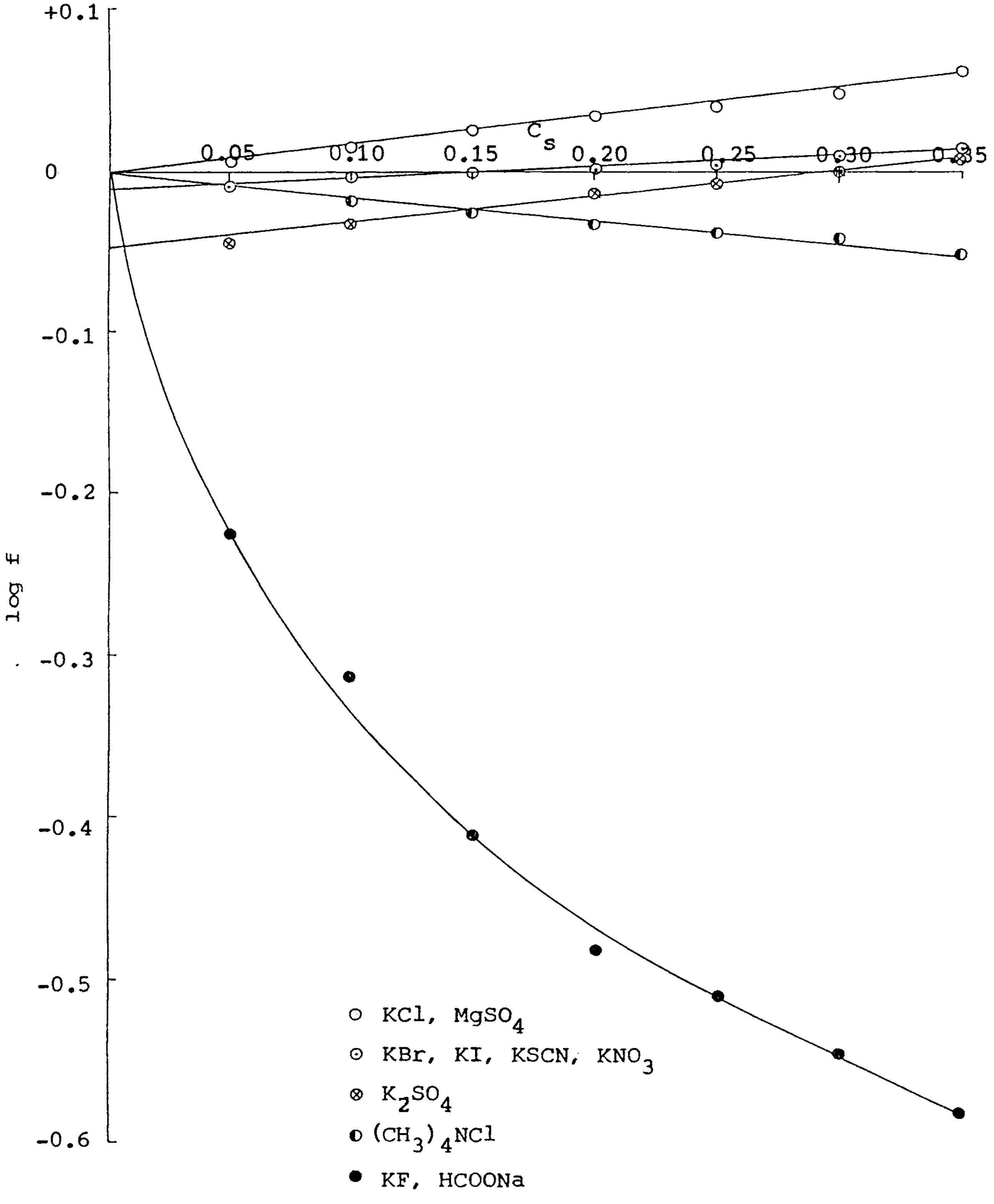
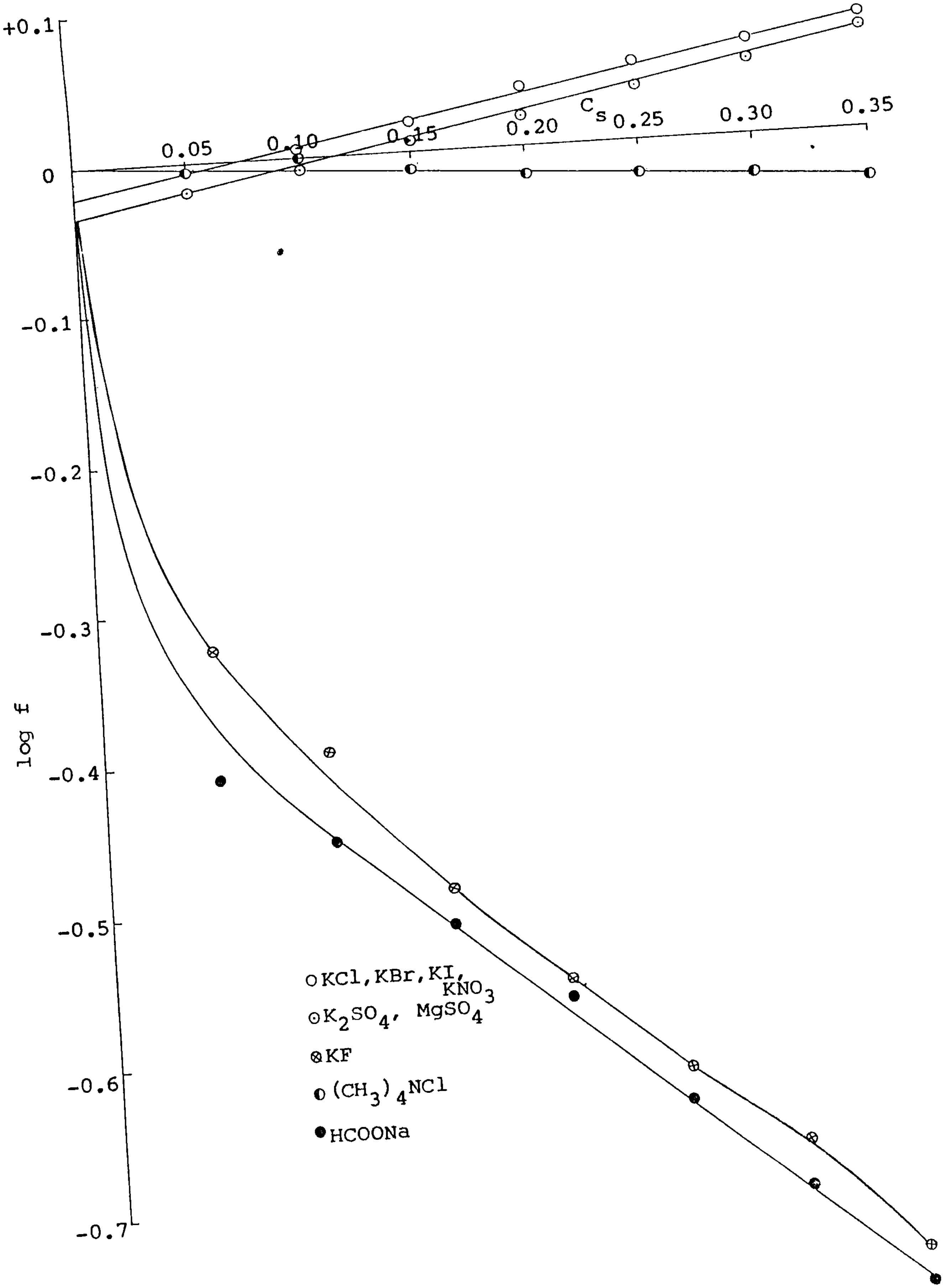


Fig.10 Effect of salts on the activity coefficient of 3-fluorobenzoic acid.


+0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
log f
C_s
0.05
0.10
0.15
0.20
0.25
0.30
0.35
○ KCl, KBr, KI, KNO₃
⊙ K₂SO₄, MgSO₄
⊗ KF
◐ (CH₃)₄NCl
● HCOONa

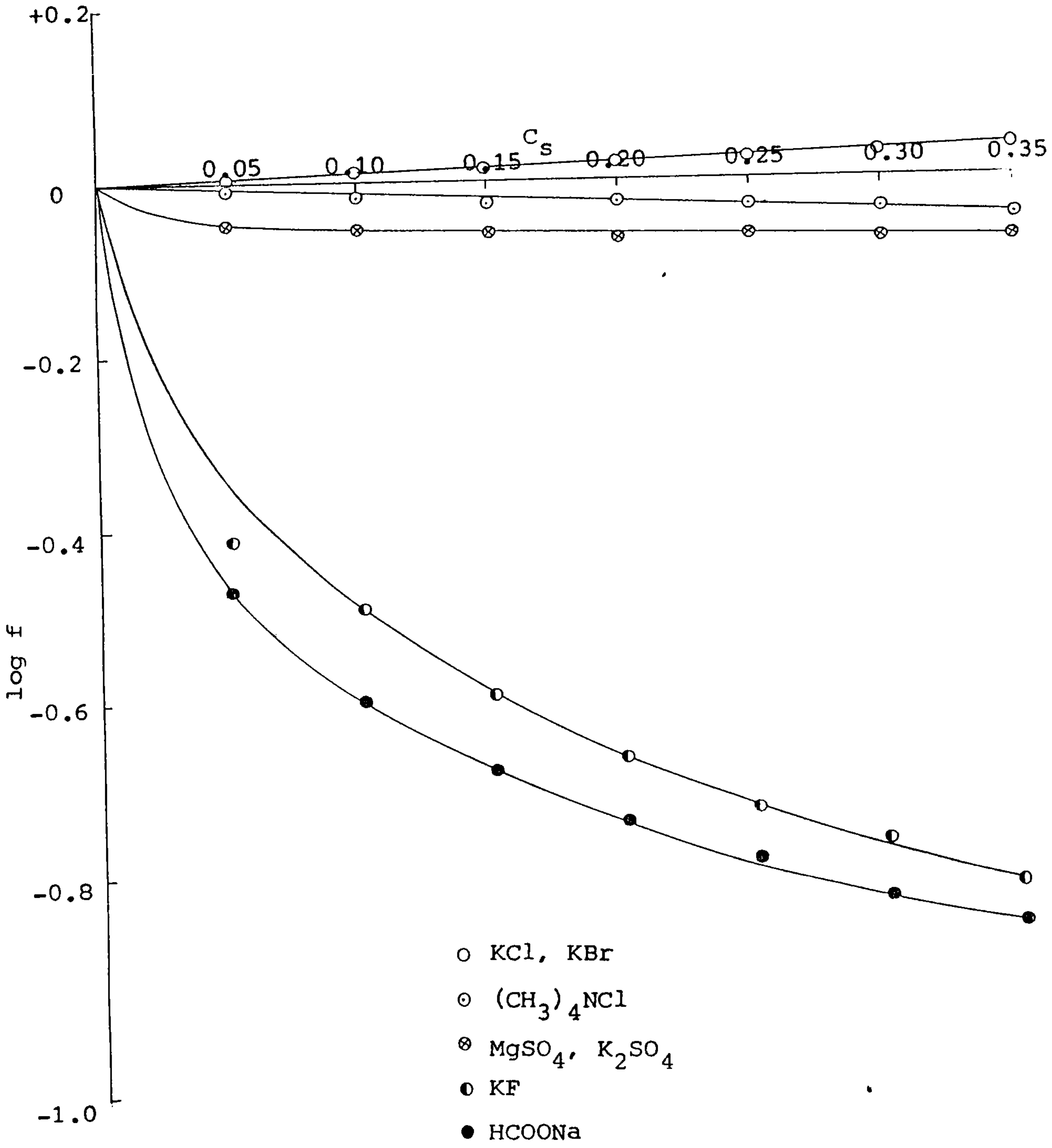


Fig.12 Effect of salts on the activity coefficient of 2-chlorobenzoic acid.

