

ACTIVITY COEFFICIENTS OF NONELECTROLYTE SOLUTES IN AQUEOUS SALT SOLUTIONS

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I. INTRODUCTION

The problem of the influence of salts on the activity coefficients of nonelectrolytes in aqueous solutions is of both fundamental and applied interest. Salt effect studies can provide considerable information of theoretical importance as to the complex interactions of ions and neutral molecules and as to the unique nature of water as a solvent. The data also have application to such related problems as kinetic salt effects and mechanisms of reactions, and they have a practical bearing on the separation of nonelectrolytes from water solutions by salting-out processes.

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Early reviews of the subject were made by Rothmund (149), Euler (42, 44), and Eyre (45). The three articles of Randall and Failey (136, 137, 138), although not complete, give a fairly good picture of the data available up to 1927. Scatchard (152, 153) in 1927, Gross (65) in 1933, and Albright (6) in 1937 compared selected data with theory. An extensive tabulation of the solubilities of gases in salt solutions is given by Markham and Kobe (114). Finally, the recent book by Harned and Owen (71) gives considerable information on both experiment and theory.

This article constitutes an analysis and interpretation of the available experimental data and of the relevant theories. It does not consider the problem of dipolar ions and proteins, since these are of sufficient importance to merit a separation treatment and have been given extensive consideration in the book edited by Cohn and Edsall (27). Furthermore, polyelectrolytes, ion-exchange resins, and salts of long-chain fatty acids (the soaps) have been specifically excluded, as have the polymeric nonelectrolytes.

II. SYMBOLS USED

The following list gives all of the symbols used in this discussion, with the exception of a few which are used only once and are defined in context.

- a_{ij} = distance of closest approach between ion j and nonelectrolyte,
- b_j = radius of ion of type j ,
- C_i = molar concentration of nonelectrolyte i in salt solution,
- C_i^0 = molar concentration of i in salt-free solution,
- C_j = molar concentration of ion species j ,
- C_e = molar concentration of electrolyte,
- C_i^R = molar concentration of nonelectrolyte in nonaqueous reference phase,
- D = dielectric constant of water–nonelectrolyte mixture,
- D_0 = dielectric constant of pure water,
- f_i = molar activity coefficient of i in salt solution,
- f_i^0 = molar activity coefficient of i in salt-free solution,
- f_i^R = molar activity coefficient of i in reference phase,
- h = Planck's constant,
- k_s = salting-out parameter,
- k_i = nonelectrolyte self-interaction parameter,
- k = Boltzmann's constant,
- K = empirical Setschenow parameter,
- N = Avogadro's number,
- p_i = partial vapor pressure of i over a solution containing electrolyte,
- p_i^0 = partial vapor pressure of i over a solution in pure water,
- P_e = "effective pressure" exerted by electrolyte in solution,
- P_w = molar polarization of water,
- P_i = molar polarization of i ,
- $\text{p}K_a$ = negative logarithm of acid ionization constant,

- pK_b = negative logarithm of basic ionization constant,
 R = gas constant,
 r_i = radius of nonelectrolyte molecule,
 S_i = solubility of nonelectrolyte in salt solution (moles/liter),
 S_i^0 = solubility of nonelectrolyte in pure water (moles/liter),
 T = absolute temperature,
 V_i = molar volume of nonelectrolyte (liters/mole),
 \bar{V}_i^0 = partial molar volume of nonelectrolyte at infinite dilution (liters/mole),
 V_s = molar volume of pure (liquid) electrolyte (liters/mole),
 \bar{V}_s^0 = partial molar volume of electrolyte at infinite dilution (liters/mole),
 V_w = molar volume of liquid water (liters/mole),
 x_i = mole fraction of nonelectrolyte i ,
 Z_j = valence of ion of type j ,
 α_j = polarizability of ion j ,
 β_0 = compressibility of pure water,
 γ_i = rational activity coefficient of i in salt solution,
 γ_i^0 = rational activity coefficient of i in salt-free solution,
 δ = dielectric decrement of aqueous solution due to nonelectrolyte solute,
 ϵ = electronic charge,
 μ = dipole moment of nonelectrolyte i ,
 μ_i = chemical potential of nonelectrolyte species i ,
 μ_i^* = chemical potential of nonelectrolyte species i in standard state, and
 ν = number of ions into which salt molecule dissociates.

III. THERMODYNAMIC RELATIONS

The rational activity coefficient of a nonelectrolyte in aqueous solution is conventionally defined by the relationship

$$\mu_i = RT \ln \gamma_i x_i + \mu_i^* \quad (1)$$

where

$$\mu_i^* = \lim_{\substack{x \rightarrow 0 \\ \text{all solutes}}} (\mu_i - RT \ln x_i)$$

For the transfer of nonelectrolyte from a solution in pure water to one in which there is added salt, the nonideal free energy change per mole will thus be

$$\Delta F = RT \ln \frac{\gamma_i^0}{\gamma_i} \quad (2)$$

Although γ may be the more significant activity coefficient to use in considering theory, molar activity coefficients (along with molar concentrations) are much more convenient to use in discussing the data. These two activity coefficients approach each other in dilute solutions. However, their logarithmic derivatives with respect to molar salt concentration, which are also of importance in salt

effect studies, do not become identical even in the case of infinite dilution.² Actually the difference is usually quite small and will be ignored in subsequent discussions, all of which will be in terms of the molar activity coefficients.

In general, f_i (or γ_i) is a function of the concentrations of all solute species, which in the present case are salt and nonelectrolyte. At a given temperature $\log f_i$ can be represented by a power series in C_s and C_i (27):

$$\log f_i = \sum_{n,m}^{\infty} k_{nm} C_s^n C_i^m$$

If, as usual, it is assumed that for low C_s and C_i the linear terms are the only important ones,

$$\log f_i = k_s C_s + k_i C_i \quad (3)$$

an expression which has been well justified experimentally for moderately dilute solutions in which there is no chemical interaction between the solute species. It has been proposed (145) that a term in the square root of the salt concentration should also enter, but there is no sufficiently accurate experimental evidence for this nor has any theoretical justification been found (156). Consequently subsequent discussion will be based on equation 3.

Most theories of salt effect are concerned with the calculation of k_s , the parameter for ion–nonelectrolyte interaction, and not with k_i , which results from the interaction of the nonelectrolyte with itself. Hence in comparing theory and experiment it is necessary to make the distinction. Experimental salting-out studies are usually made by comparing solutions of the nonelectrolyte in pure water with solutions containing added electrolyte, and the term involving k_i cannot be ignored unless the concentration of nonelectrolyte is very low in both cases or is maintained constant (or unless k_i itself is very small).

IV. EXPERIMENTAL METHODS

A variety of experimental methods has been used to obtain $\log f_i$ as a function of salt concentration. Of these the most important are solubility, distribution, and vapor-pressure measurements.

A. Solubility

Measurements of the solubility of a nonelectrolyte in pure water and in a salt solution give the activity coefficient of the nonelectrolyte directly. Since the chemical potential of a species is the same in all solutions in equilibrium with the pure substance, the activity of the species, in this case the nonelectrolyte, is constant, i.e.,

$$f_i S_i = f_i^0 S_i^0 \quad (4)$$

² The relation between these derivatives at infinite dilution is

$$\lim_{\substack{C_s \rightarrow 0 \\ C_i \rightarrow 0}} \frac{d \ln f_i}{d C_s} = \lim_{\substack{C_s \rightarrow 0 \\ C_i \rightarrow 0}} \frac{d \ln \gamma_i}{d C_s} + (\bar{V}_i^0 - \nu V_w)$$

Substituting f_i from the above into equation 3 one obtains

$$\log f_i = \log f_i^0 + \log \frac{S_i^0}{S_i} = k_s C_s + k_i S_i$$

which, since $\log f_i^0 = k_i^0 S_i^0$, gives:

$$\log \frac{f_i}{f_i^0} = \log \frac{S_i^0}{S_i} = k_s C_s + k_i (S_i - S_i^0) \quad (5)$$

If now the concentrations S_i and S_i^0 are low, the last term above can be neglected, even though, as will frequently be the case, k_i is similar in magnitude to k_s . For this case of low nonelectrolyte concentration the simple result shown in equation 6 is obtained

$$\log \frac{f_i}{f_i^0} = \log \frac{S_i^0}{S_i} = k_s C_s \quad (6)$$

which is of the same form as the well-known Setschenow equation (158, 159). However, the empirical Setschenow equation, $\log S_i^0/S_i = KC_s$, will often hold even when the last term of equation 5 is large, but in this case the constant K will not be equal to the theoretically significant salt parameter, k_s . The distinction between k_s and the overall Setschenow parameter K becomes particularly important when comparing the salting out of a nonelectrolyte of low solubility with one of high solubility.

The most obvious advantages of the solubility method are its experimental simplicity and precision. A disadvantage with liquid nonelectrolytes is that varying amounts of water and even of salts may frequently dissolve in the supposedly pure reference phase. Finally, when the solubility of the nonelectrolyte is moderate or high, equation 5 rather than equation 6 must be used and k_s can be evaluated only if separate experiments are made to determine k_i .

B. Distribution

The variation with salt concentration of the distribution of a nonelectrolyte between aqueous solutions and an immiscible nonaqueous reference phase gives a simple method for determining f_i . If for two experiments, one involving pure water and the other a salt solution, the concentration of nonelectrolyte in the reference phase is constant, the equation is

$$f_i^0 C_i^0 = b f_i^R C_i^R = f_i C_i \quad (7)$$

where b is a constant, or

$$\frac{f_i}{f_i^0} = \frac{C_i^0}{C_i}$$

In practice, one determines initially the variation of the distribution ratio for pure water and the reference phase with concentration of nonelectrolyte in the latter and uses this knowledge to calculate the C_i^0 corresponding to the C_i^R observed in an experiment with a salt solution.

Since the above equation is formally identical with that for solubilities, equations 5 and 6 apply directly to the distribution method, the symbols S_i and S_i^0 being replaced by C_i and C_i^0 .

The chief advantages of this method are: it is fairly simple experimentally; equilibrium is established rapidly; one can always arrange the experiment to have a low concentration of nonelectrolyte in the aqueous phase (and hence avoid the difficulties implicit in the last term of equation 5); and it can be used with nonelectrolytes which are miscible with water. The chief disadvantage is that it is frequently difficult to find a reference solvent which is sufficiently immiscible with water to make equation 7 applicable and for which the distribution ratio of the nonelectrolyte is such as to give adequate accuracy in the determination of f_i . Even a moderate amount of mutual solution of the reference phase and water can lead to erroneous values of f_i ; (106).

An interesting comparison of activity coefficients obtained from distribution and solubility experiments is given by Sykes and Robertson (164) for the nitrobenzoic acids, all of which exhibit low solubility in water. The agreement between the two methods is quite satisfactory.

C. Vapor pressure

For the case of two solutions of a nonelectrolyte, one in pure water and one in a salt solution, the relation between the activity coefficients and partial vapor pressures is as shown in equation 8:

$$\frac{f_i C_i}{f_i^0 C_i^0} = \frac{p_i}{p_i^0} \quad (8)$$

This equation assumes that the vapor phase is ideal, an excellent approximation at the vapor pressures normally employed.

The advantages of the vapor-pressure method arise from the simplicity and ideal character of the reference phase and the fact that it is experimentally easy to keep the concentration of the nonelectrolyte in the aqueous phase constant. When this is true, equation 8 simplifies to

$$\frac{f_i}{f_i^0} = \frac{p_i}{p_i^0} \quad (9)$$

and also complications from the self-interaction term of equation 5 are eliminated. One disadvantage of this method is that its use is restricted to volatile substances. Furthermore, the measurements are frequently of sufficient accuracy only if the concentration of the nonelectrolyte is high.

D. Other methods

Other experimental methods such as freezing point and E.M.F. are available in principle, but none has been used for any extensive studies. The freezing-point method has had occasional application and can be made quite precise; however, for ternary systems both the experiments and the analysis of the data are somewhat difficult and of course the temperature of the experiments is restricted to

the freezing point of the solutions. A typical example of the application of the freezing-point method is the study by Scatchard and Benedict (155) of the water-salt-dioxane system.

V. THEORIES OF THE SALT EFFECT

Experimentally, the effect of salts on solutions of nonelectrolytes is a very complex phenomenon. For example, figure 3 shows the decidedly varying influence of different salts on the activity coefficient of benzene in water. Most electrolytes salt out benzene, although in markedly varying degrees, but there are some which actually salt in this inert solute. (The phrases "salting out" and "salting in" are now generally used to denote, respectively, an increase and a decrease in the activity coefficient of the nonelectrolyte with increasing concentration of electrolyte.) For a more polar nonelectrolyte, such as γ -butyrolactone (figure 18), the effect of each salt is different. In addition, the relative order in the effects of the salts frequently changes (compare trimethylamine (figure 10) and succinic acid (figure 14)). This complexity is not surprising when one considers the large number of different types of intermolecular interactions which come into play. Although k_s is referred to as the "ion-nonelectrolyte" interaction parameter, molecular interactions between ion and solvent, ion and nonelectrolyte, and nonelectrolyte and solvent may all be important in determining its value.

There have been a number of qualitative and quantitative theories of the salt effect, all with common underlying aspects but emphasizing different approaches to the problem. The discussion of the theoretical material presented in this review is in four sections which reflect the different approaches; this subdivision has been made primarily for convenience of presentation and is not intended to imply that there are sharp distinctions. Since detailed developments can be found in the original references, these sections will be restricted to a statement of fundamental ideas and final results.

A. Hydration theories

The proposal that salting out results from the effective removal of water molecules from their solvent role due to hydration of the ions was discussed by Rothmund (149) and later employed by Philip (132), Glasstone (58, 59, 60), and Eucken and Hertzberg (40a), among others. Although salting out must largely be due to a preferential attraction between ions and water molecules which can loosely be referred to as "hydration," the simple idea that each ion completely ties up a share of water molecules and has no effect on the solvent properties of the rest of the water is quite inadequate. This view leads to the conclusion that hydration numbers deduced from salting-out experiments should be independent of the nonelectrolyte salted out, a conclusion which is not true. Likewise it permits no explanation of salting in. Finally, the hydration numbers do not correspond, even as to the order of the ions, with degrees of hydration obtained from other experiments.

It was suggested by Kruyt and Robinson (92) that the variations in the specific effects of salts on different nonelectrolytes might arise from the fact that the water

dipoles are oriented in the hydration shell around an ion. These authors pointed out that if there is also a preferred orientation of water molecules toward a polar nonelectrolyte, ions of one sign should have a tendency to promote its solubility while those of opposite sign, which orient water molecules unfavorably, should have an increased salting-out effect. This model does not help to explain variations in the effects of different salts on nonpolar solutes, but it is useful in interpreting some of the observed relative effects on different polar solutes. It represents the first attempt to point out that local solvent structure should play a significant role, a factor which received very little further attention until recently (37, 38, 50, 168).

B. Electrostatic theories

The theory of Debye and McAulay (32) relates salt effects to the influence of the nonelectrolyte on the dielectric constant of the solvent. The amount of work necessary to discharge the ions in pure solvent of dielectric constant D_0 and to recharge them in a solution of dielectric constant D containing the nonelectrolyte is calculated. This quantity yields the electrostatic contribution to the chemical potential of the neutral solute, and the expression for its activity coefficient becomes

$$\ln f_i = \frac{\delta_i \epsilon^2}{2kTD_0} \sum_j C_j Z_j^2 / b_j \quad (10)$$

where δ_i is defined by

$$D = D_0 (1 - \delta_i C_i)$$

Debye (31) later developed a more exact theory to take into account the heterogeneity of the mixture of water and neutral solute. Assuming that the dielectric constant varies with distance from the ion in such a manner as to minimize the total free energy of the system, the equation

$$C(r) = C_i^0 e^{-(\bar{R}_j/r)^4}$$

is obtained for the concentration of nonelectrolyte at a distance r from the ion. \bar{R}_j^4 is given by the relationship

$$\bar{R}_j^4 = \frac{\epsilon^2 Z_j^2 1000}{8\pi RTD_0} \delta_i$$

and the final expression for the activity coefficient of a nonelectrolyte (which decreases the dielectric constant of water) is

$$\frac{1}{f_i} = 1 - \frac{4\pi N}{1000} \sum_j J_j C_j \quad (11)$$

where

$$J_j = \int_{b_j}^{\infty} (1 - e^{-(\bar{R}_j)^4/r^4}) r^2 dr$$

This last theory has been extended by Gross (66), who introduced a correction for ion atmosphere effects and developed asymptotic series for the integral in equation 11 (see also reference 70). Albright and Williams (7) suggested a semi-graphical method for application of the theory to solutions containing higher concentrations of the neutral molecule, and Scatchard (154) made a calculation of the effect over the whole range of concentration for a pair of miscible non-electrolytes.

Treatments similar to that of Debye and McAulay have been offered by Altshuller and Everson (7a), Butler (20), and by Belton (8), who also developed an expression which explicitly takes into account the dipole moment and distortion polarizability of the neutral molecule, thereby avoiding the necessity of knowing δ . Falkenhagen (46) and Harned and Owen (71) give detailed discussions of the Debye theories.

More recently Kirkwood (83) has calculated the mutual electrostatic energy of a spherical ion and a neutral molecule represented as a cavity (in the surrounding dielectric) and containing an arbitrary distribution of charges. The theory, originally intended for dipolar ions but generally applicable to neutral molecules, yields a limiting law for the activity coefficient of the nonelectrolyte. For the case of a spherical molecule containing a point dipole the expression is

$$\ln f_i = \sum k_j Z_j^2 C_j \quad (12)$$

where

$$k_j = \frac{2\pi N \epsilon^2}{2303 D_0 k T} \left\{ \frac{3}{2} \frac{\mu^2}{D a_{ij} k T} - \frac{r_i^3 \Gamma(\rho)}{a_{ij}} \right\}$$

$$\rho = \frac{r_i}{a_{ij}}$$

and

$$\Gamma(\rho) = \frac{1}{3\rho^4} [(\rho^3 - 2) \log(1 + \rho) - (\rho^3 + 2) \log(1 - \rho) - 2\rho^2]$$

In all of these theories the solvent is treated as a continuous dielectric and only departures from ideality are considered which arise from electrostatic interaction involving the ionic charges. The predicted results are similar in all cases, which follows from the close correspondence in theoretical approach. Thus, under the assumption that there is a linear relationship between dielectric constant and polarization of the liquid per unit volume (127, 180), the dielectric decrement of a nonelectrolyte can be simply related to its partial molar volume and dipole moment (27) by the expression

$$-D_0 \delta_i = \frac{h P_i}{1000} - \bar{V}_i (D_0 - j)$$

where

$$P_i = \frac{4\pi N \mu^2}{9kT}$$

and h and j are empirical constants. Substitution of this relation into either the Debye or the Debye-McAulay expression gives a term in μ^2/D_0^2 and in \bar{V}_i/D_0 , in close analogy with Kirkwood's equation.

Table 1 compares experimental values of k_s with those predicted by the Debye and Kirkwood theories for a pair of typical nonelectrolytes (106, 118). The order of magnitude of the theoretical values is correct, and the general shift towards less salting out in the case of the polar nonelectrolyte is clearly indicated. However, the theories cannot reasonably account for the marked variation in the effect of different electrolytes and they fail entirely whenever there is a shift from salting out to salting in of a particular nonelectrolyte. This is not too sur-

TABLE 1
Comparison of observed salt effects with values calculated from Debye and Kirkwood theories

NONELECTROLYTE	SALT	k_s (CALCULATED)		k_s (OBSERVED)
		Debye	Kirkwood	
		liters/mole	liters/mole	
Benzene.....	NaF	0.130	0.133	0.254
	NaCl	0.126	0.125	0.195
	LiCl	0.127	0.143	0.141
	NH ₄ Cl	0.123	0.109	0.103
	NaI	0.122	0.120	0.095
	CsCl	0.121	0.105	0.088
	(CH ₃) ₄ NBr	0.110	0.093	-0.24
γ -Butyrolactone.....	NaCl	0.037	0.083	0.067
	KCl	0.035	0.075	0.035
	NaBr	0.036	0.081	0.007
	NaI	0.035	0.079	-0.088
	KI	0.033	0.071	-0.115
	NaClO ₄	0.033	0.078	-0.113
	Na ₂ SO ₄	0.087	0.213	0.369

prising since, as Debye (31) pointed out, these theories do not preclude the possibility that other types of forces may be important.

C. van der Waals forces

In the development of the foregoing theories the electrostatic interaction between an ion and a neutral molecule was shown to be of a short-range nature. For example, the leading term in Kirkwood's expression for the potential of ion-cavity repulsion varies as $1/r^4$. This suggests that other short-range forces, primarily dispersion forces, may play an appreciable role and may in part be responsible for the specific effects of the ions. Attempts have been made to take this into account, but with only partial success. Linderstrøm-Lang (102) observed a correlation between the salting-out order of the ions and the order of their molar refractivities; later, Kortüm (91) suggested that van der Waals forces may be responsible for salting in by large ions. A more specific suggestion on the

role of dispersion forces was recently made by McDevit and Long (117), who proposed a parametric equation of the form

$$\log f_i = A \sum_j Z_j^2 C_j - B \sum_j \alpha_j C_j \quad (13)$$

where the parameters A and B depend on the nonelectrolyte and to a small extent on the electrolyte but should be roughly constant for a series of similar salts, say the alkali halides. This equation was arrived at by simply introducing a term for the potential of dispersion forces into the Kirkwood development. The first term in equation 13 comes from charge-molecule interaction and the second from van der Waals interaction. For molecules whose dipole moments are not high, the first term is positive and the second negative (salting in). The constancy of A and B requires that the distance of closest approach between an ion and a neutral molecule be virtually the same for all ions. This can be well justified only when the neutral molecule is large compared to the ions.

Equation 13 is essentially a quantitative statement of the relationship noted by Linderstrøm-Lang and fits the data quite well in some cases. However, as the authors pointed out, a salting-in term resulting from the displacement of water molecules (against their own intermolecular forces) by the ion should be proportional to ionic volume and hence approximately proportional to ionic polarizability. The dispersion and "displacement" effects will be combined in the second term of equation 13 and are actually indistinguishable, since the parameter B must be obtained from the data. It will be pointed out in later sections that there is good reason to believe that the "displacement" effect is actually predominant.

At about the same time Bockris, Bowler-Reed, and Kitchener (12) made a more detailed attempt to include the effect of dispersion forces and undertook to calculate all the parameters explicitly.

Their final expression is

$$\frac{\Delta S_i}{S_i^0} = \left(P_i - P_w \frac{V_i}{V_w} \right) \frac{2\pi\epsilon^2 N}{1000D^2 kT} \sum \frac{Z_j^2 C_j}{b_j} + \left(\frac{\alpha_i \nu_i}{\nu_{s\pm} + \nu_i} - \frac{\alpha_w \nu_w}{\nu_{s\pm} + \nu_w} \frac{V_i}{V_w} \right) \frac{2\pi N h}{1000D kT} \sum \frac{\alpha_j \nu_j C_j}{b_j^3} \quad (14)$$

where ν 's are characteristic frequencies. This is similar in form to the equation of McDevit and Long, with the notable difference that the second (salting-in) term varies much less with the choice of ion. This is a consequence of taking simply the radius of the ion, b_j , rather than the sum of the ion and neutral molecule radii as the distance of closest approach. The factor b_j^3 virtually cancels out variations in polarizability and the theory predicts much less specificity in the effects of different ions than is observed.

An interesting result of this theory is that it predicts the observed salting in by large ions, such as the tetraalkylammonium ions. However, the quantitative application of the simple London formula (105) for dispersion potential to the case of complex molecules at short range is questionable. Likewise the theory

seems incomplete, in that it accounts for the water molecules displaced by the neutral solute but not for those displaced by the ions.

Both of the foregoing theories fail to indicate the anomalously low salting out generally observed for lithium and hydrogen ions, and for some nonelectrolytes they do not fit the data at all well. These uncertainties and the theoretical limitations make the theories inconclusive in establishing the role of dispersion forces. At best, the calculations of Bockris, Bowler-Reed, and Kitchener suggest that it is not negligible. The results reported in the next few sections indicate that it is only secondary in determining the relative effects of a series of ions, so that the matter must remain speculative until a more exhaustive treatment is available.

D. Internal pressure concept

The "internal pressure" concept of Tammann (166, 167) was employed by early investigators to relate salt effects to other properties of the salt solutions themselves. Euler (41) noted a connection between the order of increasing volume contractions on dissolving salts and the order of increasing salting out of ethyl acetate. Later, Geffcken (54) and Tammann (167, 169) established a similar correlation between salt effects and the relative effects of salts in decreasing the compressibility of the solution.

This approach has received little further attention until very recently, when McDevit and Long (118) pointed out that it should hold best for strictly nonpolar nonelectrolytes and developed an explicit theory for this case. By considering that the neutral molecules merely occupy volume and hence modify the ion-water interaction in this simple manner, the authors calculated the free energy of transfer of nonpolar nonelectrolyte from pure water to the salt solution and obtained a limiting law for k_s .

$$k_s = \frac{\bar{V}_i^0(V_s - \bar{V}_s^0)}{2.3\beta_0 RT} \quad (15)$$

which should be strictly applicable only for small nonelectrolyte molecules. The only quantity not readily available is V_s , the "liquid" volume of the pure salt. It can be estimated with reasonable certainty, however, and is discussed in the original reference.

It was further shown that equation 15 may also be expressed in terms of P_s , the "effective pressure" exerted by salts in solution, which was first introduced by Gibson (56). The expression,

$$k_s = \lim_{C_s \rightarrow 0} \frac{\bar{V}_i^0}{2.3RT} \frac{dP_s}{dC_s} = \frac{\bar{V}_i^0(V_s - \bar{V}_s^0)}{2.3RT\beta_0} \quad (16)$$

corresponds to the physical idea that the nonideal free energy of transfer is simply $P_s\bar{V}_i$. The linearity, up to fairly high salt concentrations, of $\log f_i$ versus C_s is well reflected by a corresponding linearity in plots of P_s against C_s . Either equation 15 or 16 may be used to calculate k_s , but the slight uncertainty concerning values of V_s is reduced whenever isothermal compressibility data are available for the calculation of dP_s/dC_s .

It was also demonstrated that for large nonpolar molecules equations 15 and 16

should predict too high an absolute value for k_s , because the finite radius of the molecule will have a limiting effect on its distance of closest approach to an ion. Exact knowledge of intermolecular potential functions are necessary to take this into account, but the predicted relative effects of various salts should still be essentially correct.

According to this viewpoint the degree of salting out or salting in of a nonpolar solute is determined by the extent to which the solvent medium is compressed or loosened when ions are present. This point will be discussed further after these expressions have been compared with the data for nonpolar solutes in Section VII.

VI. DATA ON SALT EFFECTS

A large body of data on salt effects is available in the literature for a variety of solid, liquid, and gaseous nonelectrolytes. The investigations range from quite extensive ones, emphasizing a number of salts at varying concentrations, to studies of perhaps a single salt at one concentration. A condensed summary of the data is given in the Appendix, where the tables list the nonelectrolytes, the salts studied for each, the literature references, and some comments on the experimental conditions.

In the sections which immediately follow, the data are discussed under the categories of nonpolar and polar nonelectrolytes. No attempt is made to discuss all of the available data; instead, typical examples have been chosen from the lists of the Appendix. For all of these examples, molar activity coefficients are given and salt concentrations are in either molar or normal units. These units have been used, partly because most of the original data are so expressed and partly because plots of $\log f_i$ versus C_s are commonly linear to higher salt concentrations than are those of the logarithm of the molal activity coefficient versus salt molality.

Many of the original data have been recalculated. Conversions have been made from molal or mole fraction units to molar; where necessary, corrections for dissociation have been made for weak acids and bases; and in some cases solubility data have been recalculated so as to give values of both the parameters k_i and k_s of equation 5.

VII. NONPOLAR NONELECTROLYTES

Salt effects on nonpolar nonelectrolytes merit separate discussion, since this class should be the simplest to interpret and gives a good reference point from which to consider the polar nonelectrolytes. It was assumed in Section V, C 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 solution. One of the objects of this section is to test the utility of this assumption.