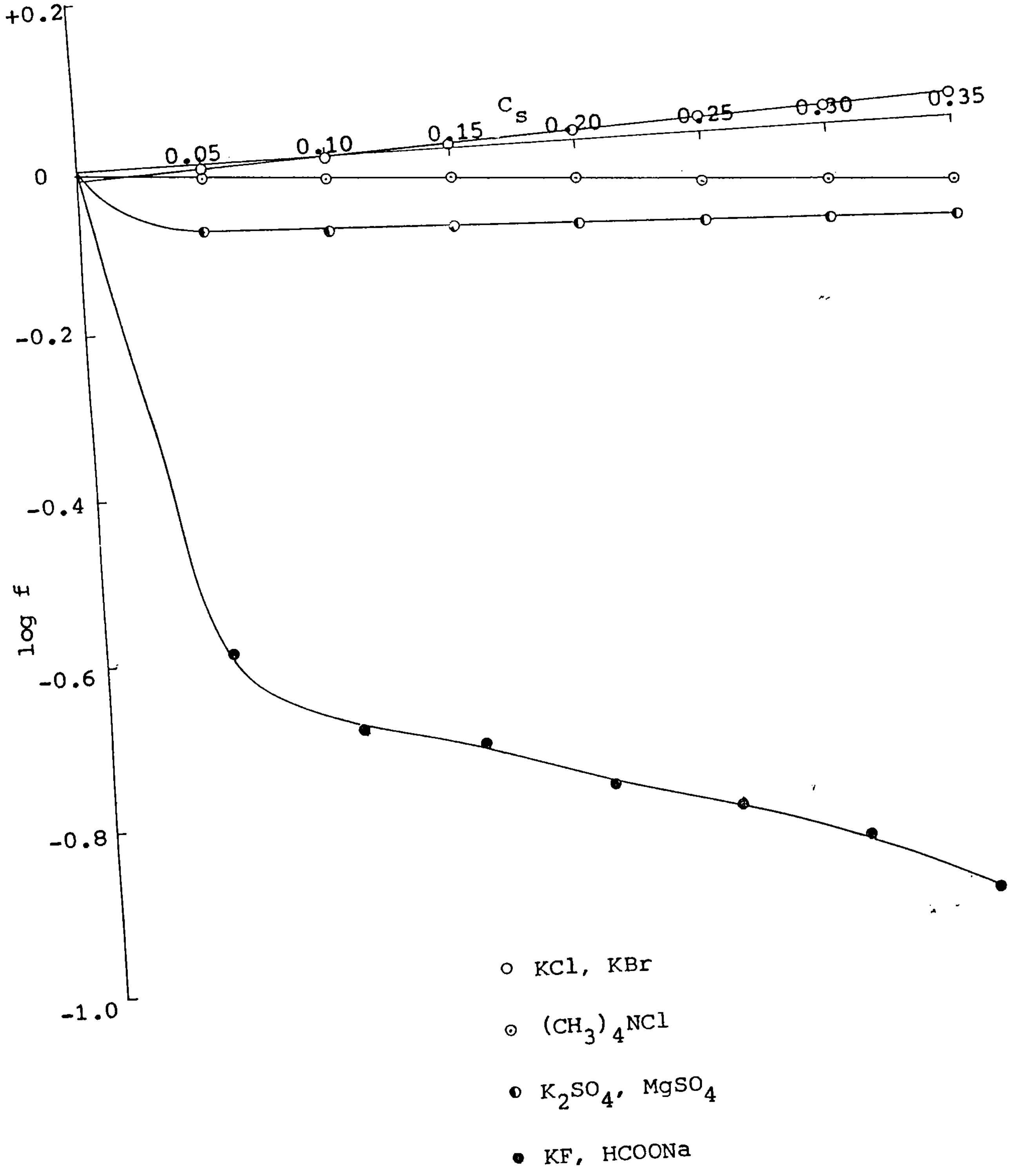


Fig.13 Effect of salts on the activity coefficient of 3-chlorobenzoic acid.

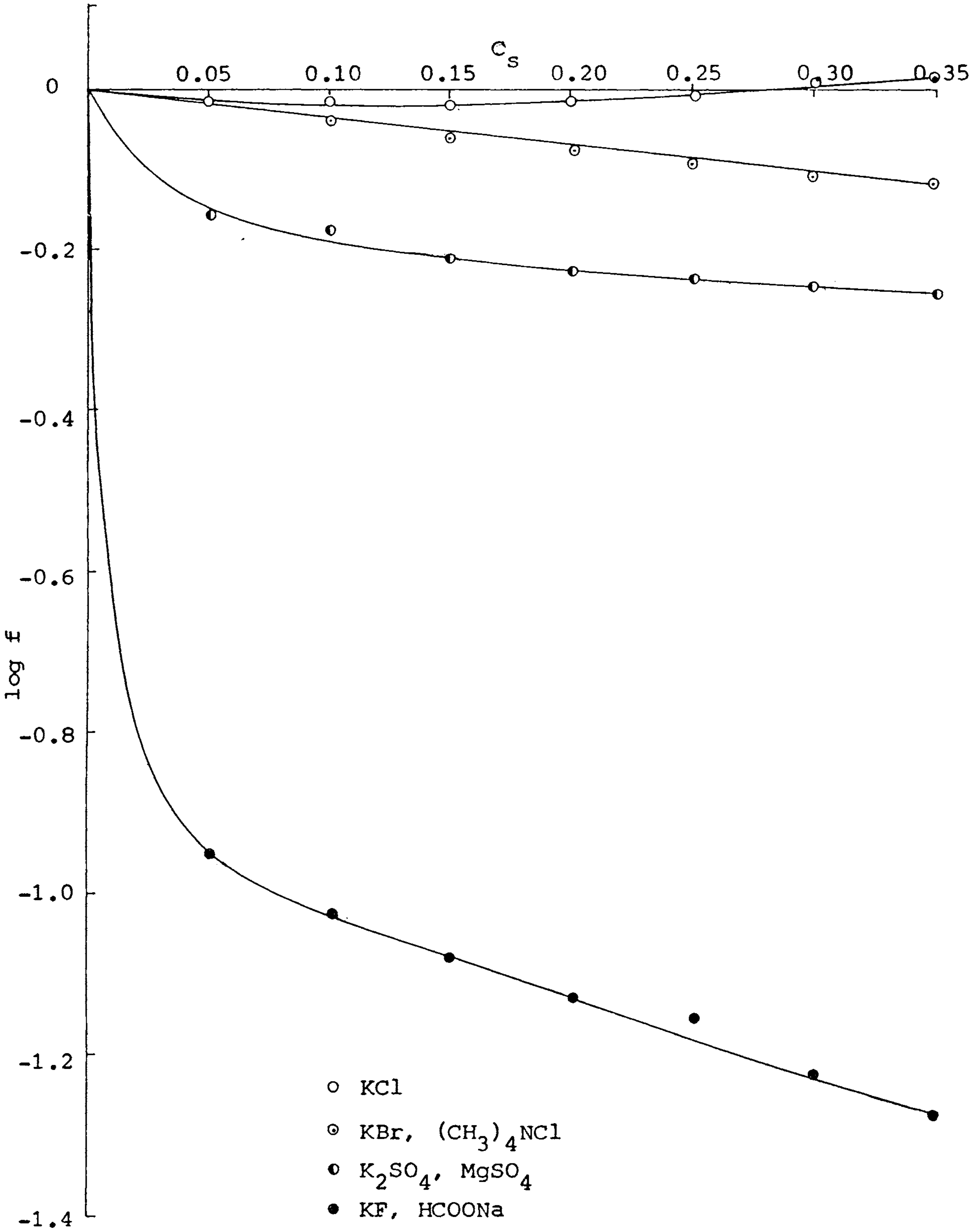


Fig.14 Effect of salts on the activity coefficient of 4-chlorobenzoic acid.

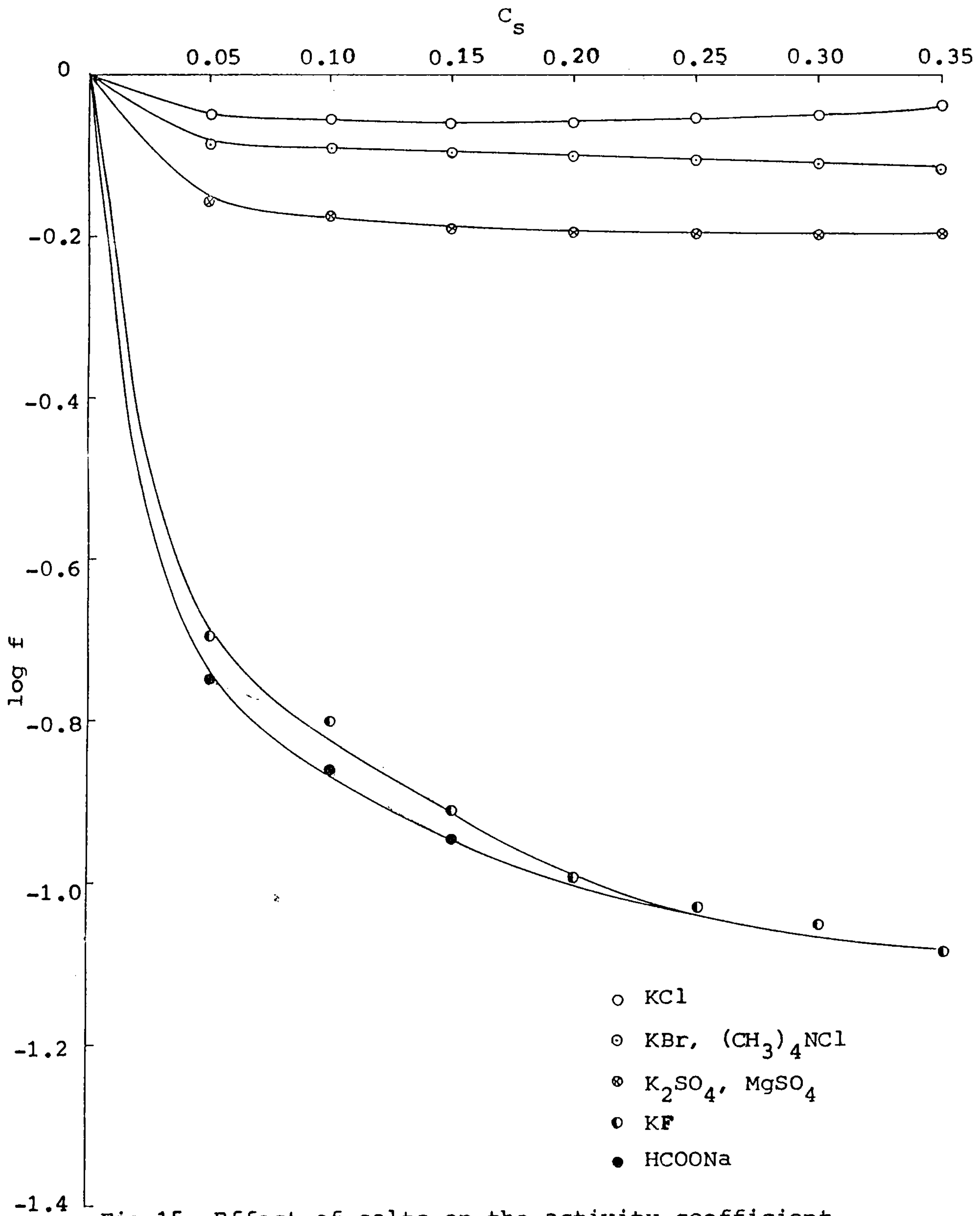


Fig.15 Effect of salts on the activity coefficient of 3-bromobenzoic acid.

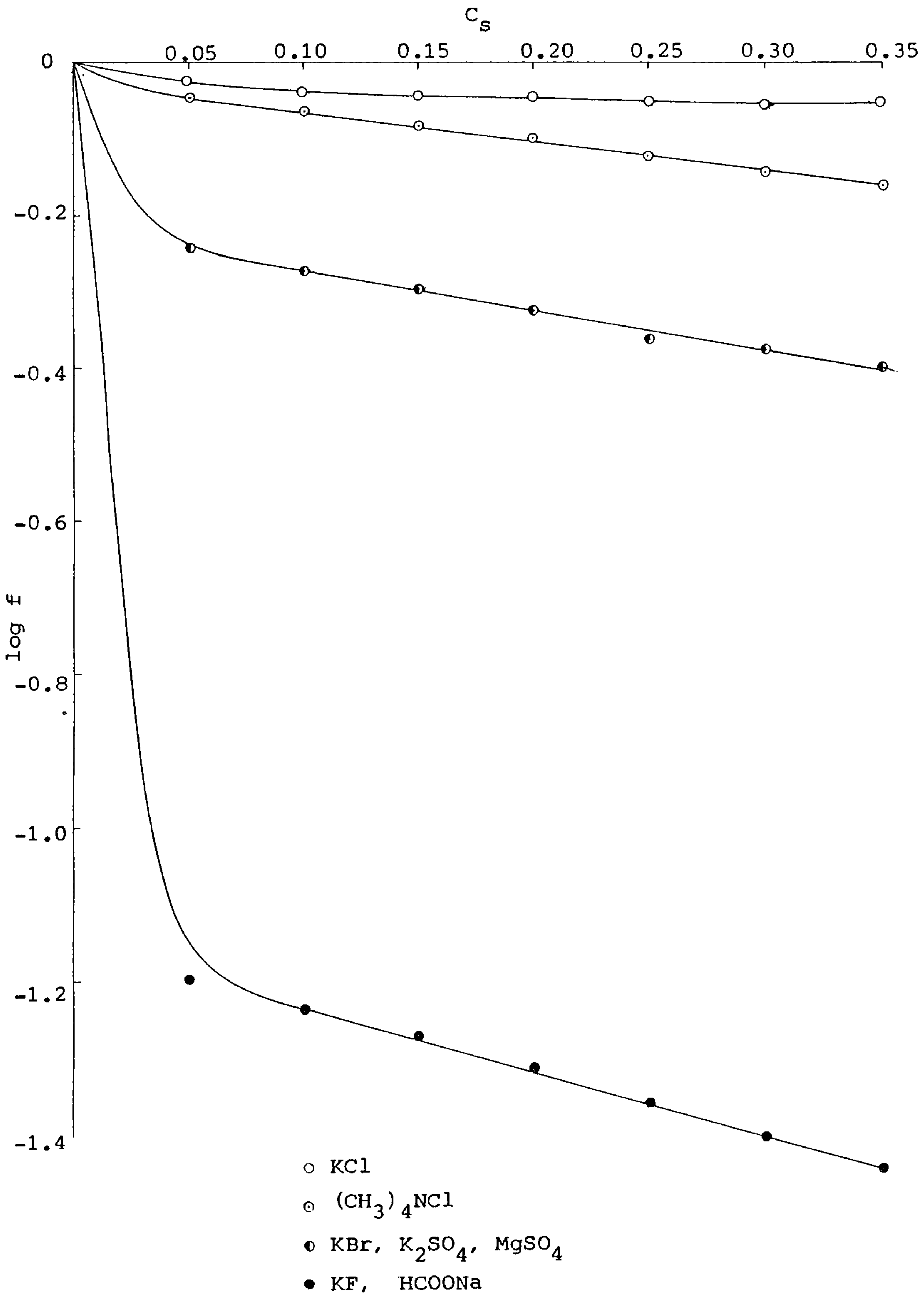


Fig.16 Effect of salts on the activity coefficient of 4-bromobenzoic acid.

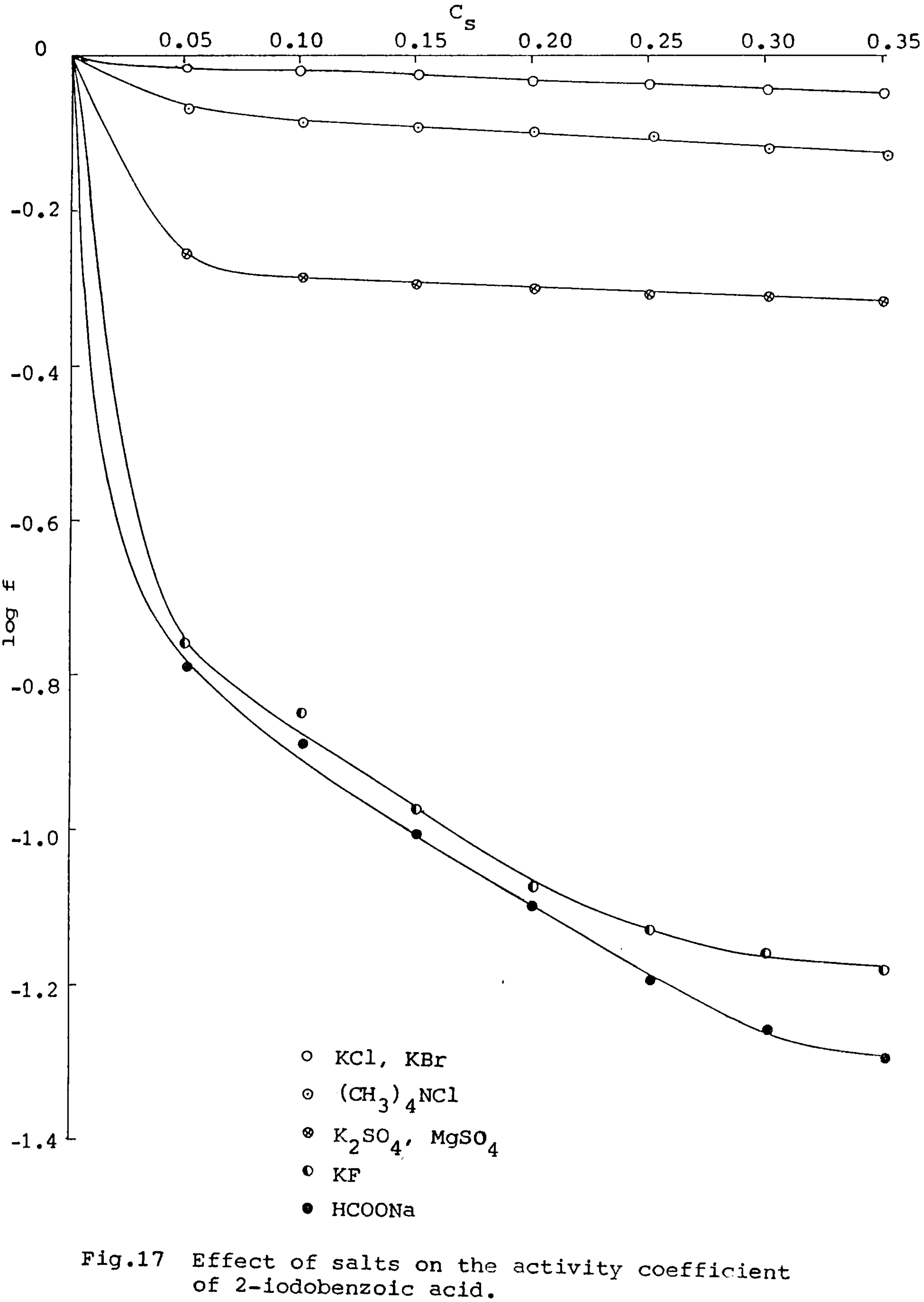


Fig.17 Effect of salts on the activity coefficient of 2-iodobenzoic acid.

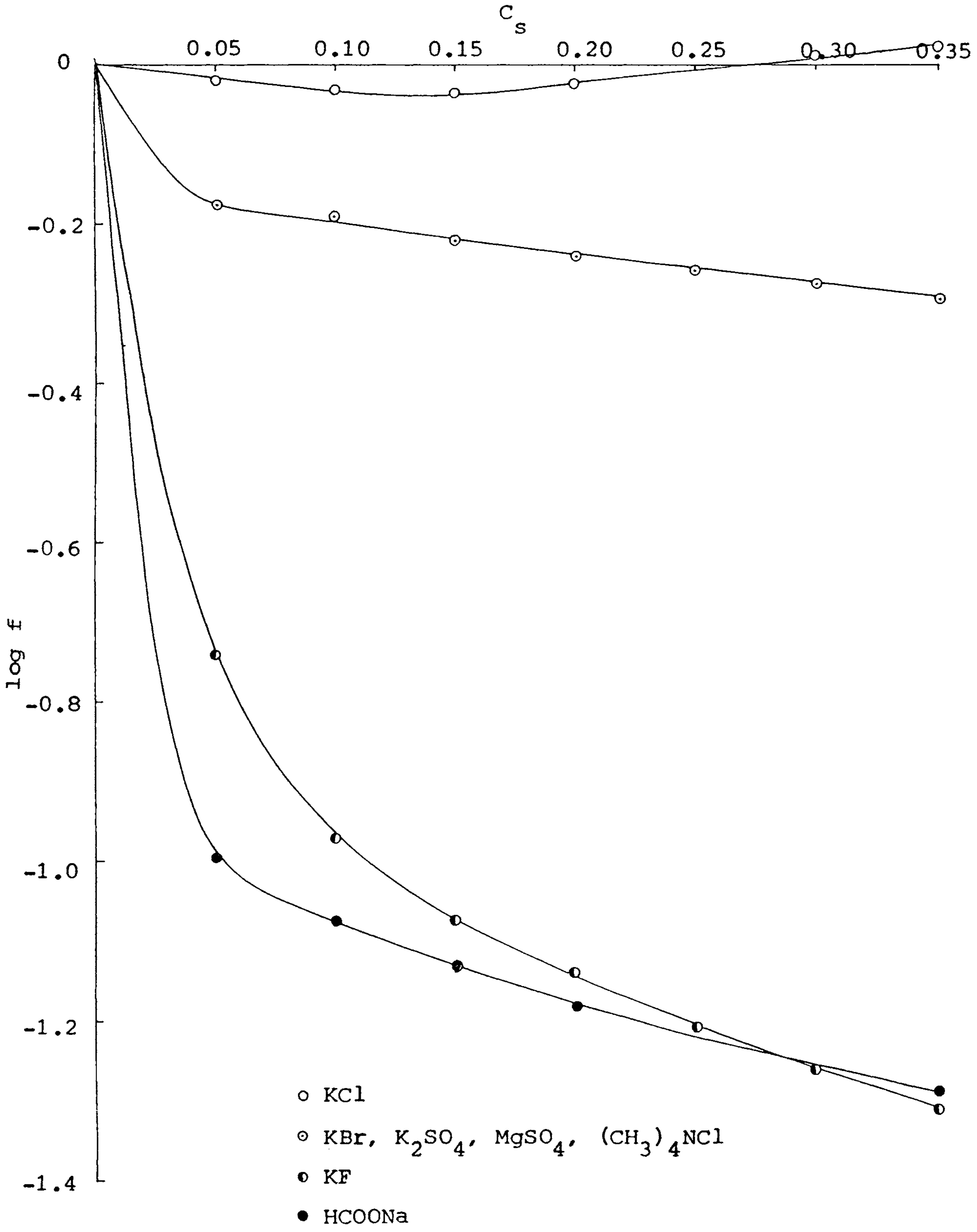


Fig.18 Effect of salts on the activity coefficient of 3-iodobenzoic acid.

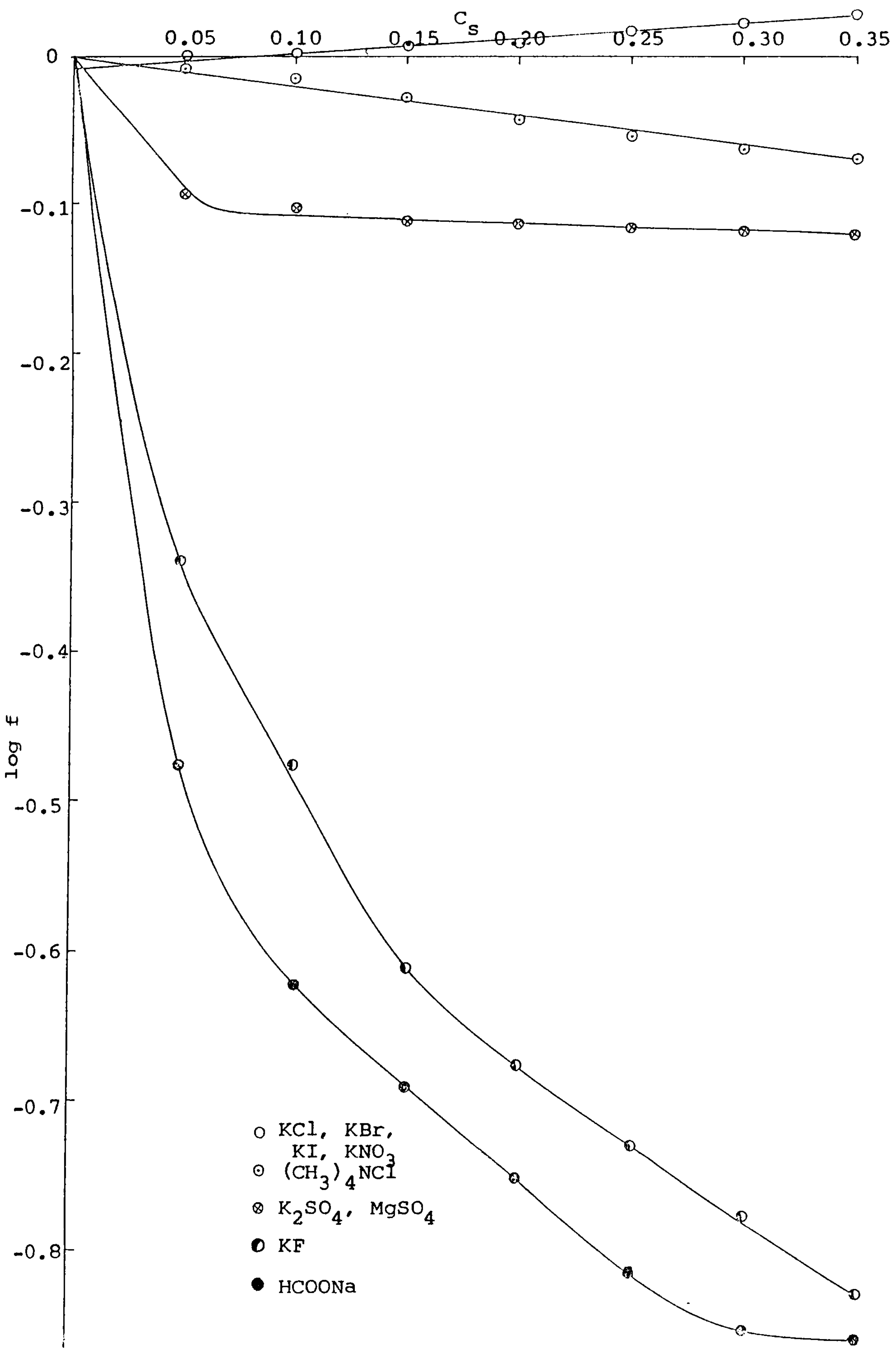


Fig.19 Effect of salts on the activity coefficient of 2-hydroxybenzoic acid.