Figures 1 to 4 give plots of $\log f_i$ versus C_s for the following nonpolar species: hydrogen (17, 54, 85, 162), oxygen (54, 108), benzene (99, 151), and nitrous oxide (54, 112).³ Although the latter is not strictly nonpolar, it is included in this

³ These and the remaining figures on salt effects do not generally include data for all of the electrolytes studied. Complete lists of the latter along with other literature references are given in the Appendix.

group since its structure and dipole moment (176) indicate that its polarity is very low. The straight lines in the figures are actually representations of the limiting slopes of $\log f_i$ vs. C_s and the numerical figures are the k_s values obtained from these. However, in most cases the linearity actually holds up to high concentrations of salt and in a few instances experimental points are plotted to illustrate this. Although the data for these examples come from solubility measurements,

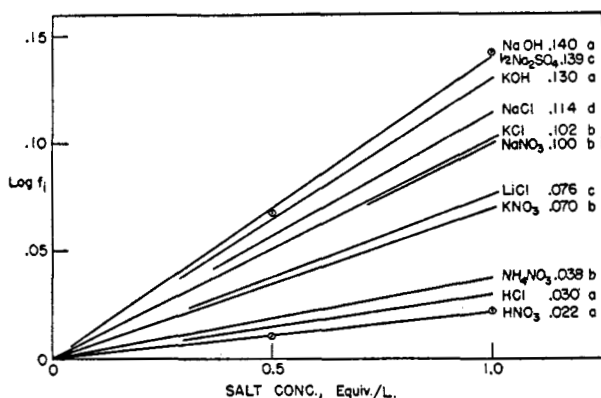


FIG. 1. Salt effects for hydrogen: (a) Geffcken (54), 25°C.; (b) Knopp (85), 20°C.; (c) Steiner (162), 15°C.; (d) Braun (17), 25°C.

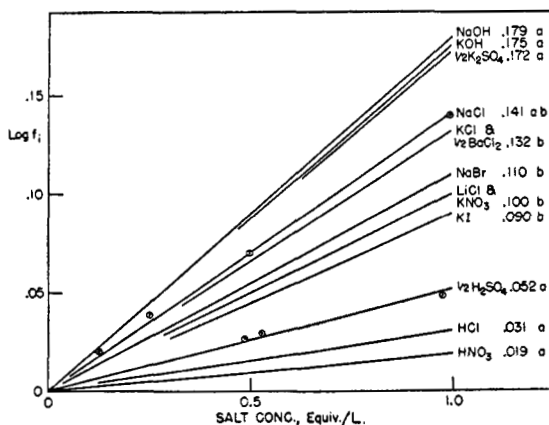


FIG. 2. Salt effects for oxygen at 25°C.: (a) Geffcken (54); (b) MacArthur (108)

in all cases the solubilities are so low that the self-interaction term of equation 5 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 facts that specificities enter even with these nonpolar molecules and are so consistent strongly suggest 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 Åkerlöf (5); observed orders of the salting parameters differed significantly in detail

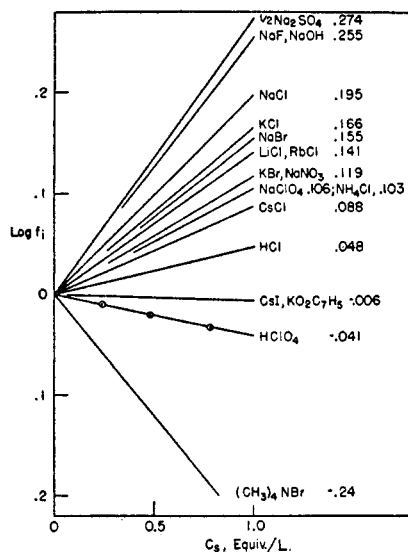


Fig. 3. Salt effects for benzene: Saylor, Whitten, Claiborne, and Gross (151), 30°C.; McDevit and Long (99), 25°C.

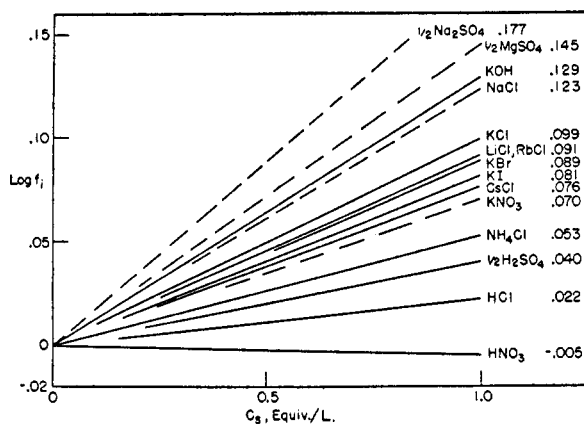


Fig. 4. Salt effects for nitrous oxide at 25°C. —, Geffcken (54); ---, Markham and Kobe (112).

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 recent value given by Eucken and Hertzberg (40a).

The data for a given nonpolar solute reveal that the contributions of the ions to the k_s values for the salts are generally additive to 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. This additivity is quite common and holds even for polar nonelectrolytes (65, 96). The obvious conclusion is that the effect of a given salt is simply the sum of the effects of the constituent ions.

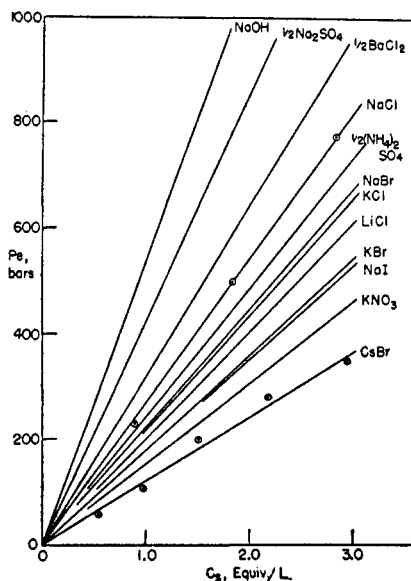


FIG. 5. Plot of P_e , the effective pressure of a salt in solution, *versus* salt concentration (Gibson (56)).

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, and in fact gives results similar to rubidium ion. Two other cations which give large salting-out effects in relation to their sizes are ammonium ion and hydrogen ion. Thus with benzene (figure 3) perchloric acid actually causes salting in and hydrochloric acid salts out only slightly.

Comparison of the data for benzene with the Debye and Kirkwood theories was discussed briefly in Section V; similar comparisons for other nonpolar molecules lead to much the same conclusions. In all cases these theories predict salting out of roughly the magnitude observed with potassium or sodium chloride. They do not predict the observed specificities or the anomalously low values of k_s for lithium salts and strong acids nor do they predict the observed salting in for salts of large ions.

In accord with equation 16 a rather good correlation exists between the

observed salt effects and those predicted from other properties of the salt solutions. From this equation it follows that the order of salt effects should be the same as the order of dP_s/dC_s for the salt solutions. Figure 5 gives a plot of Gibson's data for P_s versus C_s (56) and the salt order is seen to be very similar to that for salt effects for the various nonpolar nonelectrolytes. A more detailed comparison between theory and experiment is given in table 2, which lists observed values of k_s and those calculated from equation 16, for the species hydrogen, oxygen, and benzene. The partial molar volumes of these latter were taken as 26 (75), 31 (75), and 89.4 (172) ml./mole, respectively. For the salts,

TABLE 2
Comparison of observed k_s with values from equation 16

SALT	HYDROGEN		OXYGEN		BENZENE	
	k_s (obsd.)	k_s (calcd.)	k_s (obsd.)	k_s (calcd.)	k_s (obsd.)	k_s (calcd.)
	liters/mole	liters/mole	liters/mole	liters/mole	liters/mole	liters/mole
Na ₂ SO ₄	0.278	0.46			0.548	1.33
NaOH.....	0.140	0.25	0.179	0.29	0.256	0.85
NaCl.....	0.114	0.12	0.141	0.15	0.198	0.42
NaBr.....			0.110	0.12	0.155	0.35
KCl.....	0.102	0.10			0.166	0.34
LiCl.....	0.076	0.09	0.100	0.11	0.141	0.31
RbCl.....					0.140	0.31
NaNO ₃	0.100	0.09			0.119	0.31
KNO ₃	0.070	0.07	0.100	0.08		
NaI.....					0.095	0.27
NaClO ₄					0.106	0.26
CsCl.....					0.088	0.26
NH ₄ Cl.....					0.103	0.15
HCl.....	0.030	0.03	0.031	0.03	0.048	0.09
HClO ₄					-0.041	-0.05
(CH ₃) ₄ NBr.....					-0.24	-0.54

values of dP_s/dC_s have been used when available; otherwise values of V_s were obtained from the tabulation of Lunden (107).

For all three nonelectrolytes considered in table 2 the agreement between experimental and predicted salt orders is excellent. The only inversions occur where the measured salt effects are very similar. From this viewpoint, the observed orders of salting out of lithium salts and strong acids are not really anomalous; they are simply a reflection of the rather special properties of aqueous solutions of these electrolytes.

The actual magnitudes of the calculated k_s values for benzene are consistently too high by a factor of from 2 to 3. For a smaller molecule, hydrogen, the numerical agreement between the observed and calculated values is much better, a result which was anticipated in Section V.

The good fit with equation 16 demonstrates that the problem of salt effect for nonpolar solutes reduces largely to the problem of ion-solvent interaction, and particularly the manner in which these interactions give rise to the volume

change ($V_s - \bar{V}_s^0$). There are several excellent papers (9, 38, 50, 168) on this subject which provide some basis for speculation. As noted earlier, there is usually a contraction when ions and water are mixed. The primary effect is an attraction of water "dipoles" into the electrical fields of the ion. If water were a normal close-packed liquid, there would be a contraction due to a simple decrease in free volume. However, it is known that at ordinary temperatures a large fraction of liquid water is in an open-structured quasi-crystalline state, and much of the observed compression may come from a collapse of this open form into a more closely packed structure around an ion.

Two factors which increase with ionic size oppose this electrostriction. One is simply the decrease in electrostatic field strength, at the surface of the ion, with increasing ionic radius. The second, and perhaps more important, is the fact that water molecules are displaced by the ionic volume. If the ions were uncharged inert spheres, the accompanying separation of water molecules would result in a decrease in the cohesive energy of the system and an increase in volume. Both of these factors must play a part in the general decrease in ($V_s - \bar{V}_s^0$) with increasing ionic size, and it is not unlikely that the displacement factor becomes predominant for very large ions, resulting in the observed negative values for ($V_s - \bar{V}_s^0$).

The fact that the very small cations fall out of position, relative to their size, must be associated with the evidence that these ions have some tendency to promote rather than destroy the quasi-crystalline structure of water (9, 50). The result is a smaller overall contraction. A tentative and crude suggestion is that these small ions may be able to fit into the water structure by occupying sites normally taken by hydrogen atoms and forming between the oxygen atoms of two water molecules an electrostatic "bridge" somewhat comparable to a hydrogen bond.

The Debye and Kirkwood theories take into account only the primary electrical effect and not the "displacement" and "structural" contributions. It is interesting to note that these theories usually give the closest predictions for just the cases where the latter factors should be minimized, for example, sodium and potassium chlorides.

VIII. POLAR NONELECTROLYTES

For polar nonelectrolytes one would expect, just as with the nonpolar species, a salting-out contribution roughly proportional to the volume of the nonelectrolyte, a continuation of the specific effects characteristic of nonpolar molecules, and finally an increased salting in as the dipole moment of the molecule increases. This last is directly predicted by the Kirkwood theory (equation 12) and also by the Debye theories since, as previously noted, the dielectric decrement of a molecule decreases with increasing dipole moment.

A. Relation to dipole moment

An excellent illustration of the influence of dipole moment is shown by a comparison of the salt effects for carbon dioxide (54, 112) and sulfur dioxide (49)

(figures 6 and 7). 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 sulfur dioxide is 1.7 Debye units (176). The markedly increased salting in with sulfur dioxide is in line with predictions from either of the above theories.

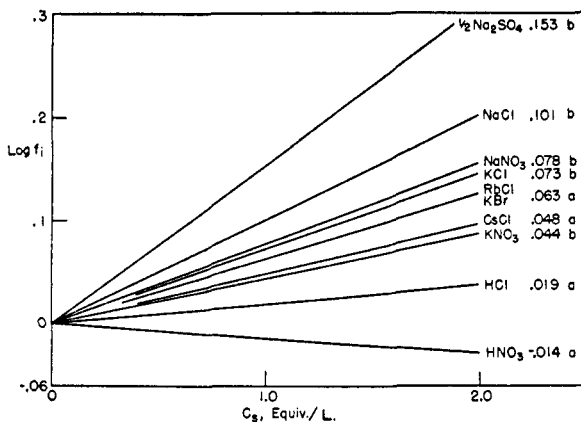


FIG. 6. Salt effects for carbon dioxide at 25°C.: (a) Geffcken (54); (b) Markham and Kobe (112).

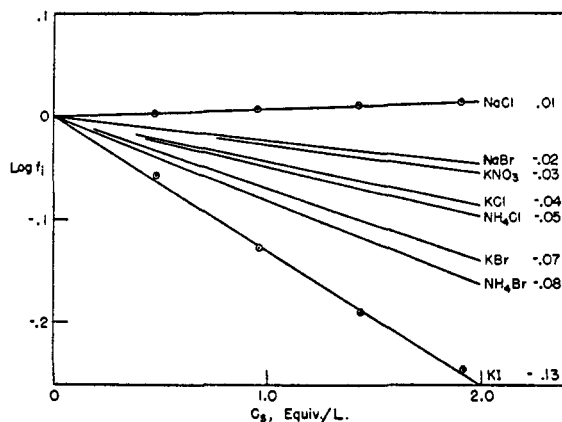


FIG. 7. Salt effects for sulfur dioxide at 25°C. (Fox (49))

Figures 6 and 7 also show that even with polar nonelectrolytes the order of the salts is similar to that found for nonpolar solutes. The primary effect of polarity is to change the overall magnitude of the salting out without greatly affecting the variations from one salt to another. The changes in order which do occur are very interesting, however, and will be considered later.

Another illustration of the effect of varying polarity was given some time ago by Gross (67, 68), who studied salt effects on acetone and on hydrogen cyanide, the first with a positive and the second with a negative dielectric decrement.

Although there were exceptions, the general results were as predicted by the Debye theories. With most salts acetone is salted out whereas hydrogen cyanide is salted in.