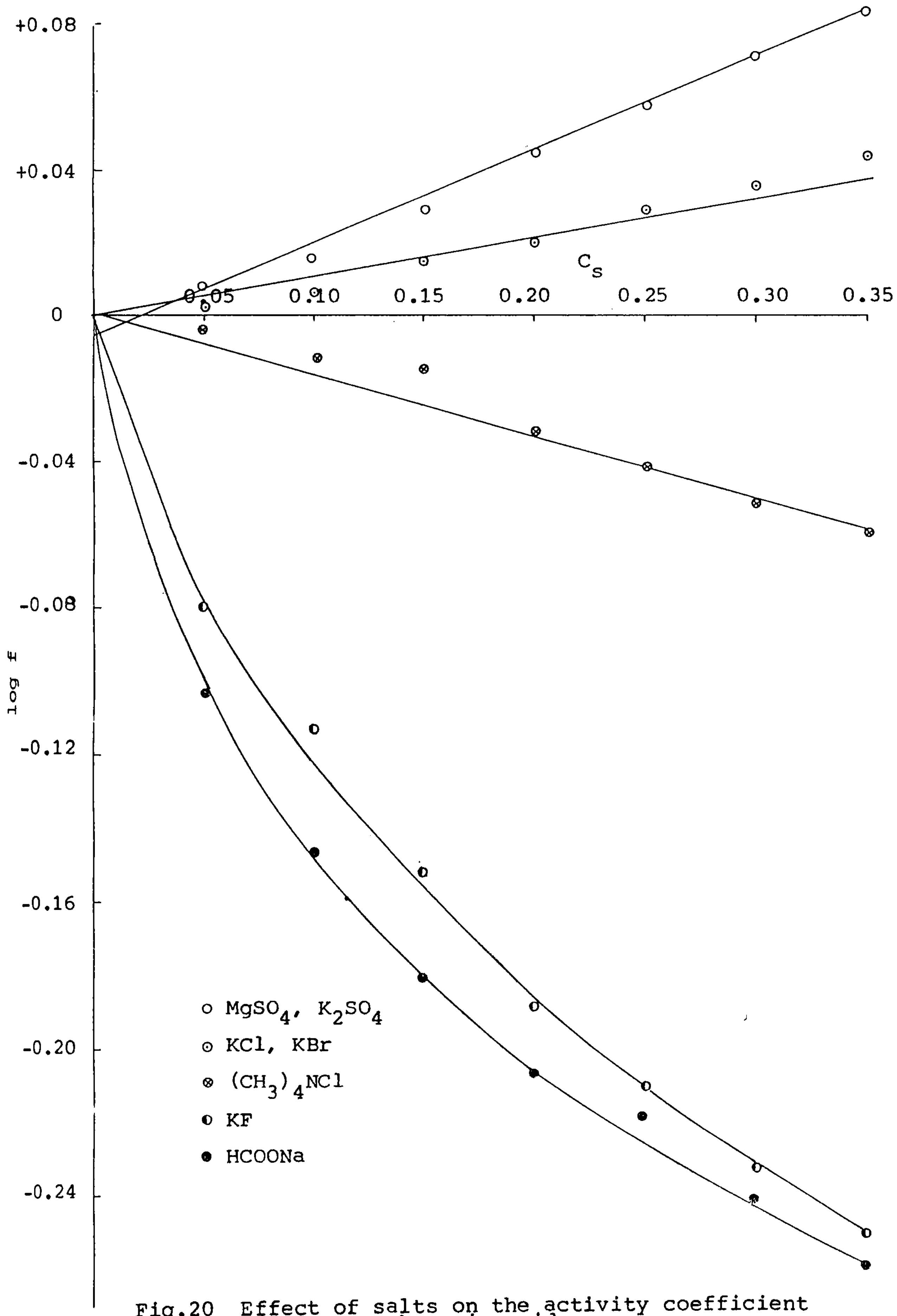


Fig.20 Effect of salts on the activity coefficient of 4-hydroxybenzoic acid.

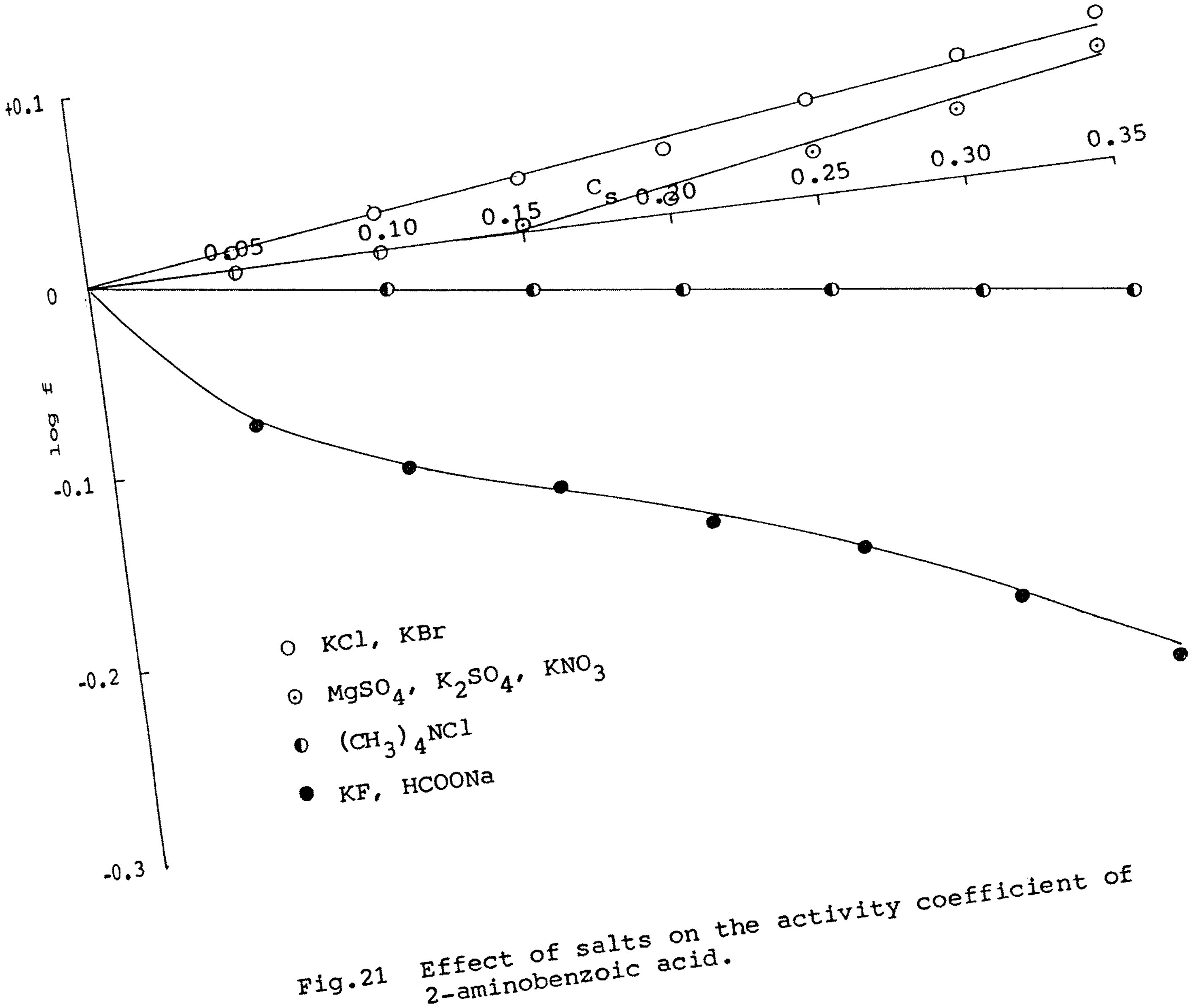


Fig.21 Effect of salts on the activity coefficient of 2-aminobenzoic acid.

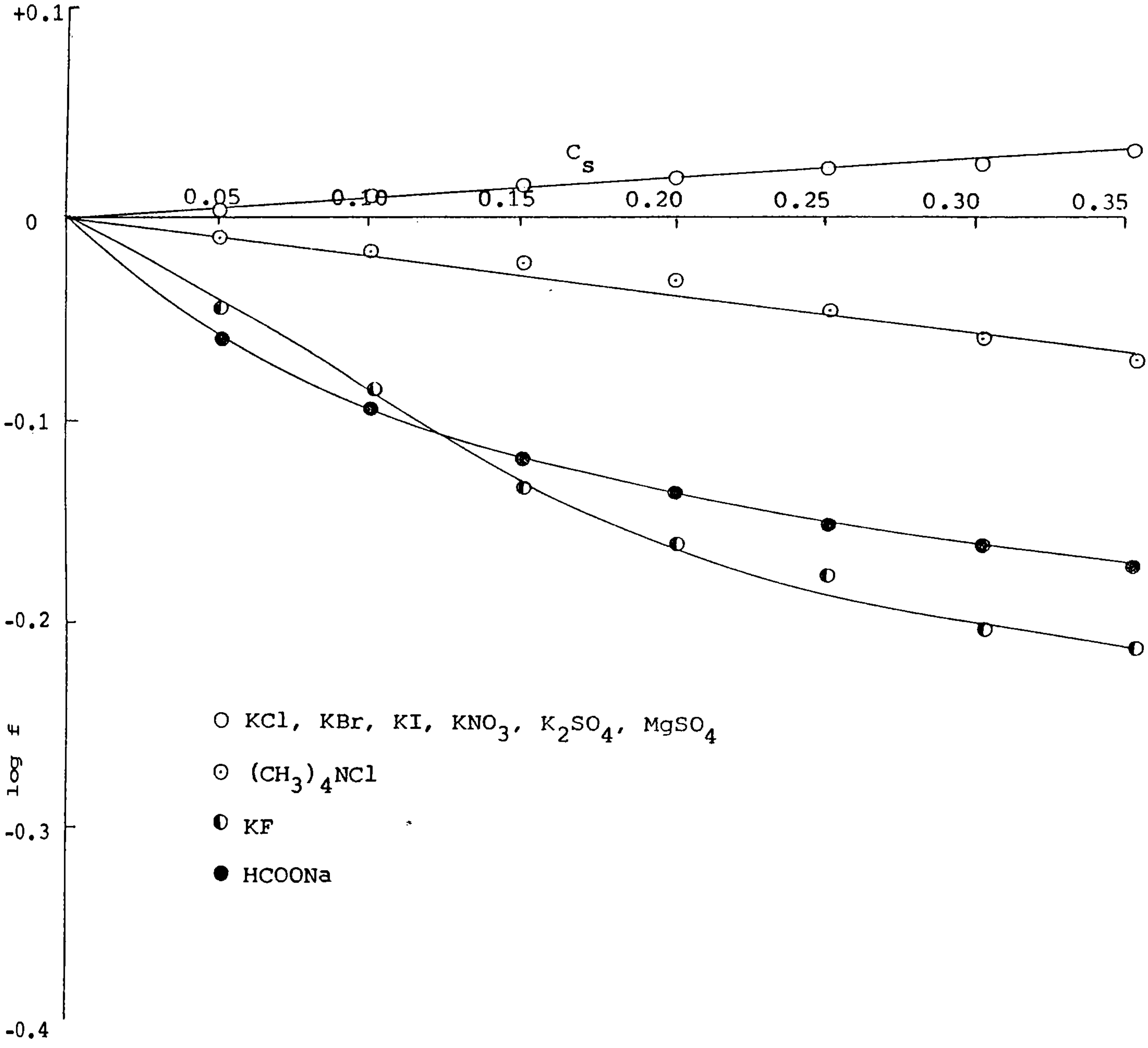


Fig.22 Effect of salts on the activity coefficient of 4-aminobenzoic acid.

benzoic acid is salted-in and does not obey the Setschenow equation with these salts.