Table 3 gives a more extensive comparison of salting-out effect with dipole moment. Values of the salting-out parameter for one salt, potassium chloride, together with values of the dipole moment, are listed for several inorganic com-

TABLE 3

Comparison of dipole moment and salt effect of potassium chloride for some inorganic nonelectrolytes*

NONELECTROLYTE	k_s (KCl)	μ	NONELECTROLYTE	k_s (KCl)	μ
	liters/mole	Debyes		liters/mole	Debyes
O ₂	0.132	0	NH ₃	0.057	1.4
H ₂	0.102	0	HCN.....	0.006	2.7
N ₂ O.....	0.099	0.1	SO ₂	-0.022	1.7
CO ₂	0.072	0	NH ₂ NO ₂	-0.07	3.8
H ₂ S.....	0.067	1.0			

* See the Appendix for references on salt effects. The values for the dipole moment are taken from the compilation by Wesson (176).

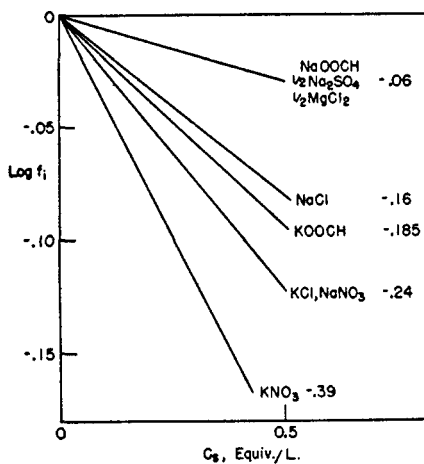


FIG. 8. Salt effects for $\text{Co}(\text{NO}_3)_3(\text{NH}_3)_3$ at 20°C. (Brønsted (18, 19, 145))

pounds. The correlation is excellent. Gross (65) gives a similar table for organic nonelectrolytes and finds a similar but less consistent parallelism. Correlations of this sort will often fail when there are several polar groups in a molecule, since the individual moments of the groups may partly or wholly cancel and yet the local effects of the groups will remain.

An interesting example of extensive salting in for a large, polar nonelectrolyte is shown in figure 8, which gives data for the inorganic molecule cobaltic trinitro-triammine (18, 19, 145). Although in this case even sodium sulfate causes marked

salting in, the general order of the salts is that expected from data for much less polar species. Somewhat analogous results are given by Meyer and Klemm (122) for glycine anhydride. The amino acids in solutions have particularly high dipole moments (and negative dielectric decrements) and, as is well known, they are quite generally salted in (27).

B. Contribution from self-interaction

In Sections III and IV it was noted that in general the activity coefficient of a nonelectrolyte depends not only on the salting-out parameter k_s , but also upon k_i , the self-interaction parameter. Contributions from the latter are most likely

TABLE 4

Comparison of distribution and solubility data for salting out of phenol at 25°C.
For distribution, C_0^d ranges from 0.05 to 0.15; for solubilities, S_i^0 is 0.90 mole/liter

SALT	SALT CONCENTRATION <i>moles/liter</i>	k_s (DISTRIBUTION)	$\frac{K(\text{sol}) = \log S_i^0/S_i}{C_s}$	k_i (CALCULATED)
NaCl.....	0.94	0.172	0.229	-0.15
	1.88	0.172	0.210	-0.13
	2.80		0.203	-0.13
KCl.....	0.93	0.133	0.191	-0.18
	1.84	0.133	0.174	-0.16
NaNO ₃	0.93	0.113	0.148	-0.14
	1.82	0.113	0.139	-0.12
	3.49		0.137	-0.14
KNO ₃	0.91	0.080	0.107	-0.14
	1.78	0.080	0.104 _s	-0.14
	3.38		0.103 _s	-0.16
Average.....				-0.14

to enter for polar nonelectrolytes, since these are frequently rather soluble in water and since studies are often made at high nonelectrolyte concentrations, particularly when activity coefficients are determined from solubility measurements. One illustration of the magnitude of the self-interaction contribution can be obtained by a comparison of the observed salt effects on phenol as determined by Endo (39, 40), using a distribution method and low concentrations of phenol in the aqueous phase, and by Morrison (123), who measured salt effects on the solubility of phenol. Table 4 lists the k_s values obtained by Endo and the much larger Setschenow K parameters obtained by Morrison. Equation 5 has been applied to these data to calculate values of k_i for phenol. The final equation is

$$k_i = \frac{1}{S_i - S_i^0} \left(\log \frac{S_i^0}{S_i} - k_s C_s \right)$$

where the solubilities are those given by Morrison and the value of k_i is that determined by Endo. As table 4 shows, the resulting values of k_i are approximately constant and independent of the choice of salt. Furthermore, the value of k_i (-0.14) is close to the value of -0.16 calculated from the freezing-point studies of Jones and Bury (81) on the phenol-water system.⁴

Another illustration of the importance of the self-interaction term for cases of high solubility is given by the calculations of McDevit and Long (119) on the data for salt effects on racemic and optically active mandelic acids reported by Ross, Morrison, and Johnson (146). The solubilities of the racemic and active acids are high and quite different, 1.335 and 0.738 moles/1000 g. of water, respectively, at 25°C. As a result, the observed salt effects on the solubilities of the two forms are very large and quite different in magnitude. Analysis of the data in terms of equation 5 leads to a constant value of the parameter k_i and to values of the salting-out parameters which are of the same order of magnitude as obtained for similar nonelectrolytes. In several other cases of salt effects on highly soluble nonelectrolytes (e.g., ethyl ether), the results suggest that there is a sizeable contribution from self-interaction but in most such cases data are not available for an independent evaluation of k_i .

C. Salting in by large ions (*hydrotropism*)

In 1916 Neuberg (124) noted that many nonelectrolytes, mostly polar but including nonpolar, are salted in by salts with large anions such as sodium benzoate and sodium *p*-toluenesulfonate. He gave the name *hydrotropism* to this phenomenon. Since then, additional studies of this effect have been made (16, 35, 52, 98, 125, 178), and it has been found that salts of both large anions and cations usually cause salting in. Typical data are shown in table 5, which gives values of the Setschenow parameter for four nonelectrolytes with several salts of large ions. The negative values of the K parameters, often quite large, show the tendency of large anions and large cations to salt in. These values are from solubility studies, so that equation 5 applies. Since the self-interaction parameter k_i is usually negative, there is a "compounding" effect as solubility increases. As a result, with nonelectrolytes whose solubility in water is initially fairly large, the salting-in effect with concentrated salt solutions is often very great. Experimentally, the Setschenow equation frequently holds well only in moderately dilute solutions of these "hydrotropic" salts (roughly up to 0.5 molar), a result which may be partly due to the contribution from self-interaction of the nonelectrolyte, and in the case of liquid nonelectrolytes partly due to solubility of salts in the latter.

⁴This analysis of the data neglects the fact that for the solubility studies the reference phase is not pure phenol but phenol saturated with water. At 25°C. for the two-phase equilibrium between phenol and water, the "phenol" phase contains 67.8 mole per cent (76). When a salt is added to the "water" phase it will change the activity of the water in this phase, the mole fraction of water in the "phenol" phase, and hence the activity of phenol in the latter. However, rough calculations show that the influence of this on the Setschenow parameters is small (of the order of 10 per cent) and will result in smaller K values than if the reference phase were constant. This tends to mask rather than exaggerate the self-interaction effect, so that the calculated k_i is minimal.

The explanation of this effect of large ions is doubtless complicated, but a large part of it is certainly that dissolution of these salts in water leads to an expansion so that the $(V_s - \bar{V}_s^0)$ term of equation 16 is negative. An illustration of this is tetramethylammonium bromide, where from the data of Lunden (107) the value of $(V_s - \bar{V}_s^0)$ can be estimated as -16 ml./mole, leading, as noted in table 2, to a prediction of large salting in of benzene by this salt. Although data are not generally available it is probable that $(V_s - \bar{V}_s^0)$ is negative for most salts of large organic ions. If the nonelectrolytes are polar (e.g., aniline or nitrobenzene), the ion-dipole attraction will enhance the salting-in effect. Finally, there may be additional effects depending upon the structures of the large ions and nonelectrolytes.

TABLE 5
Salting in by large ions

SALT	APPROXIMATE SETSCHENOW PARAMETER, K^*			
	Benzene	Benzoic acid	Aniline	Nitrobenzene
KCl.....	0.166	0.14	0.13	0.075
HClO ₄	-0.04			
NaC ₇ H ₅ O ₂		-0.22	-0.02	
KC ₇ H ₅ O ₂	-0.01	-0.23		-0.21
NH ₄ C ₇ H ₅ O ₂			-0.11	-0.21
NaC ₆ H ₄ SO ₃		-0.12		
NaC ₇ H ₇ SO ₃		-0.30		
(CH ₃) ₄ NBr.....	-0.24	-0.2		-0.17
(C ₂ H ₅) ₄ NI.....		-0.63		
Aniline nitrate.....			-0.16	-0.19
Picoline nitrate.....				-0.47

* References: benzene (118, 151); benzoic acid (12, 89, 128); aniline (43, 58); nitrobenzene (58, 151); see also references 16 and 98.

A striking illustration of differences in effects of large ions on different nonelectrolytes is the study by Linderstrøm-Lang (104) of the salt effects of a series of substituted ammonium chlorides on the solubilities of quinone and hydroquinone. With hydroquinone the salts caused markedly increased salting in, the K values ranging from 0.01 for methylammonium chloride to -0.62 for tetraethylammonium chloride. In contrast, with quinone all of these salts gave an almost constant salting-out parameter of 0.04. Further studies on the variations of both salt type and class of nonelectrolyte are clearly indicated.

A study of the salting-in effects of a homologous series of salts is given by Durand (35), who measured the solubility of benzene in solutions of the sodium salts of straight-chain carboxylic acids from C₃ to C₁₁. 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 a recent review by Klevens (84).

D. Classification

When the specific effects of salts on polar nonelectrolytes are considered more closely it is found that, although in a gross sense the salt order is similar to that for nonpolar molecules, there are significant variations in detail. Furthermore, these variations fall into two distinct groups. For one, which includes nonelectrolytes that have a definite basic character, there is an increased sensitivity to changes in the anion of the salt and also a considerable shift towards increased salting in by lithium salts. In contrast, for the group which includes the weak acids, the salting out by lithium salts is increased, relatively, and is usually larger than for sodium salts. A relatively greater sensitivity for changes in the cation is observed for this group. Finally, there is an intermediate group where the salt order is similar to that for nonpolar nonelectrolytes. Although the situation is more complicated than this simple classification implies, the data are sufficiently consistent to warrant discussion under separate headings.

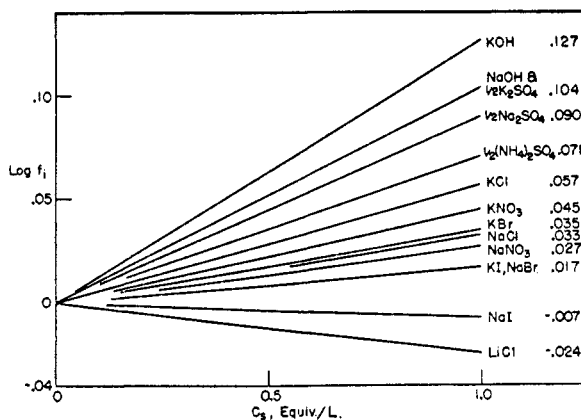


Fig. 9. Salt effects for ammonia at 20°C. (Dawson and McCrae (30))

E. Basic nonelectrolytes

Figures 9 to 11 give plots of $\log f_i$ versus salt concentration for three typical basic nonelectrolytes: ammonia (30), trimethylamine (74),⁵ and aniline (43, 58). The first of these shows the typical salt order for a basic solute particularly clearly. The cation order is inverted to the extent that sodium salts actually salt in more than potassium salts—an inversion of the nonpolar order—and lithium chloride causes marked salting in. Similar but less marked specificities are shown for the larger molecule, trimethylamine. With the weaker base, aniline, the cation order is much closer to that for nonpolar solutes. However aniline, as

⁵ The limiting slopes given in figure 10 for the effect of sodium and potassium sulfates on trimethylamine are half the values actually calculated from the data of Herz and Stanner (74). This change has been made, since a comparison of the data given in the same paper for phenol with the results for the latter reported by Endo (39) indicate that the concentration units for the sulfates in the Herz and Stanner investigation are probably molar rather than normal as stated.

well as the other two examples, shows the other characteristic of basic nonelectrolytes, a relatively greater sensitivity (than would be expected for a nonpolar molecule) to changes in the anion. These characteristics are quite general with basic nonelectrolytes and are shown, for example, by *p*-phenylenediamine (92), dipropylamine (74), and glycine anhydride (122). Quinone, which is less obviously a base, shows a similar sensitivity to anions (102).

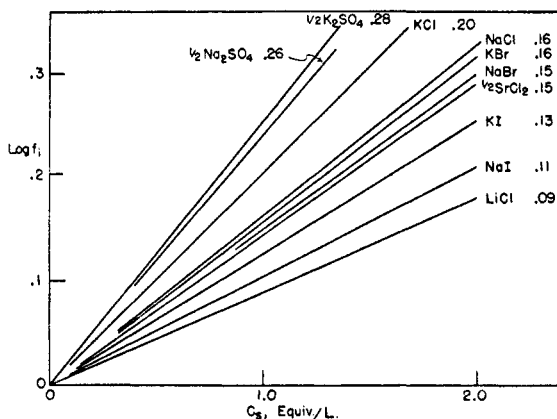


FIG. 10. Salt effects for trimethylamine at 25°C. (Herz and Stanner (74))

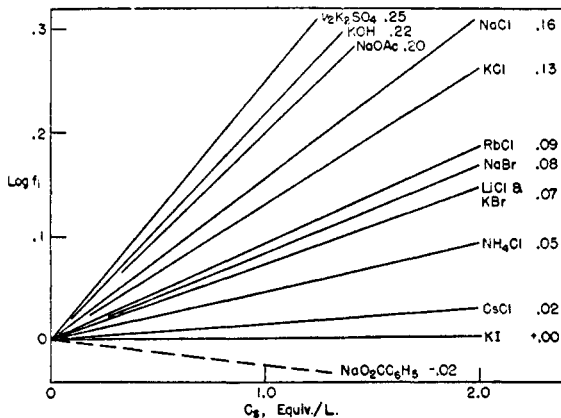


FIG. 11. Salt effects for aniline at 25°C. —, Glasstone, Bridgman, and Hodgson (58); ---, Euler and Svanberg (43)).