Let us first consider the effect of sulphate ion on those solutes where the Setschenow equation is valid and salting-out is observed. Sulphate ion is a strong structure-maker.[23] This will reduce the solubility because the proportion of $(H_2O)_d$ molecules will be reduced. In other words, the immobilization of water molecules by the highly charged and compact sulphate ion increases the cohesive energy density fdorcing the solute to be squeezed out of the 'cavity' in solution resulting salting-out. Since Mg^{2+} is a powerful structure-maker and K^+ is structure breaker, $MgSO_4$ produces more salting-out than K_2SO_4 in accordance with the expectation. This is also true wherever salting-in is observed; that is to say $MgSO_4$ produces less salting-in than K_2SO_4. However, it is to be noted that the difference in salting-in/salting-out action between $MgSO_4$ and K_2SO_4, though present, is nominal in all the cases.

Before going to assess the effect of sulphate ion on other acids, for example, on nitrobenzoic acids it must be borne in mind that sulphate ion possesses two anionic charges which can experience electrostatic attraction between the positive end of the dipole of the water molecules and the hydrogen of the carboxyl group. This factor will definitely serve to increase solubility while the first factor, the structure-making property of the sulphate ion, reduces the solubility. We believe that the combined effect of these two factors are adequate to account for the results.

In nitrobenzoic acids, the electron-withdrawing nature of the nitro group makes the carboxyl proton more acidic. Such a behaviour cannot be seen in any other acids even in fluorobenzoic acids. The nitro group in nitrobenzoic acid make hydrogen bonds through the OH_f and the carboxyl group through the LP_f of the water molecules. The inductive effect of the nitro group favours this process by making both the nitro group and the carboxyl proton more sensitive to hydrogen bonding. However, it is to be noted that the contribution of the hydrogen bonding and hence to the total solubility by the two sites are not independent. In fluorobenzoic acids, the hydrogen bonding ability of the fluoro group and the carboxyl proton are independent of each other to a great extent so that the contribution due to the fluoro and carboxyl group to the total hydrogen bonding capacity of the system are additive.

As already stated, the sulphate ion, on its part increase the solubility through an electrostatic attraction between the negative end of the dipole of the water molecules and the hydrogen of the carboxyl group. The immobilization of water molecules by sulphate ion caused by the hydrogen bonding through the OH_f of water molecules will expose the LP_f site of water molecule to hydrogen bond with carboxyl proton of the acid solute. Thus acidity of the carboxyl proton plays the most significant role in the salt effect of the sulphate ion. The relationship between acidity and solubility has been discussed from similar studies on picric acid.[34] The results observed are also on the expected lines: The sulphate ion salted-in nitrobenzoic acids, chlorobenzoic acids, bromo- and iodobenzoic acids. Our argument is further substantiated by the salting-in of 2-hydroxybenzoic acid but not 4-hydroxybenzoic acid, fluorobenzoic acids, aminobenzoic acids and methylbenzoic acids (see the p^{ka} values - Table 14). The favourable effect on solubility due to the electrostatic effect will be important only when hydrogen-bonding occurs between the carboxyl group and the LP_f of the water molecules. This can be seen if we look into the corresponding data for the phthalic acid. There the Setschenow parameters have positive values.

Another point which deserves our attention is this: 4-hydroxybenzoic acid while salted-out by the potassium and magnesium sulphate, 2-hydroxybenzoic acid is salted-in. In 2-hydroxybenzoic acid, there is intramolecular hydrogen-bonding which increases the acidity of carboxyl proton. The p^{ka} value of 2.98 for 2-hydroxybenzoic acid thus suggest that the solubility increase is due to the increased hydrogen bonding through this proton. This is not the case with 4-hydroxybenzoic acid.

Comparing the salting-out action of potassium sulphate and magnesium sulphate, it is noted that in majority of the systems, magnesium sulphate salts-out more than potassium sulphate. According to Desnoyers *et al*[35] cation-anion structural hydration interaction promotes

Table 14

$p^{k}a$ values of monosubstituted benzoic acids at 25°C

Nonelectrolyte	$p^{k}a$ at 25°C
Benzoic acid	4.21
2-Nitrobenzoic acid	2.18
3-Nitrobenzoic acid	3.46
4-Nitrobenzoic acid	3.67
2-Methylbenzoic acid	3.90
3-Methylbenzoic acid	4.25
4-Methylbenzoic acid	4.37
2-Fluorobenzoic acid	3.47
3-Fluorobenzoic acid	3.85
4-Fluorobenzoic acid	3.85
2-Chlorobenzoic acid	2.92
3-Chlorobenzoic acid	3.82
4-Chlorobenzoic acid	3.98
3-Bromobenzoic acid	3.81
4-Bromobenzoic acid	3.97
2-Iodobenzoic acid	2.86
3-Iodobenzoic acid	3.79
2-Hydroxybenzoic acid	3.00
4-Hydroxybenzoic acid	6.25
2-Aminobenzoic acid	6.97
4-Aminobenzoic acid	4.92

the water structure by increasing hydrogen bonding while the cation-cation and anion-anion interactions lead to disordering of the surrounding water molecules. It has also been suggested that cation-cation interaction will prevail if the two ions are alike in their influence on the water structure which may be structure-promoting or structure-breaking. Thus in the case of magnesium sulphate, in aqueous solution Mg^{2+}- Mg^{2+} interactions will prevail since both Mg^{2+} and SO_4^{2-} ions are structure-makers. But, for K_2SO_4 cation-anion structural hydration prevails promoting water structure as the potassium ion and the sulphate ions have opposite influence on the water-structure. It follows from the above fact that salting-out parameter would be more for K_2SO_4 contrary to our observation. We are of the view that the total effect of the electrolyte on the structuredness of water will be sum of the independent contributions of constituent ions. If we assume this be the case, then definitely $MgSO_4$ will cause more salting-out than K_2SO_4. However, it is also admitted that the difference in the K_s values for these electrolytes on different solutes is very meagre.

Among halobenzoic acids, the salting-out of fluorobenzoic acid can be explained on the basis of structure-making action of sulphate ions. With the remaining acids, the gradual change from salting-out to salting-in and the total breakdown of the Setschenow equation as we go from fluorobenzoic acids to iodobenzoic acids can also be explained on similar lines as with the potassium halides. Here the polarizability of the halogens and the acidity of the carboxyl proton of the solutes affect the solubility of the latter.

B. Thermodynamics of transfer of monosubstituted benzoic acids from water to salt solutions

Thermodynamic parameters of transfer such as the free energy, the enthalpy and entropies of transfer of nitro-, methyl-, fluoro-, chloro-, bromo-, iodo-, hydroxy-, and aminobenzoic acids from water to 0.1 mol dm^{-3} of the salt solutions at 298°K are reported in the tables 15 to 24. The method of evaluating these parameters is discussed in detail in Chapter IV. As already stated within the limitations of this method, the objective underlying this investigation is to see to what extent the trend in the values of thermodynamic parameters of transfer agree with the interpretation which have been offered to explain the results of solubility in the presence of the various salts.

Table 15

1. Sodium formate (0.1 mol dm^{-3})

Temperature: 25°C

Mono substituted benzoic acid	ΔG (Jmol^{-1})	ΔH (Jmol^{-1})	ΔS (JK^{-1}mol^{-1})
2-nitro	-2949	-11830	-29.7
3-nitro	-2926	-9680	-22.6
4-nitro	-6161	-13290	-23.9
2-methyl	-2559	-8920	-21.3
3-methyl	-1887	-2370	14.3
4-methyl	-3109	-7040	-13.2
2-fluoro	-1715	-7220	-18.5
3-fluoro	-2293	-6420	-13.8
4-fluoro	-2826	-4970	-7.2
2-chloro	-4325	-8520	-14.1
3-chloro	-4277	-6430	-7.2
4-chloro	-6186	-9590	-11.4
3-bromo	-5255	-12570	-24.2
4-bromo	-7414	-9960	-8.5
2-iodo			
3-iodo	-6331	-6930	-2.0
2-hydroxy	-3890	-9350	-18.3
4-hydroxy	-897	-1740	-2.8
2-amino	-696	-4970	-14.3
4-amino	-730	-4230	-11.7

Table 16

2. Potassium fluoride (0.1 mol dm^{-3})

Temperature: 25°C

Mono substituted benzoic acid	ΔG ($Jmol^{-1}$)	ΔH ($Jmol^{-1}$)	ΔS ($JK^{-1}mol^{-1}$)
2-nitro	-2351	-12860	-35.2
3-nitro	-2200	-2450	-0.8
4-nitro	-5329	-8830	-11.7
2-methyl	-1890	170	6.9
3-methyl	-1812	3660	18.3
4-methyl	-2868	2660	18.5
2-fluoro	-1286	-730	-20.2
3-fluoro	-1905	-4140	-7.5
4-fluoro	-2370	-4610	-7.5
2-chloro	-3442	-6690	-10.8
3-chloro	-3880	-6360	-8.3
4-chloro	-6698	-9560	-9.6
3-bromo	-4826	-7520	-9.0
4-bromo	-7637	-10250	-9.0
2-iodo	-7214	-6170	3.5
3-iodo	-6664	-6420	0.8
2-hydroxy	-3056	-8530	-18.3
4-hydroxy	-852	-6090	-17.6
2-amino	-741	-4250	-11.7
4-amino	-556	-2830	-7.6

Table 17

3. Potassium chloride (0.1 mol dm^{-3})

Temperature: 25°C

Mono substituted benzoic acid	ΔG ($Jmol^{-1}$)	ΔH ($Jmol^{-1}$)	ΔS ($JK^{-1}mol^{-1}$)
2-nitro	-200	-1380	-3.9
3-nitro	-199	-940	-2.5
4-nitro	-212	-1260	-3.5
2-methyl	119	1920	6.0
3-methyl	244	1610	4.6
4-methyl	99.4	2890	9.4
2-fluoro	162	500	1.1
3-fluoro	115	110	3.4
4-fluoro	146	940	2.7
2-chloro	45	1460	-4.8
3-chloro	-34.1	-770	-2.5
4-chloro	-89	-1180	-3.6
3-bromo	-380	-1450	-3.6
4-bromo	-273	-820	-1.8
2-iodo	-216	-1750	-5.1
3-iodo	-204	-1690	-4.9
2-hydroxy	1.54	-170	-0.6
4-hydroxy	26.2	-600	-2.1
2-amino	34.1	1060	3.4
4-amino	91.8	890	2.7

Table 18

4. Potassium bromide (0.1 mol dm^{-3})

Temperature: 25°C

Mono substituted benzoic acid	ΔG ($Jmol^{-1}$)	ΔH ($Jmol^{-1}$)	ΔS ($JK^{-1}mol^{-1}$)
2-nitro	-299	-2570	-7.6
3-nitro	-301	-2690	-8.0
4-nitro	-251	-1220	-3.3
2-methyl	97.6	1790	5.7
3-methyl	209	2110	6.4
4-methyl	-18.7	2620	8.8
2-fluoro	143	600	1.5
3-fluoro	74.3	1430	4.5
4-fluoro	61.2	910	2.8
2-chloro	-12.3	1310	4.4
3-chloro	-191	-2740	-8.5
4-chloro	-557	-2610	-6.9
3-bromo	-568	-2100	-5.1
4-bromo	-742	-860	-3.8
2-iodo	-248	-1720	-4.9
3-iodo	-465	-5070	-15.4
2-hydroxy	61.2	-460	-1.3
4-hydroxy	11.4	-360	-1.2
2-amino	-16.5	970	3.3
4-amino	513	920	2.9