A possible explanation for the cation order is chemical interaction, specifically complex-ion formation between the cations and the nonelectrolytes. Most of the basic nonelectrolytes are derivatives of ammonia and all have a tendency to form complex ions. Furthermore, it is well known that for the alkali metal cations the tendency for complex-ion formation is largest for lithium ion and decreases strongly with increasing atomic weight. Thus the inversion of sodium and potassium salts and the strong salting in by lithium salts is consistent with general

chemical properties. However, this "chemical" explanation does not predict the observed sensitivity to anions and also suffers from the fact that it cannot be used to explain the quite different salt order shown by acidic nonelectrolytes.

A more likely interpretation of these salt orders can be given in terms of the "localized hydrolysis" hypothesis developed by Harned and Owen (71) to explain inversions in salt order for activity coefficients of strong electrolytes and the water orientation hypothesis suggested by Kruyt and Robinson (92) (and in a somewhat different manner by Meyer and Dunkel (121)). The basic assumption is that the interactions which occur between acidic and basic nonelectrolytes and water molecules are greatly affected by the orientation of the water molecules in the hydration sphere of an ion. With cations the surrounding water molecules will be oriented with their protons outward and there will then be an attraction between these protons and a basic nonelectrolyte and a repulsion with an acidic nonelectrolyte. With anions the orientation of the water molecules and thus the interactions with nonelectrolytes will be the inverse. These effects should enter in particularly for the small or highly charged ions which are strongly hydrated—for example, lithium, hydrogen, hydroxide, fluoride, and sulfate ions—and are probably negligible for large ions.

From this picture one would expect for basic nonelectrolytes, relative to nonpolar solutes, an increased salting in by lithium ion and perhaps by sodium ion and an increased salting out by sulfate and hydroxide ions. The observed cation order for ammonia and trimethylamine is in agreement with this, as is the wider spread observed for the anions. With ammonia the salting out by hydroxide ion compared to chloride ion is large and the salting in by lithium ion compared to potassium ion is also large, compared to the results for nonpolar solutes of similar size, indicating that the ammonia molecule is actually attracted to lithium ion and repelled by hydroxide ion.

A further prediction from this model of localized hydrolysis is that the amount of attraction or repulsion should depend on the acid strength of the nonelectrolyte. With the basic nonelectrolytes not enough data are available to test this definitely but for the two molecules of similar size, aniline and trimethylamine, the latter, which is the stronger base, shows much more markedly the predicted changes in cation order.

More extensive data are available on acidic nonelectrolytes; in the next section the observed results are considered in terms of this same explanation.

F. Acidic nonelectrolytes

Figures 12 to 14 give the observed salt effects on undissociated phthalic (144), benzoic (12, 89), and succinic (102) acids. The salt orders for these three are quite similar and differ considerably from those for the basic solutes. For all of these acids the cation order for the alkali metal ions parallels ion size, i.e., lithium salts now actually salt out more than sodium salts. Furthermore, these acids are all relatively much more sensitive to changes of cation than to changes of anion. A similar salt order is shown by a variety of acidic nonelectrolytes, ranging from

benzene derivatives (see Section VIII, H) through such aliphatic acids as succinic and acetic (150, 163).

These characteristics of the salt orders for acidic nonelectrolytes are in complete accord with the localized hydrolysis picture discussed in the previous

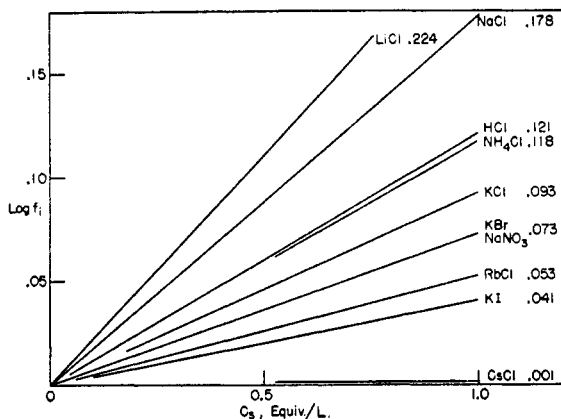


FIG. 12. Salt effects for phthalic acid at 25°C. (Rivett and Rosenblum (144))

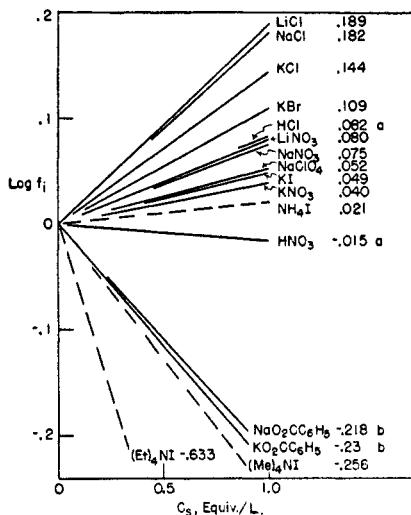


FIG. 13. Salt effects for benzoic acid at 25°C. ---, Bockris, Bowler-Reed, and Kitchener (12); —, Kolthoff and Bosch (89), except (a) Kendall and Andrews (82) and (b) Larsson (94) at 18°C.

section. In the present case it is possible to check in more detail on the prediction that the extent of variation from the salt order characteristic of nonpolar solutes should depend on the acid strength of the nonelectrolyte. The three acids phthalic, benzoic, and phenol (the data for which are given in figure 15) are of comparable

size but of considerably different acid strength. The dipole moments of the last two are almost equal and that for undissociated *o*-phthalic acid is undoubtedly higher. Hence for a given salt, for example, potassium chloride, one might expect benzoic acid and phenol to give similar k_s values and phthalic acid to show less salting out. The observed k_s values for a few salts with these three acids as well as with benzene are given in table 6. It is seen that for the salts potassium bromide

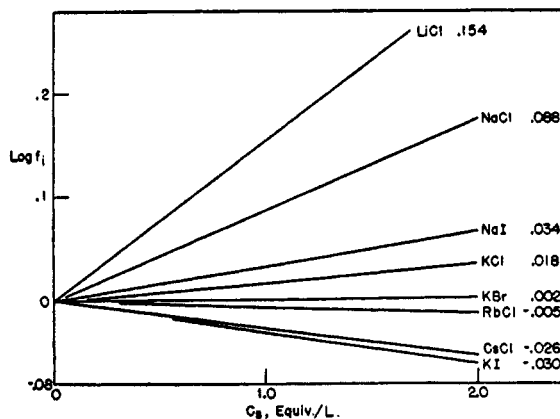


FIG. 14. Salt effects for succinic acid at 18°C. (Linderstrøm-Lang (102))

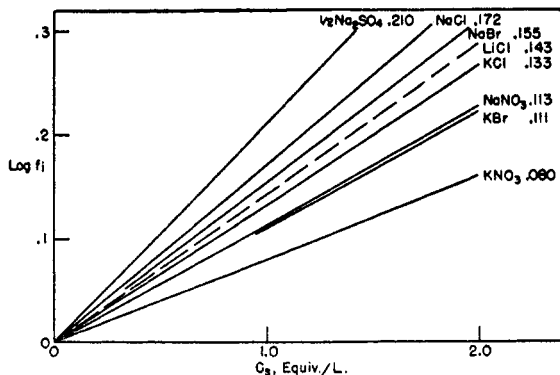


FIG. 15. Salt effects for phenol at 25°C. —, Endo (40); ---, Herz and Stanner (74)

and chloride the values for phenol and benzoic acid are similar and the values for phthalic acid are indeed considerably lower. However, for sodium chloride the k_s values are comparable for the three acids. Finally, for lithium chloride the k_s values increase considerably from phenol to benzoic to phthalic acid and the latter actually gives the highest k_s value of all even though, from the standpoint of simple polarity, more salting in is expected. In fact, for both phthalic and benzoic acid the k_s values for lithium chloride and hydrochloric acid are actually higher than they are in the case of benzene, clearly indicating that a

repulsion enters between the acidic nonelectrolyte and both lithium and hydrogen ions.

Although further studies with other acidic and basic solutes would be desirable, on the basis of the available data the model of localized hydrolysis does provide an adequate qualitative explanation of the observed variations in salt orders.

TABLE 6
Salting parameters for acidic nonelectrolytes of similar size

SALT	k_s			
	Benzene	Phenol $pK = 9.9$	Benzoic acid $pK = 4.2$	Phthalic acid $pK = 2.9$
	<i>liters/mole</i>	<i>liters/mole</i>	<i>liters/mole</i>	<i>liters/mole</i>
KBr.....	0.119	0.111	0.109	0.073
KCl.....	0.166	0.133	0.144	0.093
NaCl.....	0.195	0.172	0.182	0.178
LiCl.....	0.141	0.143	0.189	0.224
HCl.....	0.048		0.082	0.121

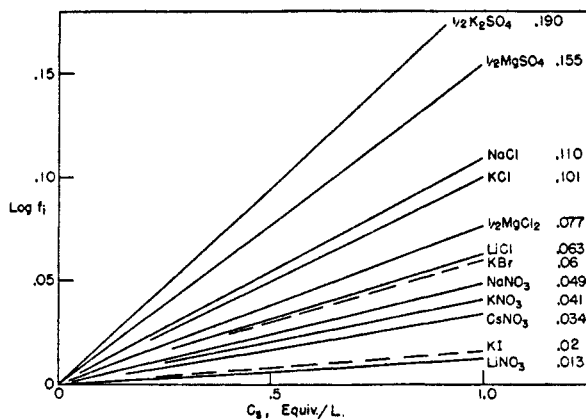


FIG. 16. Salt effects for acetone. —, Gross (67, 68), 15°C.; ---, Herz and Stanner (74), 25°C.

G. Intermediate nonelectrolytes

It would be expected that nonelectrolytes with neither pronounced acidic or basic character would give salt orders similar to those for nonpolar solutes, and several such cases have been studied. Figures 16 to 18 give the data for three typical examples: acetone (67, 68, 74), diacetone alcohol (4), and γ -butyrolactone (106). These vary considerably in polarity (the dipole moment of acetone is 2.74 and that for the lactone is 4.2), and consequently the amount of salting out differs considerably, but the salt order is similar to that for nonpolar molecules in all three cases. Other examples are ethyl acetate (59, 60, 133, 134), phenylthiourea (11, 148), and ethyl ether (42, 170). An interesting example of a substance which

is actually a weak acid but which gives no indications of the specificities characteristic of acidic nonelectrolytes is hydrogen sulfide (120), a small molecule which has the possibility of fitting easily into the water structure.

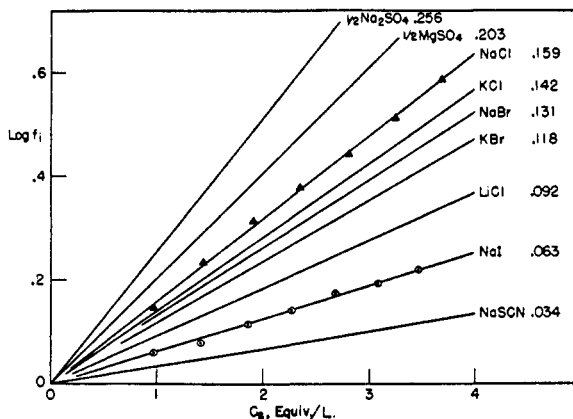


FIG. 17. Salt effects for diacetone alcohol at 24°C. (Åkerlöf (4))

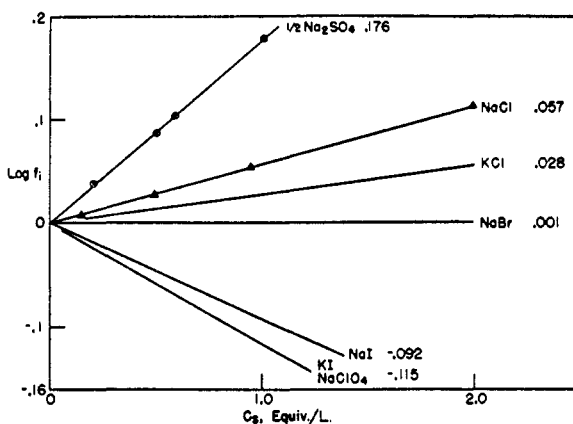


FIG. 18. Salt effects for γ -butyrolactone at 25°C. (106)

H. Benzene derivatives

The points which have been made in the preceding sections can be summarized by an examination of some of the data for benzene and its derivatives. Since all of the molecules are of similar size, complications from changes in molecular volume are minimized.

In table 7 the dipole moments of several benzene derivatives are listed, along with the k_s values for potassium chloride. Although in a broad sense decreased salting out accompanies an increasing dipole moment, the comparison shows 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. For example, the presence of a second amino group causes *p*-phenylenediamine to be salted out far less than aniline, in spite of the negligible difference in their total moments.

Relative variations in the order of the individual ions for effects on benzene derivatives are illustrated in figures 19 to 21. For the cations, potassium ion has been taken as a reference and for each nonelectrolyte the relative values for the other ions have been obtained by taking the difference between the k_s value for a salt with that cation and the k_s value for the potassium salt with the same anion. The anions have been treated similarly, chloride ion being chosen as the reference.

Figure 19 shows the consistent trends towards relatively greater salting out by the smaller cations when basic groups are removed and acidic groups added. This result is in agreement with the discussion of Section VIII, F and further

TABLE 7

Dipole moments (176) and k_s values with potassium chloride for several benzene derivatives

COMPOUND	μ <i>Debyes</i>	k_s (KCl)
<i>p</i> -Phenylenediamine	1.5	0.018
Aniline	1.5	0.13
<i>m</i> -Nitroaniline	4.7	0.077
<i>p</i> -Nitroaniline	6.5	0.049
Benzene	0	0.166
Phenol	1.6	0.133
Benzoic acid	1.7	0.144
Salicylic acid	2.6	0.126
Nitrobenzene	4.0	0.166
<i>p</i> -Nitrophenol	5.0	0.050

indicates that there is an effective repulsion between small cations and the carboxyl groups as well as an attraction between the cations and an amino group.

The connection between acidity or basicity and the salt effect order of anions is shown in figure 20. With increasing acidity the spread in the individual effects is reduced. Sulfate ion shows a consistently decreasing salting-out tendency entirely analogous to the increase noted for lithium ion, indicating, as expected, that oppositely charged ions of high field strength have opposite effects on the acidic and basic groups.