Table 19

5. Potassium iodide (0.1 mol dm^{-3})

Temperature: 25°C

Mono substituted benzoic acid	ΔG ($Jmol^{-1}$)	ΔH ($Jmol^{-1}$)	ΔS ($J\ mol^{-1}$)
2-nitro	-320	-2700	-7.9
3-nitro	-322	-2670	-7.9
4-nitro	-320	-1490	-3.9
2-methyl	52.1	2600	8.6
3-methyl	41.4	2480	8.2
2-fluoro	72.4	560	1.6
3-fluoro	-28.6	1450	4.8
4-fluoro	27.8	870	3.2
2-hydroxy	-83.5	-550	-1.6
2-amino	-50.7	640	2.7
4-amino	34.8	1280	4.2

Table 20

6. Potassium thiocyanate (0.1 mol dm^{-3})

Temperature: 25°C

Mono substituted benzoic acid	ΔG ($Jmol^{-1}$)	ΔH ($Jmol^{-1}$)	ΔS ($JK^{-1}mol^{-1}$)
2-nitro	-353	-3130	-9.3
3-nitro	-371	-2830	-8.3
4-nitro	-391	-1460	-3.6
2-fluoro	47.6	660	2.1
3-fluoro	-6.1	830	2.8

Table 21

7. Potassium nitrate (0.1 mol dm^{-3})

Temperature: 25°C

Mono substituted benzoic acid	ΔG ($Jmol^{-1}$)	ΔH ($Jmol^{-1}$)	ΔS ($JK^{-1}mol^{-1}$)
2-nitro	-207	-1370	-3.9
3-nitro	-206	-730	-1.71
4-nitro	-259	-1170	-3.1
2-methyl	-25.3	-790	-2.6
3-methyl	-109	2350	8.3
2-fluoro	162	1780	5.4
3-fluoro	36.1	1920	6.3
4-fluoro	188	1330	4.4
2-hydroxy	-185	-1570	-4.7
2-amino	84.5	880	2.7
4-amino	26.1	1010	3.3

Table 22

10. Tetramethylammonium chloride (0.1 mol dm^{-3})

Temperature: 25°C

Mono substituted benzoic acid	ΔG ($Jmol^{-1}$)	ΔH ($Jmol^{-1}$)	ΔS ($JK^{-1}mol^{-1}$)
2-nitro	-287	-570	-0.9
3-nitro	-317	-2620	-7.7
4-nitro	-273	-2220	-6.5
2-methyl	-27.1	920	3.2
3-methyl	49.9	2660	8.8
4-methyl	31.1	580	2.1
2-fluoro	-56	1630	5.7
3-fluoro	-47.9	1930	6.6
4-fluoro	-10.4	1190	4.1
2-chloro	-46.8	1120	3.9
3-chloro	-241	-1850	5.4
4-chloro	-193	1080	4.3
3-bromo	-536	1250	-2.4
4-bromo	-460	-2990	-8.5
2-iodo	-654	-5900	-17.6
3-iodo	-390	-5760	-15.5
2-hydroxy	-51.7	-1590	5.5
4-hydroxy	-29.5	-600	-1.9
2-amino	-31.6	-720	-2.3
4-amino	-159	-1560	-4.7

Table 23

8. Potassium sulphate (0.1 mol dm^{-3})

Temperature: 25°C

Mono substituted benzoic acid	ΔG ($Jmol^{-1}$)	ΔH ($Jmol^{-1}$)	ΔS ($JK^{-1}mol^{-1}$)
2-nitro	-882	-3240	-7.9
3-nitro	-393	-2640	-7.5
4-nitro	-1103	-1570	-1.6
2-methyl	-63.8	-2460	-8.1
3-methyl	50.0	2080	6.8
4-methyl	-85.7	-1490	-4.7
2-fluoro	11.0	-920	-3.1
3-fluoro	-22.4	-1080	-2.9
4-fluoro	-224	-1340	-3.8
2-chloro	-606	-1340	-2.5
3-chloro	-597	-810	-6.9
4-chloro	-1124	-2630	-5.1
3-bromo	-1071	-2630	-5.2
4-bromo	-1656	-2400	-2.5
2-iodo	-1710	-5800	-13.7
3-iodo	-1245	-4710	-14.6
2-hydroxy	-553	1170	5.8
4-hydroxy	-405	1430	6.2
2-amino	18.2	-1320	4.5
4-amino	40.1	-201	-0.8

Table 24

9. Magnesium sulphate (0.1 mol dm^{-3})

Temperature: 25°C

Mono substituted benzoic acid	ΔG ($Jmol^{-1}$)	ΔH ($Jmol^{-1}$)	ΔS ($JK^{-1}mol^{-1}$)
2-nitro	-763	-3970	-10.8
3-nitro	-298	-2530	-7.5
4-nitro	-984	-2060	-3.6
2-methyl	64.3	-2690	-9.3
3-methyl	138.7	1710	5.3
4-methyl	-11.1	-3040	-10.2
2-fluoro	129	-1270	-4.7
3-fluoro	-35.9	-2640	-8.7
4-fluoro	50.0	-600	-18.6
2-chloro	-448	1210	-2.5
3-chloro	-418	-1590	-3.9
4-chloro	-925	-3130	-7.4
3-bromo	-886	-2190	-4.4
4-bromo	-1179	-1570	-1.3
2-iodo	-1487	-6400	-16.5
3-iodo	-1085	-5710	-15.5
2-hydroxy	-405	-1430	6.2
4-hydroxy	476	-1010	-3.5
2-amino	74.8	-640	-2.2
4-amino	20.9	-370	-1.3

i) Potassium fluoride and sodium formate

The results show (i) the free energy of transfer is highly negative, (ii) except for 2-, 3-, and 4-methylbenzoic acids, the entropy term is negative, and (iii) the enthalpy of transfer is negative and is appreciable except for methylbenzoic acids and that too only for the electrolyte KF.

The observed fact of increased solubility in potassium fluoride and sodium formate is supported by the appreciably large negative free energy of transfer of the solute from water to salt solutions. It is to be noted that the free energy may be negative because the enthalpy may be more negative than $T \Delta S_{tr}$ or $T\Delta S_{tr}$ may be more positive than ΔH_{tr} or due to both negative ΔH_{tr} and positive $T \Delta S_{tr}$ term. In the present case, it is seen that ΔH_{tr} and not $T \Delta S_{tr}$ contribute favourably to the ΔG_{tr} term.

It has been suggested earlier that the reason for the steep increase in the solubility of benzoic acids in presence of added potassium fluoride and sodium formate is due to some sort of acid-base interaction between the carboxyl proton of the solute and the fluoride/formate ion. The salting-in occurs despite the fact that the $\bar{F}$ and $HCO\bar{O}$ are powerful structure-makers. As proposed above, if acid-base interaction be the reason of increased solubility, then the favourable enthalpy of transfer can be rationalized. Since both these ions are powerful structure-makers, energy will be required to desolvate the ions, which may offset to an unknown extent by the formation of the hydrogen bond with the fluoride and formate ions. This desolvation should be attended by a large increase in entropy, which, likewise may be offset by the hydrogen-bonding with the fluoride/formate ion. If the interpretation is correct the results should show that the dominant term responsible for the free energy decrease is of entropic origin. However, the negative entropy values in majority of the cases suggest that the water molecules liberated during the desolvation process are still under the influence of the electrical field of the fluoride/formate ion. This results in ordering of water molecules around the 'solute-ion' species decreasing the entropy. In other words, the desolvation phenomenon is the driving force for the dissolution process. The enthalphy term is negative suggesting that the endothermicity of desolvation is essentially balanced by the exothermicity of the acid-base interaction between the solute and the fluoride/formate ion.

In the case of methylbenzoic acids, the data can be rationalized by suggesting that the spontaneity of the dissolution process is possible due to the entropy term operating against the highly unfavourable enthalpy. The thermodynamic data on these solutes with the fluoride ion indicate that the compact F^- with high electrical density is solvated extensively through ion-dipole interaction and the energy required for desolvation is more than to compensate for the energy gain through the acid-base interaction. The liberated water molecules constitute what we call a 'chaotropic medium' which makes the dissolution process spontaneous.

ii) Potassium chloride, potassium bromide, potassium iodide, potassium thiocyanate and potassium nitrate

The results can be summarized as follows: (1) The free energy of transfer of nitrobenzoic acids, bromobenzoic acids and iodobenzoic acids are all negative. However the values are extremely small and are within ±1 kJ mole^{-1}. (ii) With fluoro-, chloro-, methyl-, amino-, and hydroxybenzoic acids ΔG_{tr} is positive. It is to be noted that as the size of the anion increases, the free energy of transfer decreases and becomes negative. Here also the ΔG_{tr} values are very small. (iii) As regards the enthalpy values, the observed results do not conform to any regular trend. Nonetheless, the results can be classified into two: when the electrolyte salted-in the solutes, it is accompanied by a negative enthalpy factor and negative entropy term, and when the electrolyte salted-out the solutes enthalpy is positive and entropy is positive. However, both the enthalpy and entropy parameters are very small in all cases. There are exceptions to this pattern also.

Because of the small values of thermodynamic parameters of transfer it is not fruitful to try to assess their significance excepting in a very general way. When the effect of these electrolytes on the activity coefficient of different solutes is analysed emphasis has been laid on the fact that such diverse results could not be accounted by a single theory of the salt effect. For example, the salting-in of nitrobenzoic acid is explained by the structure-breaking action of the ions. The structure-breaking action of the ions thus will directly increase the entropy factor and indirectly make the enthalpy more exothermic because the structure-breaking action enhances the probability of hydrogen bonding with the liberated water molecules. Thus our view on the solubility of nitrobenzoic acids in presence of these salts is vindicated by the thermodynamic parameters.

On the other hand, the salting-out of methyl-, fluoro-, amino-, and hydroxybenzoic acid is considered to be due to the electrostriction produced by these salts forcing the solutes to "come out" of the hole created for it in the solution. The electrostriction will definitely reduce both entropy and exothermicity. Arnett *et al.*[36] has reported that the free energy of salting-out for a number of nonelectrolytes by simple inorganic salts is dominated by an endothermic trend in enthalpy at nearly constant entropy. All we can say from the results is that they do not militate against the interpretations offered earlier.

iii) Tetramethylammonium chloride

The results are: (i) the free energy of transfer for all the solutes are negative and is small. (ii) With fluoro-, chloro-, and methylbenzoic acids, the enthalpy of transfer is positive; in other cases it is negative. (iv) Entropy is positive where enthalpy is positive and vice-versa.

The negative ΔG_{tr} for the transfer process in presence of tetramethylammonium chloride shows that the solubility of all solutes is increased by the addition of $(CH_3)_4NCl$. The explanation provided for KCl, KBr etc. also holds good for tetramethylammonium chloride. The negative entropy observed in certain cases may be due to the partial ordering of the liberated water molecules around the solute species. In the case of methyl-, fluoro-, and chlorobenzoic acids, the striking feature is that the increased solubility (exhibited by an increasingly negative free energy of dissolution) occurs inspite of a rapidly increasing endothermic trend in the heat of dissolution. Thus, here the salting-in of these acids in presence of $(CH_3)_4NCl$ is entirely the result of a favourable trend in entropy operating in opposition to an unfavourable trend in the enthalpy.

iv) Potassium sulphate and magnesium sulphate

The following are the results: (i) The free energy of transfer is small and is within ±1 kJ $mole^{-1}$. (ii) The enthalpy of transfer is negative in all cases except for 2-hydroxybenzoic acid where ΔH_{tr} is positive. (iii) The entropy is negative in majority of the cases. However, with 2-aminobenzoic acid and 2-hydroxybenzoic acid ΔS_{tr} is positive.

Potassium sulphate and magnesium sulphate shows exceptionally high solubility with nitrobenzoic acids, and 2-hydroxybenzoic acid. The highly negative free energy of transfer lends support to the above observation. However in the former case the negative free energy is accompanied by a favourable enthalpy and an unfavourable entropy while an unfavourable enthalpy and a positive entropy gain in the latter. It is a known fact that sulphate ion is a powerful structure-maker and possesses two sites for hydrogen bonding. So the enthalpy of transfer process should have contributions from two compensating effects namely, an endothermic component due to the desolvation of the sulphate ion and an exothermic component due to the desolvation of the sulphate ion and an exothermic component due to the greater hydrogen bonding with the solute molecules. But we should expect the latter factor to be more important so that the net enthalpy should have been negative. This is the case with all solutes except 2-hydroxybenzoic acid. The unfavourable entropy term indicates that some of the liberated water molecules are still under the influence of the strong electric field of the sulphate ion causing a partial ordering and decreasing the entropy as in the case of the fluoride and formate ion.

In 2-hydroxybenzoic acid, there is intramolecular hydrogen bonding between the hydroxyl group and the carboxyl proton of the acid. The increased solubility of 2-hydroxybenzoic acid is due to the hydrogen bonding with the water molecules through the hydroxyl and carboxyl group. But the fact is that both the groups hydrogen bond with water molecules through LP_f site of the latter while in 2-nitrobenzoic acid and 2-fluorobenzoic acid, the fluoro- and nitro group make use of the OH_f site of water molecules for H-bonding. According to the localized hydrolysis models, the protons of water molecules will be oriented towards the sulphate ions and hydrogen bond formation with the carboxyl and hydroxyl groups will thus be enhanced through the LP_f of water molecules bound with the sulphate ion. The only unfavourable situation is the intramolecular hydrogen bond. We are unable to interpret this alone would be the reason for the reversal of both the enthalpy and entropy while the free energy of the solution continues in a spontaneous direction as their resultant.

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Chapter IV

EXPERIMENTAL

Materials

The electrolytes used for the study were potassium halides, potassium nitrate, potassium thiocyanate, potassium sulphate, magnesium sulphate, tetramethylammonium chloride and sodium formate. All the electrolytes were of A.R. Grade and were used as such without further purification.

The solutes selected were monosubstituted benzoic acids, and included ortho-, meta- and para-nitrobenzoic acids, methylbenzoic acids, fluorobenzoic acids, chlorobenzoic acids, meta- and para-bromobenzoic acids, ortho- and meta-iodobenzoic acids, ortho- and para-aminobenzoic acids, and ortho- and para hydroxy benzoic acids. Except amino- and hydroxy benzoic acids, all other compounds were of synthetic grade and were checked for purity by comparing their melting points to literature values, and were recrystallized if found necessary (Table 25). Amino and hydroxy benzoic acids were purified by repeated recrystallization from hot water.

Table 25

The observed and literature values for the melting points of the compounds studied

Compound	Melting point Observed (°C)	Literature value (°C)[8]
Benzoic acid	122	122.4
2-Nitrobenzoic acid	148	147.5
3-Nitrobenzoic acid	142	142.0
4-Nitrobenzoic acid	241	240.0
2-Methylbenzoic acid	107	105.0
3-Methylbenzoic acid	111	110.0
4-Methylbenzoic acid	182	180.0
2-Fluorobenzoic acid	125	122.0
3-Fluorobenzoic acid	125	124.0
4-Fluorobenzoic acid	185	185.0
2-Chlorobenzoic acid	142	140.2
3-Chlorobenzoic acid	155	154.3
4-Chlorobenzoic acid	240	239.7
3-Bromobenzoic acid	155	157.0
4-Bromobenzoic acid	250	253.0
2-Iodobenzoic acid	161	162.0
3-Iodobenzoic acid	190	188.0
2-Hydroxybenzoic acid	159	158.3
4-Hydroxybenzoic acid	214	215.5
2-Aminobenzoic acid	147	147.0
4-Aminobenzoic acid	189	188.0

Procedures

We have used the solubility method to study the salt effect because this method has been used extensively for various classes of organic compounds such as amino acids[1,2], phenols and cresols[3], toluene[4] benzoyltrifluoroacetone[5], hydrocarbons and substituted benzenes[6], monoalkylbenzene[7] etc. The solubilities of the above acidic solutes were determined in water, and in aqueous electrolyte solutions of concentrations in the range 0.05 mol dm^{-3} to 0.35 mol dm^{-3} of the electrolyte by spectroscopic methods. Doubly distilled water was used throughout the experiment.

The general procedure was to mix a small quantity of the solute and the salt solutions at different concentrations in a boiling tube filled with mercury sealed apparatus to minimise the loss due to evaporation. The whole system is kept in a thermostated bath (Haake E3 Model) at 35°C. The solution is then shaken thoroughly by an indigenously fabricated shaking machine, the speed of which can be regulated. To check whether the sample attains equilibrium 1 ml aliquots were withdrawn periodically and spectroscopical measurements were carried out on it after proper dilution. It was found that in majority of the cases, the equilibration of the sample was achieved within five hrs. when the optical density readings were constant within one to two per cent.

Spectral measurements were made at a number of wavelengths near the wavelength maximum for each of the solute in order to note whether any shifts occur in the absorption spectrum of the compound. This was for detecting the development of colloidal dispersion and for detecting the incursion of chemical reactions. The wavelength maximum for each compound at which solubility measurements were made, were given in Table 26.

The electrolytes KI, KNO_3 and KSCN have strong absorptions in the wavelength region 225 nm to 250 nm where some of the solutes studied also have strong absorptions. To avoid interference due to the high absorption of these electrolytes, spectral observations were made at a wavelength outside this region (Table 27). It has been noted that the absorbance and molar extinction coefficients were relatively small.

Table 26

The wavelength maximum at which the optical density measurements were made for each compound

Compound	exptal $\lambda^{(nm)}$
Benzoic acid	273.0
2-Nitrobenzoic acid	268.4
3-Nitrobenzoic acid	265.2
4-Nitrobenzoic acid	272.0
2-Methylbenzoic acid	229.6
3-Methylbenzoic acid	231.6
4-Methylbenzoic acid	238.8
2-Fluorobenzoic acid	228.0
3-Fluorobenzoic acid	228.0
4-Fluorobenzoic acid	228.0
2-Chlorobenzoic acid	230.0
3-Chlorobenzoic acid	228.0
4-Chlorobenzoic acid	230.0
3-Bromobenzoic acid	228.0
4-Bromobenzoic acid	239.6
2-Iodobenzoic acid	225.0
3-Iodobenzoic acid	225.0
2-Hydroxybenzoic acid	297.0
4-Hydroxybenzoic acid	249.0
2-Aminobenzoic acid	323.0
4-Aminobenzoic acid	276.0

Table 27

The solutes and its corresponding λ_{max} at which spectral measurements were conducted and is applicable only when studied in the presence of the electrolytes KI, KNO_3 and KSCN

Compound	Wavelength λ_{max} (nm)
1-methyl benzoic acid	275
3-methyl benzoic acid	278
2-fluorobenzoic acid	274
3-fluorobenzoic acid	276
4-fluorobenzoic acid	265

When the sample attained equilibrium, 2 ml aliquots were withdrawn, and the absorbance of the solution was measured on a UV spectrophotometer (Hitachi Model 200). Beer's law test were made on the solute by proper dilution of the most concentrated solutions with doubly distilled water. All experiments were done in duplicate.

To determine the thermodynamic parameters of transfer from water to salt solutions, the solubilities of the above solutes were also determined at temperatures 20°C, 25°C, 35°C and 40°C in water and in 0.1 mol dm^{-3} of the salt solutions, using similar procedure.

Treatment of data and results

The results of the solubility experiments were reported in Tables 4 - 13 (see Results and Discussion). The values reported were the equilibrium solubilities of the solutes in unionized form obtained from optical density measurements.

In analysing the solubility data, inconsistency was found in the absorbance measurements for 2-bromo-benzoic acid and 4-iodobenzoic acid. It is to be noted that spectral readings were taken for these compounds even after 36 hrs. of equilibration. However, we could not decide what phenomenon might be occurring either colloidal dispersion or some chemical reaction.

The values of log f were calculated by dividing the solubility of each compound in water by the solubility of that compound in electrolyte solutions. This gives the solubility in salt solution relative to the solubility in water. The logarithm of this relative solubility is log f, which is equivalent to defining the activity coefficient of the pure substance as unity. Since the solubilities were of the order of 10^{-2} mol dm^{-3} or less the value of log f is found as a function of salt concentration only in majority of the cases.

In order to compare relative salt effects in salt solutions, the Setschenow constants were evaluated for those solute-electrolyte pairs where Setschenow equation was obeyed, from plots of log f versus C_s, the concentrations of the electrolyte in moles dm^{-3}. This data is also presented in Tables 4 - 13 (see Chapter III). The K_s values were evaluated by the least squares method and the probable errors[9] were also computed.

The standard free energy of transfer of a mole of nonelectrolyte from pure water to a salt solution of concentration C_s was calculated from the equation

$$\Delta G = 2{\cdot}303\ RT\ K_s$$

The enthalpy of transfer was determined by applying the Van't Hoff isochore to K_s, the salting coefficients at different temperatures. The log f values versus the inverse of the temperature are plotted and their slopes give the ΔH_{tr} values. The ΔH_{tr} values were also computed by the method of least squares and are reported in the Table 15-24 The entropy of transfer is obtained from the relation

$$\Delta S_{tr} = \frac{\Delta H - \Delta G}{T}$$

Table 28

Solubility of 2-nitrobenzoic acid in water (10^2 mol dm^{-3}): 2.690 (20°C), 2.986 (25°C), 4.145 (35°C), 4.916 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electroylte	Solubility (10^2 mol dm^{-3}) at 0.1 ml dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	9.470	9.962	11.705	12.762
KF	7.482	7.869	8.972	9.899
KCl	2.938	3.250	4.401	5.195
KBr	3.071	3.395	4.521	5.265
KI	3.111	3.409	4.545	5.311
KSCN	3.152	3.460	4.620	5.299
KNO_3	2.961	3.237	4.406	5.226
K_2SO_4	3.926	4.259	5.672	6.590
$MgSO_4$	3.729	4.112	5.367	6.176
$(CH_3)_4NCl$	3.068	3.384	4.654	5.529

Table 29

Solubility of 3-nitrobenzoic acid in water (10^2 mol dm^{-3}): 1.407 (20°C), 1.911 (25°C), 2.708 (35°C), 3.200 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electroylte	Solubility (10^2mol dm^{-3}) at 0.1 ml dm^{-3} salt solutions 20°C	25°C	35°C	40 °C
HCOONa	4.840	6.319	7.748	8.615
KF	3.474	4.639	6.386	7.397
KCl	1.538	2.064	2.901	3.406
KBr	1.624	2.147	2.952	3.433
KI	1.632	2.173	2.985	3.454
KSCN	1.666	2.221	3.021	3.525
KNO_3	1.541	2.069	2.915	3.432
K_2SO_4	1.678	2.238	3.073	3.555
$MgSO_4$	1.618	2.150	2.946	3.445
$(CH_3)_4NCl$	1.630	2.165	2.988	3.447

Table 30

Solubility of 4-nitrobenzoic acid in water (10^3 mol dm^{-3}): 1.015 (20°C), 1.237 (25°C), 1.689 (35°C), 1.922 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electroylte	Solubility (10^3mol dm^{-3}) at 0.1 ml dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	13.255	15.024	16.870	17.897
KF	9.204	10.643	13.068	13.755
KCl	1.118	1.343	1.811	2.044
KBr	1.134	1.366	1.840	2.077
KI	1.168	1.404	1.890	2.121
KSCN	1.201	1.448	1.938	2.190
KNO_3	1.137	1.371	1.849	2.085
K_2SO_4	1.598	1.931	2.595	2.897
$MgSO_4$	1.527	1.841	2.461	2.731
$(CH_3)_4NCl$	1.149	1.384	1.830	2.056

Table 31

Solubility of 2-methylbenzoic acid in water (10^3 mol dm^{-3}): 6.060 (20°C), 7.889 (25°C), 11.896 (35°C), 13.831 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electroylte	Solubility (10^3mol dm^{-3}) at 0.1 ml dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	17.948	22.430	29.437	32.776
KF	12.989	16.909	25.465	29.831
KCl	5.705	7.573	11.609	13.698
KBr	5.765	7.573	11.679	13.799
KI	5.835	7.709	12.073	14.232
KNO_3	6.243	8.037	11.924	13.661
K_2SO_4	6.316	8.109	11.814	13.531
$MgSO_4$	6.010	7.682	11.255	12.739
$(CH_3)_4NCl$	6.090	7.970	12.185	14.226

Table 32

Solubility of 3-methylbenzoic acid in water (10^3 mol dm^{-3}): 7.860 (20°C), 9.146 (25°C), 11.341 (35°C), 12.632 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electroylte	Solubility (10^3 mol dm^{-3}) at 0.1 ml dm^{-3} salt solutions 20°C	25°C	35°C	40°C
HCOONa	16.403	19.836	24.969	28.275
KF	15.929	19.011	24.628	28.244
KCl	7.043	8.273	10.581	11.749
KBr	7.114	8.411	10.722	12.082
KI	7.606	8.964	11.604	12.977
KNO_3	8.078	9.573	12.201	13.831
K_2SO_4	7.578	8.990	11.425	12.877
$MgSO_4$	7.363	8.616	10.987	12.340
$(CH_3)_4NCl$	7.576	8.947	11.514	13.041