Figure 21 shows the influence of the introduction of a nitro group on the cation order. There is clearly a greater salting out by lithium ion as well as by sodium ion when a nitro group is present. This is qualitatively consistent with the fact that the nitro group decreases the basic and increases the acidic ionization constants. However, the "acid" effect of this group is appreciably greater than would be predicted from the changes in pK values. The nitro group influences the anion order much less. The shift for sulfate ion is in the direction expected from the more acidic character of the nitro derivatives but the spread among the halide ions is increased rather than decreased.

Studies on *o*-, *m*- and *p*-chlorobenzoic acids (128) show that, although the dipole moments of these acids are slightly higher and the pK_a values lower than for benzoic acid itself, both the magnitude and the order of the salt effects are very

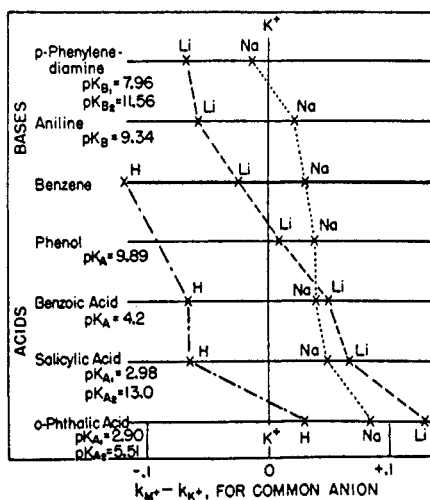


FIG. 19

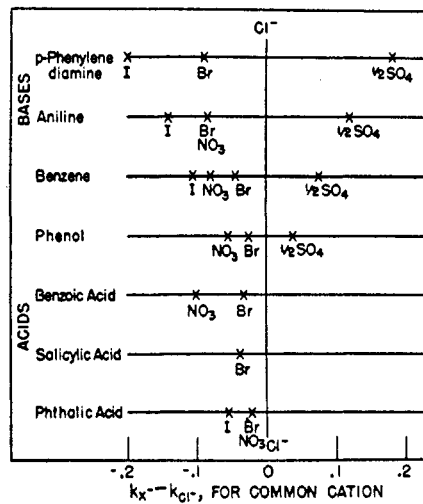


FIG. 20

FIG. 19. Salt effects of cations, relative to potassium ion, on benzene derivatives. See table A-2 for references.

FIG. 20. Salt effects of anions, relative to chloride ion, on benzene derivatives

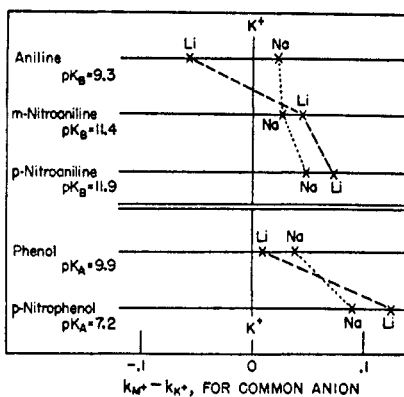


FIG. 21

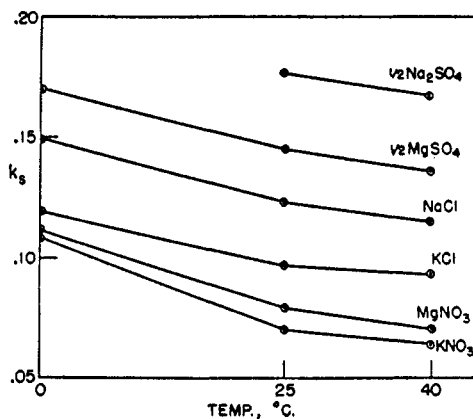


FIG. 22

FIG. 21. Salt effects of cations, relative to potassium ion, on nitro compounds

FIG. 22. Salting-out parameters for nitrous oxide as a function of temperature (Markham and Kobe (112)).

close to those for benzoic acid. The different effects of the nitro and chloro groups indicate that the question goes beyond the simple matter of relative acidity and basicity. More complete experimental data on nitrobenzene and

chlorobenzene, as well as on the substituted acids and bases, would help to clarify matters.

IX. TEMPERATURE COEFFICIENT

Most studies of the influence of temperature on the activity coefficients of nonelectrolytes in the presence of salts have utilized the solubility method and data are usually given for the change in the ratio S_i^0/S_i at a given salt concentration as a function of temperature. Thus, in 1899 Bohr (15) studied the solubility of carbon dioxide in water and in 6.52 and 17.62 weight per cent solutions of sodium chloride and reported data at 5° temperature intervals over the range 0–60°C.

The temperature coefficient of the activity coefficient ratio can be related to the enthalpy and entropy of the transfer of nonelectrolyte from pure water to the salt solution by differentiating equation 2. The results are:

$$\frac{d \ln f_i/f_i^0}{dT} = - \frac{\Delta H}{RT^2} \quad (17)$$

and

$$R \frac{d(T \ln f_i/f_i^0)}{dT} = -\Delta S \quad (18)$$

The first of these was employed many years ago by Rothmund (149), who noted that the value of ΔH was close to zero for a variety of nonelectrolytes. More recently Frank and Evans (50) have attempted to interpret the observed ΔS changes in terms of the structure of aqueous solutions.

The temperature coefficient of k_s is proportional to that for $\log f_i$ only when the self-interaction term is negligible. Intuitively one would predict a negative temperature coefficient for k_s on the simple basis that solutions should become more nearly ideal as temperature increases. This temperature coefficient should be calculable from the available theories, but for either the Debye or the Kirkwood theories definite predictions are not easily made. For example, in the Debye-McAulay theory, as Morrison (123) pointed out, a positive temperature coefficient is predicted from the product $D_o T$, which falls with rising temperature. Unfortunately the dielectric decrement, δ , probably also varies with temperature, and data on this are not readily available.

For the case of nonpolar nonelectrolytes an estimate of the expected temperature coefficient can be obtained by differentiating equation 15. This results in several terms of which one, that in $d\bar{V}_s^0/dT$, is dominant, and, since the others roughly cancel each other, the predicted temperature coefficient is approximated by the following equation:

$$\frac{dk_s}{dT} \cong - \frac{\bar{V}_i^0}{2.3RT} \frac{d\bar{V}_s^0}{dT} \quad (19)$$

Table 8 gives calculated values of dk_s/dT for the solute nitrous oxide, along with data to indicate the expected change of this quantity with temperature. The second column of the table lists values of $d\bar{V}_s^0/dT$ at 25°C. from the com-

pilation of Harned and Owen (71) and the data of Gibson and Kincaid (57). The third column gives the calculated values of dk_s/dT from equation 19 (using a \bar{V}_s^0 value for nitrous oxide of 33 ml./mole). The last two columns list values from Geffcken (55) of $\Delta\bar{V}_s^0/\Delta T$ for some of the salts in the temperature intervals 0–25°C. and 25–50°C. The important points from the table are as follows: the calculated values of dk_s/dT are small and negative; the predicted temperature coefficients are much larger in the interval 0–25°C. than for 25–50°C., since $\Delta\bar{V}_s^0/\Delta T$ decreases with temperature; the predicted temperature coefficients vary considerably for salts, in particular, that for lithium chloride is quite low and that for potassium nitrate is relatively high.

Some of these predictions can be tested with data from the careful study by Markham and Kobe (112) of salt effects on the solubilities of nitrous oxide and carbon dioxide at the temperatures 0.2°, 25°, and 40°C. Values of k_s at the various

TABLE 8

Calculated temperature coefficient of k_s for nitrous oxide and values of $\Delta\bar{V}_s^0/\Delta T$ to show variation with temperature

SALT	$10^2 \frac{d\bar{V}_s^0}{dT}$ (25°C.)	$10^3 \frac{dk_s}{dT}$ (25°C.) (CALCULATED)	$10^2 \frac{\Delta\bar{V}_s^0}{\Delta T}$ (0–25°C.)	$10^2 \frac{\Delta\bar{V}_s^0}{\Delta T}$ (25–50°C.)
LiCl.....	2.5	–0.3	7	0
NaCl.....	9.3	–1.2	16	6
KCl.....	8.5	–1.1	14	5
KBr.....	10.2	–1.3	16	6
NaI.....	15	–1.9	21	11
NaOH.....	11.7	–1.5		
$\frac{1}{2}$ Na ₂ SO ₄	11.1	–1.4		
KNO ₃	15.6	–2.0		

temperatures have been calculated from these data and those for nitrous oxide are plotted as a function of temperature in figure 22. It is evident that the theoretical predictions are well substantiated. In all cases the temperature dependence is negative and it is smaller in the interval 25–40°C. than for the interval 0–25°C. Furthermore, the values for potassium and magnesium nitrates are definitely larger than those for the chlorides. Finally, the values of the observed temperature coefficients are fairly close to the calculated ones of table 8. Very similar results, even as to the actual values of the temperature coefficients, are shown by the data for carbon dioxide.

Values of temperature coefficients which are very similar in magnitude to those for nitrous oxide and carbon dioxide have recently been reported by Eucken and Hertzberg (40a) for the nonpolar solutes argon, xenon, oxygen, methane, and ethane. Less precise temperature studies for polar nonelectrolytes of low solubility show similar results, i.e., the temperature coefficient of k_s is always small and usually negative. Examples are acetone (67, 68), benzoic acid (61, 77), and quinone (102). An example of a study at a high but constant concentration of nonelectrolyte, where again the temperature coefficient is quite small,

is the study of salt effects on the vapor pressure of ammonia solutions (142). A discussion of temperature coefficients is given by Calvet (15), who also discusses the relation between salt effects and the mobilities of the solute.

When studies of salt effects are made at various temperatures on a nonelectrolyte whose solubility is fairly high, the Setschenow parameter K frequently varies considerably with temperature and commonly the change with temperature of K parallels the change of nonelectrolyte solubility in pure water (123). In view of the discussion in Section IV, this is to be expected since, even though k_s is virtually constant, the term $k_i(S_i - S_i^0)$ will vary with the solubilities and will in fact change sign in going from salting out to salting in.

X. SUMMARY

The magnitude of the effect of salts on the activity coefficient of a nonelectrolyte in aqueous solution depends strongly on properties of both the nonelectrolyte and the salt, and several theories, both qualitative and quantitative, have been advanced to explain the results. The well-known electrostatic theories—for example, those of Debye and Kirkwood—predict the correct order of magnitude of the effect for such ordinary electrolytes as sodium and potassium chlorides but they do not predict the large variations with salt which commonly occur. Thus with all nonelectrolytes, salts of large ions, for example, tetramethylammonium or naphthalenesulfonate ion, lead to pronounced salting in even though salts of smaller ions usually give marked salting out.

A considerable specificity in the effect of salts is shown even with nonpolar nonelectrolytes. However, the detailed salt order, i.e., the relative values of the salting-out parameter, k_s , for various salts, is virtually the same for all nonpolar solutes. For example, with the alkali metal cations the order of increased salting out is quite generally $\text{Cs} < \text{Rb} \cong \text{Li} < \text{K} < \text{Na}$ and a similar consistency holds for the anion order. In accord with the theoretical predictions, the observed salt effects for the nonpolar nonelectrolytes correlate rather well with the volume changes ($V_s - \bar{V}_s^0$) which occur when (liquid) salt is dissolved in water. This suggests that a better understanding of the salt effects on nonelectrolytes depends on a more detailed understanding of the properties of the salt solutions themselves. A large part of the variation in the effects of different salts probably arises from the displacement of water molecules by the added ions but special structural factors doubtless also enter for such ions as lithium and hydrogen.

For polar nonelectrolytes the magnitude of the salt effects depends strongly on the size and polarity of the neutral molecule but in a rough sense the specific effects of salts observed with nonpolar species still persist. However, there are significant differences between the salt effects on acidic and basic nonelectrolytes. Acidic nonelectrolytes are commonly more sensitive than are nonpolar solutes to changes in the cation of the salt and frequently the cation order changes from that observed with the nonpolar solutes to increased salting out in the order $\text{K} < \text{Na} < \text{Li}$. For acidic nonelectrolytes of comparable size the extent of the shift from the nonpolar order correlates fairly well with the acid strength. With basic nonelectrolytes there is increased sensitivity to anions and the salting-out

order of the alkali metal cations frequently shifts to $\text{Li} < \text{Na} < \text{K}$. Qualitatively, these effects can be explained in terms of interactions between the acidic and basic nonelectrolytes and water molecules in the hydration spheres of the ions.

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XII. APPENDIX

The two tables of this appendix (tables A-1 and A-2) list studies of salt effects for nonpolar and polar nonelectrolytes, respectively. The research methods which were employed are indicated in the third column of these tables by using

TABLE A-1
Salt effects for nonpolar nonelectrolytes

NONELECTROLYTE	T	METHOD	SALTS	NOTES*	REFER- ENCES
Acetylene.....	°C. 15	S	H ₂ SO ₄ ; NaOH, Na ₂ SO ₄ ; KOH; Ba(OH) ₂	abd	(10)
	25	S	NaCl, NaBr, NaNO ₃ , Na ₂ SO ₄ ; KCl, KBr, KNO ₃ , K ₂ SO ₄ ; NH ₄ Cl, NH ₄ Br, (NH ₄) ₂ SO ₄ ; MgCl ₂ , Mg(NO ₃) ₂ , MgSO ₄ ; CaCl ₂ , Ca- (NO ₃) ₂ ; BaCl ₂ ; Zn(NO ₃) ₂ , ZnSO ₄ ; MnSO ₄ ; FeSO ₄ ; CoSO ₄ ; NiSO ₄ ; AlCl ₃ , Al(NO ₃) ₃ , Al ₂ (SO ₄) ₃ ; FeCl ₃ , Fe ₂ (SO ₄) ₃ ; Cr ₂ (SO ₄) ₃	bd	(110)
Argon.....	25	S	HClO ₄ ; LiCl; NaCl, NaNO ₃ ; KCl; MgCl ₂ ; CaCl ₂ ; SrCl ₂ ; BaCl ₂ ; AlCl ₃	bd	(5)
	0; 20	S	NaCl	abd	(40a)
Benzene.....	16	S	Sodium salts of aliphatic and aro- matic acids	abd	(35)
	30	S	HCl; LiCl; NaF, NaCl; KCl, KBr KC ₇ H ₅ O ₂ ; CsCl; NH ₄ Br; (CH ₃) ₄ NBr	abd	(151)
	25	S	HCl, HClO ₄ ; LiCl; NaOH, NaCl, NaBr, NaI, NaNO ₃ , NaClO ₄ , Na ₂ SO ₄ ; KCl, KBr; RbCl; CsCl, CsI; NH ₄ Cl; BaCl ₂	abd	(118)
Biphenyl.....	25	S	HCl, HClO ₄ ; LiCl; NaCl, NaBr, NaClO ₄ , Na ₂ SO ₄ ; KCl	abd	(130)
Bromine.....	22	S	H ₂ SO ₄ ; bromides	bce	(177)
	25	S + D	NaNO ₃ , Na ₂ SO ₄ ; K ₂ SO ₄	abde	(80)
	25	S	NaCl, NaNO ₃ , Na ₂ SO ₄ ; KCl, KNO ₃ , K ₂ SO ₄ ; NH ₄ Cl, NH ₄ NO ₃ , NH ₄ C ₂ H ₅ O ₂ , (NH ₄) ₂ SO ₄	bce	(120)
Carbon tetrachlo- ride.....	25	S	KCl; MgSO ₄	acd	(64)
Chlorine.....	25	S	H ₂ SO ₄ ; chlorides	abd	(161)
Ethane.....	0; 20	S	NaCl	abd	(40a)
Ethylene.....	15	S	NaOH, Na ₂ SO ₄ ; KOH	abd	(10)
Helium.....	25	S	HClO ₄ ; LiCl, LiI; NaCl, NaNO ₃ ; KCl	bcd	(5)
Hydrogen.....	5-25	S	NaCl; BaCl ₂	abd	(17)
	15	S	LiCl; NaCl, NaNO ₃ , Na ₂ SO ₄ , Na ₂ CO ₃ ; KCl, KNO ₃ , K ₂ CO ₃ ; MgSO ₄ ; CaCl ₂ ; ZnSO ₄ ; AlCl ₃		
	20	S	NaNO ₃ ; KCl, KNO ₃ ; NH ₄ NO ₃	abd	(85)
	25	S	HCl, HNO ₃ , H ₂ SO ₄ ; NaOH; KOH	abd	(54)
	38	S	NaCl	acd	(174)

TABLE A-1—Concluded

NONELECTROLYTE	T	METHOD	SALTS	NOTES*	REFER-ENCES
Iodine.....	°C.				
	25	D	NaNO ₃ , Na ₂ SO ₄ ; K ₂ SO ₄	abd	(80)
	25	S	NaCl, NaBr, NaNO ₃ , Na ₂ SO ₄ ; KCl, KBr, KNO ₃ , K ₂ SO ₄ ; NH ₄ Cl, NH ₄ Br, NH ₄ NO ₃ , NH ₄ C ₂ H ₂ O ₃ , (NH ₄) ₂ SO ₄ , (NH ₄) ₂ C ₂ O ₄	bcd	(120)
	15 25; 35	D S	KCl, KBr, KNO ₃ , K ₂ SO ₄ , K ₂ C ₂ O ₄ HNO ₃ , H ₂ SO ₄ ; NaCl, NaNO ₃ , Na ₂ SO ₄ , NaH ₂ PO ₄	abd bd	(28) (23)
Methane.....	0; 20	S	NaCl	abd	(40a)
Naphthalene.....	25	S	HCl, HClO ₄ ; LiCl; NaCl, NaBr, NaClO ₄ , Na ₂ SO ₄ ; KCl	abd	(130)
Nitrogen.....	5-25	S	NaCl; BaCl ₂	abd	(17)
	25; 38	S	NaCl, Na ₂ CO ₃ , NaHCO ₃	acd	(173)
Nitrous oxide....	8-22	S	LiCl, Li ₂ SO ₄ ; NaCl, Na ₂ SO ₄ ; KCl, K ₂ SO ₄ ; MgSO ₄ ; CaCl ₂ ; SrCl ₂	bd	(63)
	5-25	S	H ₂ C ₂ O ₄ , H ₃ PO ₄ ; NaCl	abd	(147)
	20	S	NaNO ₃ ; KNO ₃	abd	(85)
	15; 25	S	HCl, HNO ₃ , H ₂ SO ₄ ; LiCl; KOH, KCl, KBr, KI; RbCl; CsCl, NH ₄ Cl	abd	(54)
	25	S	HCl, HNO ₃ , HIO ₄ , H ₂ SO ₄ , H ₃ PO ₄ ; NaCl, NaBr, NaNO ₃ , Na ₂ SO ₄ , Na ₂ HPO ₄ , Na ₃ PO ₄ ; KCl, KBr, KNO ₃ , KIO ₄ , K ₂ SO ₄ ; NH ₄ Cl, NH ₄ Br, NH ₄ NO ₃ , (NH ₄) ₂ SO ₄ ; Mg(NO ₃) ₂ , MgSO ₄ ; CaCl ₂ , Ca(NO ₃) ₂ ; BaCl ₂ ; Zn(NO ₃) ₂ , ZnSO ₄ ; Cd(NO ₃) ₂ ; CuSO ₄ ; MnSO ₄ ; FeSO ₄ ; CoSO ₄ ; NiSO ₄ ; Al(NO ₃) ₃ , Al ₂ (SO ₄) ₃ ; Fe ₂ (SO ₄) ₃ ; Cr ₂ (SO ₄) ₃	bd	(110)
	0-40	S	NaCl, Na ₂ SO ₄ ; KCl, KNO ₃ ; Mg(NO ₃) ₂ , MgSO ₄	abd	(112)
Oxygen.....	15; 25	S	HCl, HNO ₃ , H ₂ SO ₄ ; NaOH, NaCl; KOH, K ₂ SO ₄	abd	(54)
	25	S	LiCl; NaCl, NaBr, Na ₂ SO ₄ ; KCl, KBr, KI, KNO ₃ , K ₂ SO ₄ ; RbCl; CsCl; NH ₄ Cl; MgCl ₂ ; CaCl ₂ ; BaCl ₂	abd	(108)
	0-25	S	LiCl; NaCl; KCl; MgCl ₂	abd	(40a)
Radon.....	18	S	NaCl; KCl, KMnO ₄ ; NH ₄ Cl; AgNO ₃ ; CuSO ₄ ; ZnSO ₄ ; FeSO ₄ ; Pb(NO ₃) ₂ ; HgCl ₂	abd	(88)
Xenon.....	0; 20		NaCl	abd	(40a)

* See page 168 for definition of abbreviations.

TABLE A-2
 Salt effects for polar nonelectrolytes

NONELECTROLYTE	T	METHOD	SALTS	NOTES*	REFER- ENCES
	°C.				
Acetal.....	0; 25	D	LiCl, LiNO ₃ ; NaOH, NaCl, NaNO ₃ , NaClO ₄ ; KCl, KNO ₃	d	(126)
Acetic acid.....	-3	FP	KBr	ace	(1)
	25	D	HCl, HNO ₃ , H ₂ SO ₄ ; LiNO ₃ ; KCl, KClO ₃ , K ₂ SO ₄ ; NH ₄ NO ₃ ; Ba(NO ₃) ₂	abe	(150)
	25	D	LiCl, LiBr, LiNO ₃ , LiBrO ₃ , LiIO ₃ ; NaCl, NaBr, NaNO ₃ , NaClO ₃ , NaBrO ₃ , NaIO ₃ , Na ₂ SO ₄ ; KCl, KBr, KNO ₃ , K ₂ SO ₄ ; CaCl ₂ , CaBr ₂ , Ca(NO ₃) ₂ ; SrCl ₂ , SrBr ₂ , Sr(NO ₃) ₂ ; BaCl ₂ , BaBr ₂ , Ba(NO ₃) ₂	abd	(163)
	100	VP	LiCl; NaCl, NaC ₂ H ₃ O ₂ , Na ₂ SO ₄ ; KCl, KNO ₃ , KSCN	abde	(116)
Acetone.....	20	D	LiCl; NaCl; KCl	abd	(133)
	25	D	LiCl; NaCl, NaBr, NaI; KCl, KBr, KI; MgCl ₂ ; CaCl ₂ ; SrCl ₂ ; BaCl ₂	bce	(74)
	15; 25	D	LiNO ₃ ; KCl, KNO ₃ ; CsNO ₃	abd	(68)
	15; 25	D	LiCl; NaCl, NaNO ₃ ; K ₂ SO ₄ ; MgCl ₂ , MgSO ₄ ; La ₂ (SO ₄) ₃	abde	(67)
Ammonia.....	0-24	VP	NaNO ₃ ; KOH; NH ₄ Cl, NH ₄ NO ₃ ; Ca(NO ₃) ₂	be	(139)
	-3	FP	KBr	ace	(1)
	25	VP	NaOH, NaCl; KCl; NH ₄ Cl, NH ₄ I, NH ₄ NO ₃ , NH ₄ CNS, (NH ₄) ₂ SO ₄ , (NH ₄) ₂ C ₂ O ₄ , NH ₄ tartrate; MgCl ₂ ; CaCl ₂ ; SrCl ₂ ; BaCl ₂	ace	(53)
	60	VP	LiCl; NaOH, NaCl, NaC ₂ H ₃ O ₂ , NaCHO ₂ , Na ₂ CO ₃ ; KOH, KCl, KBr, KI, KNO ₃ , KC ₂ H ₃ O ₂ , K ₂ SO ₄ , K ₂ CO ₃ , K ₂ C ₂ O ₄ ; NH ₄ Cl, (NH ₄) ₂ SO ₄ ; CaCl ₂ ; SrCl ₂ ; BaCl ₂ , Ba(C ₂ H ₃ O ₂) ₂ , Ba(CHO ₂) ₂	bce	(90)
	20	D	LiCl, Li ₂ SO ₄ ; NaOH, NaCl, NaI, NaNO ₃ , NaClO ₃ , Na ₂ SO ₄ , Na ₂ CO ₃ ; KOH, KCl, KBr, KI, KNO ₃ , KClO ₃ , K ₂ SO ₄ , K ₂ CO ₃ , K ₂ C ₂ O ₄ ; NH ₄ Cl, NH ₄ Br, NH ₄ NO ₃ , (NH ₄) ₂ SO ₄	abe	(30)
	20-60	VP	K ₂ SO ₄ ; NH ₄ Cl	ace	(131)

TABLE A-2—Continued

NONELECTROLYTE	T	METHOD	SALTS	NOTES*	REFER- ENCES
Ammonia— <i>Cont'd.</i>	°C.				
	25	VP	LiOH, LiCl, LiBr, LiI; NaOH, NaCl, NaBr, NaI, Na ₂ S; KOH, KF, KCl, KBr, KI, KNO ₂ , KNO ₃ , KClO ₃ , KBrO ₃ , KIO ₃ , KCN, KSCN, KBO ₂ , KC ₂ H ₃ O ₂ , KCHO ₂ , K ₂ SO ₄ , K ₂ SO ₃ , K ₂ CO ₃ , K ₂ C ₂ O ₄ , K ₂ CrO ₄ , K ₂ HPO ₄	abe	(2)
	35	VP	NaOH, NaCl, Na ₂ CO ₃ ; KOH, KCl, KC ₂ H ₃ O ₂ , K ₂ CO ₃ , K ₂ C ₂ O ₄	ace	(142)
	10-30	VP	NH ₄ CNS	be	(48)
	25	D	NH ₄ Cl	ad	(115)
Aniline	18	S	LiCl; NaOH, NaCl, Na ₂ SO ₄ ; KCl; CaCl ₂	abe	(42)
	25	D	KBO ₂ , K ₂ SO ₄ ; Ca(OH) ₂ ; Ba(OH) ₂ ; Sr(OH) ₂	acd	(141)
	18	S	NaCl, NaC ₂ H ₃ O ₂ , NaC ₇ H ₅ O ₂ , aniline nitrate; other salts of organic acids	bce	(43)
	25; 50	S	LiCl, LiBr, LiI; NaCl, NaBr, NaI, NaNO ₃ , Na ₂ SO ₄ , Na citrate; KOH, KF, KCl, KBr, KI, KNO ₃ , KClO ₃ , KC ₂ H ₃ O ₂ , K ₂ SO ₄ , K ₂ CO ₃ , K ₂ C ₂ O ₄ , K ₂ CrO ₄ , K ₃ Fe(CN) ₆ ; RbCl, RbBr, RbI; CsCl, CsBr, CsI; NH ₄ Cl, NH ₄ Br, NH ₄ I, (NH ₄) ₂ C ₂ O ₄ ; MgSO ₄ ; Sr(NO ₃) ₂ ; BaCl ₂ , Ba(NO ₃) ₂	abe	(58)
	Benzoic acid	25; 45	S	NaCl, NaNO ₃ ; KCl, KNO ₃	abd
25		S	KCl, KSCN	abd	(51)
25		S	HCl, HNO ₃	abd	(82)
25		S	NaCl, NaNO ₃ , Na ₂ SO ₄ ; MgSO ₄ ; BaCl ₂ , Ba(NO ₃) ₂	abd	(145)
20		S	NaC ₆ H ₅ SO ₃ , NaC ₇ H ₇ SO ₃ , NaC ₈ H ₉ SO ₃	abd	(52)
25		S	NaCl; KCl, KBr; MgCl ₂	abd	(73)
25		D	LiCl; NaBr, NaCl, NaI; KCl, KBr, KI; SrCl ₂ ; BaCl ₂	bcd	(74)
25		S	KCl	abd	(25)
18		S	NaCl, NaC ₂ H ₃ O ₂ , NaCHO ₂ , NaC ₂ H ₂ ClO ₂ , NaC ₇ H ₅ O ₂	abd	(93)
18		S	NaC ₇ H ₅ O ₂ ; KC ₇ H ₅ O ₂	abd	(94)
18		S	NaCl; KCl	abd	(95)