Table 33

Solubility of 4-methylbenzoic acid in water (10^3 mol dm^{-3}): 1.930 (20°C), 2.428 (25°C), 3.421 (35°C), 3.919 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electrolyte	Solubility (10^3 mol dm^{-3}) at 0.1 ml dm^{-3} salt solutions 20°C	25°C	35°C	40°C
HCOONa	7.083	8.558	10.832	12.050
KF	6.020	7.723	11.328	13.068
KCl	1.827	2.317	3.412	3.990
KBr	1.909	2.452	3.551	4.166
K_2SO_4	2.020	2.509	3.478	3.939
$MgSO_4$	1.978	2.443	3.295	3.716
$(CH_3)_4NCl$	1.946	2.460	3.490	4.013

Table 34

Solubility of 2-fluorobenzoic acid in water (10^2 mol dm^{-3}): 4.235 (20°C), 5.191 (25°C), 7.368 (35°C), 8.450 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electroylte	Solubility (10^2mol dm^{-3}) at 0.1 ml dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	8.881	10.380	13.372	14.681
KF	7.522	8.623	11.381	12.248
KCl	3.951	4.868	6.951	7.989
KBr	3.980	4.901	7.004	8.071
KI	4.096	5.004	7.208	8.295
KSCN	4.131	5.100	7.286	8.395
KNO_3	3.917	4.868	7.062	8.194
K_2SO_4	4.243	5.166	7.255	8.257
$MgSO_4$	4.050	4.949	6.898	7.821
$(CH_3)_4NCl$	4.283	5.304	7.732	8.894

Table 35

Solubility of 3-fluorobenzoic acid in water (10^2 mol dm^{-3}): 1.476 (20°C), 1.724 (25°C), 2.401 (35°C), 2.682 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electrolyte	Solubility (10^2 mol dm^{-3}) at 0.1 mol dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	3.866	4.387	5.545	5.974
KF	3.270	3.729	4.890	5.346
KCl	1.397	1.647	2.326	2.617
KBr	1.418	1.675	2.370	2.679
KI	1.447	1.700	2.421	2.727
KSCN	1.474	1.724	2.433	2.734
KNO_3	1.437	1.697	2.427	2.744
K_2SO_4	1.626	1.889	2.593	2.872
$MgSO_4$	1.524	1.750	2.355	2.584
$(CH_3)_4NCl$	1.484	1.759	2.512	2.837

Table 36

Solubility of 4-fluorobenzoic acid in water (10^3 mol dm^{-3}): 4.385 (20°C), 5.317 (25°C), 7.292 (35°C), 8.308 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electrolyte	Solubility (10^3mol dm^{-3}) at 0.1 ml dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	14.185	16.654	21.271	23.659
KF	12.022	13.455	17.827	19.938
KCl	4.107	5.014	6.969	7.972
KBr	4.244	5.200	7.198	8.246
KI	4.312	5.277	7.368	8.457
KNO_3	4.307	5.254	7.320	8.358
K_2SO_4	4.839	5.827	7.845	8.855
$MgSO_4$	4.493	5.424	7.387	8.375
$(CH_3)_4NCl$	4.366	5.339	7.454	8.524

Table 37

Solubility of 2-chlorobenzoic acid in water (10^2 mol dm^{-3}): 0.837 (20°C), 1.018 (25°C), 1.360 (35°C), 1.613 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electrolyte	Solubility (10^2 mol dm^{-3}) at 0.1 mol dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	5.073	5.831	6.976	7.811
KF	3.508	4.078	5.037	5.642
KCl	0.814	0.999	1.360	1.631
KBr	0.834	1.023	1.390	1.663
K_2SO_4	1.076	1.303	1.707	2.003
$MgSO_4$	1.011	1.221	1.601	1.890
$(CH_3)_4NCl$	0.847	1.038	1.404	1.682

Table 38

Solubility of 3-chlorobenzoic acid in water (10^3 mol dm^{-3}): 1.799 (20°C), 2.295 (25°C), 3.273 (35°C), 3.710 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electrolyte	Solubility (10^3 mol dm^{-3}) at 0.1 mol dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	10.532	12.965	16.716	18.505
KF	8.958	11.096	14.131	15.870
KCl	1.833	2.325	3.297	3.696
KBr	1.968	2.477	3.512	3.719
K_2SO_4	2.309	2.906	4.125	4.649
$MgSO_4$	2.157	2.709	3.794	4.261
$(CH_3)_4NCl$	2.008	2.529	3.528	3.940

Table 39

Solubility of 4-chlorobenzoic acid in water (10^4 mol dm^{-3}): 3.007 (20°C), 3.568 (25°C), 5.071 (35°C), 6.001 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electrolyte	Solubility (10^4 mol dm^{-3}) at 0.1 mol dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	39.130	43.121	53.882	60.781
KF	40.576	47.570	66.391	77.592
KCl	3.143	3.685	5.234	6.034
KBr	3.825	4.478	6.152	7.123
K_2SO_4	4.813	5.631	7.674	8.996
$MgSO_4$	4.441	5.220	7.051	8.204
$(CH_3)_4NCl$	3.227	3.855	5.559	6.622

Table 40

Solubility of 3-bromobenzoic acid in water (10^3 mol dm^{-3}): 1.005 (20°C), 1.232 (25°C), 1.757 (35°C), 2.088 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electrolyte	Solubility (10^3 mol dm^{-3}) at 0.1 mol dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	9.544	10.639	12.829	14.289
KF	7.375	8.698	11.122	12.645
KCl	1.188	1.429	2.009	2.371
KBr	1.283	1.547	2.149	2.522
K_2SO_4	1.576	1.899	2.614	3.058
$MgSO_4$	1.460	1.756	2.449	2.855
$(CH_3)_4NCl$	1.260	1.527	2.145	2.532

Table 41

Solubility of 4-bromobenzoic acid in water (10^4 mol dm^{-3}): 1.368 (20°C), 1.669 (25°C), 2.335 (35°C), 2.776 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electrolyte	Solubility (10^4 mol dm^{-3}) at 0.1 mol dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	29.551	32.665	40.532	45.940
KF	31.556	37.022	44.084	49.593
KCl	1.541	1.857	2.566	3.064
KBr	1.849	2.262	3.122	3.672
K_2SO_4	2.717	3.240	4.445	5.145
$MgSO_4$	2.227	2.684	3.671	4.342
$(CH_3)_4NCl$	1.680	2.008	2.711	3.146

Table 42

Solubility of 2-iodobenzoic acid in water (10^3 mol dm^{-3}): 1.568 (20°C), 1.771 (25°C), 2.446 (35°C), 2.894 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electrolyte	Solubility (10^3 mol dm^{-3}) at 0.1 mol dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	13.482	14.690	18.317	20.720
KF	12.943	13.977	18.032	20.191
KCl	1.723	1.946	2.603	3.051
KBr	1.755	1.954	2.645	3.093
K_2SO_4	3.248	3.504	4.643	5.060
$MgSO_4$	2.976	3.224	4.151	4.652
$(CH_3)_4NCl$	2.118	2.322	2.931	3.370

Table 43

Solubility of 3-iodobenzoic acid in water (10^4 mol dm^{-3}): 2.202 (20°C), 2.926 (25°C), 4.363 (35°C), 5.417 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electrolyte	Solubility (10^4mol dm^{-3}) at 0.1 ml dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	30.048	36.921	51.565	60.996
KF	34.739	41.406	59.294	70.755
KCl	2.420	3.172	4.643	5.685
KBr	2.742	3.534	4.968	5.882
K_2SO_4	3.762	4.863	6.721	8.003
$MgSO_4$	3.544	4.518	6.357	7.444
$(CH_3)_4NCl$	2.680	3.413	4.794	5.605

Table 44

Solubility of 2-hydroxybenzoic acid in water (10^2mol dm^{-3}): 1.531 (20°C), 1.861 (25°C), 2.805 (35°C), 3.211 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electrolyte	Solubility (10^2mol dm^{-3}) at 0.1 ml dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	7.787	9.057	11.766	12.949
KF	5.529	6.431	8.655	9.281
KCl	1.531	1.861	2.798	3.197
KBr	1.573	1.909	2.860	3.260
KI	1.590	1.924	2.879	3.287
KNO_3	1.666	2.008	2.956	3.358
K_2SO_4	1.899	2.326	3.561	4.107
$MgSO_4$	1.789	2.186	3.367	3.890
$(CH_3)_4NCl$	1.548	1.900	2.913	3.391

Table 45

Solubility of 4-hydroxybenzoic acid in water (10^2 mol dm^{-3}): 2.771 (20°C), 3.688 (25°C), 7.181 (35°C), 8.814 (40°C) and at 0.1 mol dm^{-1} salt solutions at different temperatures.

Electrolyte	Solubility (10^2 mol dm^{-3}) at 0.1 ml dm^{-3} salt solutions 20°C	25°C	35°C	40°C
HCOONa	4.033	5.294	10.056	12.265
KF	4.097	5.169	9.323	11.090
KCl	2.752	3.649	7.066	8.607
KBr	2.765	3.671	7.115	8.713
K_2SO_4	2.810	3.709	7.081	8.606
$MgSO_4$	2.739	3.621	6.939	8.489
$(CH_3)_4NCl$	2.816	3.731	7.214	8.814

Table 46

Solubility of 2-aminobenzoic acid in water (10^2 mol dm^{-3}): 2.904 (20°C), 3.561 (25°C), 5.352 (35°C), 6.550 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electroylte	Solubility (10^2 mol dm^{-3}) at 0.1 ml dm^{-3} salt solutions			
	20°C	25°C	35°C	40°C
HCOONa	4.389	5.137	6.967	8.086
KF	4.029	4.545	6.941	8.126
KCl	2.844	3.512	5.352	6.595
KBr	2.904	3.586	5.458	6.718
KI	2.944	3.644	5.515	6.780
KNO_3	2.786	3.448	5.230	6.438
K_2SO_4	2.916	3.522	5.223	6.342
$MgSO_4$	2.839	3.449	5.184	6.254
$(CH_3)_4NCl$	2.952	3.612	5.584	6.535

Table 47

Solubility of 4-aminobenzoic acid in water (10^2 mol dm^{-3}): 3.076 (20°C), 3.767 (25°C), 5.498 (35°C), 6.631 (40°C) and at 0.1 mol dm^{-3} salt solutions at different temperatures.

Electroylte	Solubility (10^2mol dm^{-3}) at 0.1 ml dm^{-3} salt solutions 20°C	25°C	35°C	40°C
HCOONa	4.219	4.974	6.832	7.966
KF	3.929	4.704	6.648	7.844
KCl	2.946	3.631	5.360	6.501
KBr	2.992	3.689	5.435	6.616
KI	3.012	3.707	5.511	6.709
KNO_3	3.027	3.724	5.498	6.697
K_2SO_4	3.032	3.703	5.403	6.494
$MgSO_4$	3.056	3.738	5.427	6.525
$(CH_3)_4NCl$	3.319	4.009	5.753	6.856

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Chapter V

CONCLUSION

Salt effect studies on the activity coefficient of monosubstituted benzoic acids led to the following conclusions.

1. The effect of added salts on these acidic polar nonelectrolytes, unlike nonpolar solutes, are highly specific. It depends both on the nature of the solute and the electrolyte.

2. Contrary to the general expectation, potassium fluoride and sodium formate salted-in all solutes extensively accompanied by large negative free energy, negative enthalpy and a quite insignificant entropy factor for the transfer of the solute from water to salt solutions. The deviation from normal salt effect in the presence of electrolytes has been construed as a specific acid-base interaction involving the carboxyl proton and anion of the respective salt. The total breakdown of the Setschenow equation could also be rationalized on the basis of appreciable solubility of the solutes to which the above limiting equation could not be applied.

3. The effect of potassium sulphate and magnesium sulphate differs as the nature of the solute varied. Sulphate ion with its very high hydrogen bonding potential has the ability to make hydrogen bonds with the carboxyl group. Thus it is the acidity of the carboxyl proton that decides the direction of the salting process.

4. The behaviour of sulphate ion with other solutes where the acidity of the solute is not appreciable, it is the water-structure affecting properties of the sulphate ion which determines the path of the salt effect. Being a powerful structure-maker, sulphate ion produced salting-out with methylbenzoic acids, fluorobenzoic acids etc.

5. With other electrolytes, the salt effect could be rationalized on the basis of localized hydrolysis model and on the basis of the requirement of structure affecting properties of the ions.

6. It is also concluded that the number and nature of the functional groups present in the solute definitely plays a crucial role.

7. The thermodynamic parameters of transfer of solute from water to salt solution is found to be helpful to corroborate the data on K_s values obtained from activity coefficient measurements for different solute-electrolyte pairs.