TABLE A-2—Continued

NON-ELECTROLYTE	T	METHOD	SALTS	NOTES*	REFERENCES
Benzoic acid— <i>Cont'd.</i>	°C.				
	18	S	LiCl, LiNO ₃ ; NaNO ₃ , NaClO ₄ , NaC ₂ HCl ₂ O ₂ , NaC ₂ Cl ₃ O ₂ , NaC ₆ H ₅ SO ₃ , NaC ₁₀ H ₇ SO ₃ ; KBr, KI, KNO ₃ ; RbCl; CsCl; MgCl ₂ ; CaCl ₂ , Ca(NO ₃) ₂ ; SrCl ₂ , Sr(NO ₃) ₂ ; BaCl ₂ , Ba(NO ₃) ₂	abd	(96)
	25	S	LiCl, LiI, LiNO ₃ ; NaCl, NaNO ₃ , NaClO ₄ ; KCl, KBr, KI, KNO ₃ , K ₂ SO ₄ ; Mg(NO ₃) ₂ ; CaCl ₂ , Ca(NO ₃) ₂ ; SrCl ₂ , Sr(NO ₃) ₂ ; BaCl ₂ , Ba(NO ₃) ₂	abd	(89)
	25	S	NaC ₆ H ₅ SO ₃ , NaC ₇ H ₇ SO ₃ , NaC ₁₀ H ₇ SO ₃ ; CsCl	abd	(128)
	35	S	LiCl; NaCl, NaBr, NaI; KCl, KBr, KI; BaCl ₂	abd	(61)
	25-85	S	NaCl; KCl, KNO ₃ ; NH ₄ Cl	bd	(123)
25-85	S	NH ₄ I; (CH ₃) ₄ NI; (C ₂ H ₅) ₄ NI; (C ₂ H ₇) ₄ NI; (C ₄ H ₉) ₄ NI	abd	(12)	
Boric acid.....	25	S	NaNO ₃ , Na ₂ SO ₄ ; KCl, KNO ₃ , K ₂ SO ₄	abe	(14)
	12-24	S	HCl; LiCl; NaCl; KCl, KI; RbCl; CsCl; MgCl ₂ ; CaCl ₂ ; BaCl ₂	abe	(102)
	25	S	HCl, HNO ₃	abe	(82)
Butyl alcohol.....	115	S	NaCl, NaBr, NaI, NaNO ₃ , NaSCN	ae	(140)
γ-Butyrolactone.....	25	D	NaCl, NaBr, NaI, NaClO ₄ , Na ₂ SO ₄ ; KCl, KI; BaCl ₂	abd	(106)
Carbon dioxide.....	8-22	S	NaCl; KCl; NH ₄ Cl; CaCl ₂ ; SrCl ₂ ; BaCl ₂	abd	(109)
	15-26	S	H ₂ SO ₄ ; LiCl; NaCl, NaBr, NaNO ₃ , NaClO ₃ , NaC ₂ H ₃ O ₂ , Na ₂ SO ₄ ; KCl, KBr, KI, KNO ₃ , KSCN, KC ₂ H ₃ O ₂ ; NH ₄ Cl, NH ₄ NO ₃ ; MgSO ₄ ; CaCl ₂ ; BaCl ₂ , Ba(C ₂ H ₃ O ₂) ₂ ; ZnSO ₄	abd	(159)
	0-60	S	NaCl	bd	(15)
	15; 25	S	HCl, HNO ₃ , H ₂ SO ₄ ; KCl, KBr, KI, KNO ₃ ; RbCl; CsCl	abd	(54)
	15.5	S	H ₂ SO ₄ ; LiCl; NaCl; KCl, KBr, KI, KNO ₃ , K ₂ SO ₄ , KHSO ₄ , KHSO ₄ , KH ₂ AsO ₄ , KH ₂ PO ₄ , K ₂ HAsO ₄ , K ₂ HPO ₄ ; (NH ₄) ₂ SO ₄ ; MgSO ₄ ; ZnSO ₄ ; CuSO ₄ ; (also mixed solvents)	bcd	(26)

TABLE A-2—Continued

NONELECTROLYTE	T	METHOD	SALTS	NOTES*	REFER- ENCES
	°C.				
Carbon dioxide —Cont'd.....	25	S	KCl; NH ₄ Cl; BaCl ₂ ; Fe(NH ₄)- (SO ₄) ₂	abd	(47)
	38	S	HCl, H ₂ PO ₄ ; NaCl, NaH ₂ PO ₄ , Na lactate; KCl, KH ₂ PO ₄ , KHC ₂ O ₄ , K lactate	ad	(175)
	25	S	H ₂ SO ₄ ; NaCl, Na ₂ SO ₄ ; MgCl ₂ ; CaCl ₂ ; ZnCl ₂ ; AlCl ₃ ; Al ₂ (SO ₄) ₃	bcd	(87)
	0-40	S	NaCl, NaNO ₃ , Na ₂ SO ₄ ; KCl, KNO ₃ ; Mg(NO ₃) ₂ , MgSO ₄	abd	(112)
	25	S	HClO ₄ , H ₂ SO ₄	abd	(113)
Chloroacetic acid....	25	D	NaCl, NaC ₂ H ₂ ClO ₂ ; KCl, KBr, KNO ₃ ; BaCl ₂	abd	(138)
<i>o</i> -Chlorobenzoic acid	25	S	LiCl; NaCl, NaClO ₄ , NaC ₆ H ₅ SO ₃ , NaC ₇ H ₄ ClO ₂ , NaC ₇ H ₇ SO ₃ , NaC ₁₀ H ₇ SO ₃ ; KCl, KBr; CsCl	abd	(128)
<i>m</i> -Chlorobenzoic acid.....	25	S	LiCl; NaCl, NaClO ₄ , NaC ₆ H ₅ SO ₃ ; KCl, KBr	abd	(128)
<i>p</i> -Chlorobenzoic acid	25	S	KCl	abd	(128)
Cobaltitrinitrotri- amine.....	20	S	NaCl, NaNO ₃ , NaCHO ₂ , Na ₂ SO ₄ ; KCl, KNO ₃ , KCHO ₂ , K ₂ SO ₄ ; MgCl ₂ , MgSO ₄	ad	(18, 145)
	20	S	KCl	abd	(19)
<i>m</i> -Cresol.....	25	S	HCl, H ₂ SO ₄ ; NaCl, Na ₂ SO ₄ ; MgCl ₂ , MgSO ₄	abe	(24)
Diacetone alcohol...	24	D	LiCl, Li ₂ SO ₄ ; NaCl, NaBr, NaI, NaSCN, Na ₂ SO ₄ ; KCl, KBr, KI, KSCN; MgSO ₄ ; Al ₂ (SO ₄) ₃	abd	(4)
Dichloroacetic acid..	25	D	NaCl; KNO ₃ , KC ₂ HCl ₂ O ₂ ; BaCl ₂	abd	(138)
1,1-Dichloroethane..	25	S	KCl; MgSO ₄	acd	(64)
1,2-Dichloroethane..	25	S	KCl; MgSO ₄	acd	(64)
1,2-Dichloropropane	25	S	KCl; MgSO ₄	acd	(64)
1,3-Dichloropropane	25	S	KCl; MgSO ₄	acd	(64)

TABLE A-2—Continued

NONELECTROLYTE	T	METHOD	SALTS	NOTES*	REFER- ENCES
	°C.				
Dimethylacetal.....	25	D	NaCl		(126)
Dinitrophenol.....	25	S	NaCl, NaClO ₄ ; KCl, KClO ₄ ; BaCl ₂	abd	(69)
Dioxane.....	0	FP	LiCl; NaCl; KCl	abe	(155)
Dipropylamine.....	25	S	LiCl; NaCl, NaBr, NaI; KCl, KBr, KI	abe	(74)
Dipropylformal.....	25	D	HCl; NaCl; KCl, KBr, KI		(126)
Ethyl acetate.....	28	S	NaCl, Na ₂ SO ₄ ; KCl, KNO ₃ ; MgSO ₄ ; ZnSO ₄	abe	(41)
	-2	FP	LiCl; NaCl, NaBr, NaNO ₃ ; KCl, KBr, KI, KNO ₃ , K ₂ SO ₄ ; MgCl ₂ , Mg(NO ₃) ₂ ; BaBr ₂ , Ba(NO ₃) ₂ ; CuSO ₄	ae	(143)
	20	D	LiCl; NaCl; KCl	abd	(133)
	20	D	Li ₂ SO ₄ ; NaNO ₃ , Na ₂ SO ₄ ; KNO ₃ , K ₂ SO ₄ ; NH ₄ Cl, NH ₄ NO ₃ , (NH ₄) ₂ SO ₄ ; MgSO ₄	abd	(134)
	25; 50	S	LiCl, LiBr, LiI; NaCl, NaBr, NaI, KCl, KBr, KI; RbCl, RbBr, RbI; CsCl, CsBr, CsI; NH ₄ Cl, NH ₄ Br, NH ₄ I	abe	(60)
	25	S	NaNO ₃ , Na ₂ SO ₄ ; KF, KNO ₃ , KClO ₃ , K ₂ SO ₄ , K ₂ CrO ₄ , K ₄ Fe(CN) ₆ , K ₃ Fe(CN) ₆ , NH ₄ NO ₃ , NH ₄ C ₂ H ₃ O ₂ , (NH ₄) ₂ C ₂ O ₄ ; MgSO ₄ ; Ca(NO ₃) ₂ ; Sr(NO ₃) ₂ ; BaCl ₂ , Ba(NO ₃) ₂ ; CuCl ₂ , CuSO ₄ ; ZnSO ₄ ; NiSO ₄ ; Pb(NO ₃) ₂	abe	(59)
	15-50	S	NaCl; KBr, KI	abe	(157)
Ethyl alcohol.....	-3	FP	KBr	ace	(1)
	25	VP	LiCl	abe	(21, 160)
Ethyl ether.....	-16 to 38	S	HCl	bee	(33)
	18	S	LiCl; NaCl, Na ₂ SO ₄ ; KCl, KNO ₃	bee	(42)
	28	S	NaF, NaCl, NaBr, NaI, NaC ₂ H ₃ O ₂ , Na ₂ SO ₄ , Na ₂ CrO ₄ , Na ₂ Cr ₂ O ₇ , Na ₂ MoO ₄ , Na ₂ WO ₄ , Na ₂ PO ₄ , Na ₂ AsO ₄ , Na succinate, Na citrate, Na tartrate, Na phthalate, Na cinnamate, NaC ₇ H ₅ O ₂ , NaC ₇ H ₄ (OH)O ₂ , NaC ₈ H ₅ SO ₃ ; NH ₄ NO ₃ , (NH ₄) ₂ C ₂ O ₄ ; FeSO ₄ ; Hg(CN) ₂ ; FeCl ₃ ; Al ₂ (SO ₄) ₃	ace	(170)

TABLE A-2—Continued

NONELECTROLYTE	T	METHOD	SALTS	NOTES*	REFER- ENCES
Ethyl ether— <i>Cont'd.</i>	15; 25	S	NaCl	abe	(171)
	18	S	H ₂ SO ₄ ; NaOH, NaCl, NaC ₂ H ₃ O ₂ , Na ₂ SO ₄ , Na picrate, Na lactate, Na maleate, Na phenoxide	abe	(99)
	18; 25	S	HCl, HClO ₄ , H ₂ SO ₄ , H ₃ PO ₄	be	(111)
Glycine anhydride...	20	S	LiBr, LiI; NaCl, NaBr, NaI; KF, KCl, KBr, KI	abd	(122)
Hydrogen cyanide...	15; 25	D	LiNO ₃ ; NaNO ₃ ; KCl, KNO ₃ ; CsNO ₃	abd	(68)
	15	D	LiCl; NaCl, NaNO ₃ ; K ₂ SO ₄ ; MgCl ₂ , MgSO ₄ ; La ₂ (SO ₄) ₃	abd	(67)
Hydrogen sulfide....	25	VP, S	HCl, H ₂ SO ₄ ; NaCl, NaBr, NaNO ₃ , Na ₂ SO ₄ ; KCl, KBr, KI, KNO ₃ , K ₂ SO ₄ ; NH ₄ Cl, NH ₄ Br, NH ₄ NO ₃ , NH ₄ C ₂ H ₃ O ₂ , (NH ₄) ₂ SO ₄	abd	(120)
	25	S	HCl	abd	(82)
Hydroquinone.....	12-24	S	HCl, H ₂ SO ₄ ; LiCl; NaCl, Na ₂ SO ₄ ; KCl, KBr, KI; RbCl; CsCl; MgCl ₂ ; CaCl ₂ ; SrCl ₂ ; BaCl ₂ ; AlCl ₃ ; LaCl ₃	abe	(102)
	18	S	(NH ₄) ₂ SO ₄	be	(103)
	18	S	NH ₄ Cl; CH ₃ NH ₃ Cl; C ₂ H ₅ NH ₃ Cl; C ₄ H ₉ NH ₃ Cl; (CH ₃) ₃ (C ₂ H ₅)NCl; (C ₂ H ₅) ₄ NCl	abe	(104)
	24	S	KBr, KI, KNO ₃ , K ₂ SO ₄	bce	(92)
<i>o</i> -Hydroxybenzoic acid.....	25; 35	S	NaCl; KCl, KNO ₃	abd	(77)
	25	S	NaCl; KCl	abd	(73)
	25	S	HCl, HNO ₃	abd	(82)
	25	S	NaC ₂ H ₃ O ₂ , NaCHO ₂ , NaC ₂ H ₂ ClO ₂	ad	(93)
	25	S	HCl	bd	(86)
	25	S	LiCl; NaCl, NaClO ₄ , NaC ₆ H ₅ SO ₃ , NaC ₇ H ₇ SO ₃ , NaC ₁₀ H ₇ SO ₃ ; KCl, KBr	abd	(129)
<i>m</i> -Hydroxybenzoic acid.....	25	S	KCl	abd	(129)
<i>p</i> -Hydroxybenzoic acid.....	25	S	KCl	abd	(129)

TABLE A-2—Continued

NONELECTROLYTE	T	METHOD	SALTS	NOTES*	REFER-ENCES
	°C.				
γ -Hydroxybutyric acid.....	25	D	NaCl, NaBr, NaClO ₄	abd	(106)
Isobutyl alcohol. ...		FP	CuSO ₄	ace	(165)
Mandelic acid.....	25	S	LiCl, LiNO ₃ ; NaCl, NaNO ₃ ; RbCl, RbNO ₃ ; CsCl, CsNO ₃ ; NH ₄ Cl, NH ₄ NO ₃ ; TiNO ₃ ; MgCl ₂ ; CaCl ₂ ; SrCl ₂ ; BaCl ₂ ; also mandelates	abe	(146)
	25	S	HCl, H ₂ SO ₄	be	(86)
Mesityl oxide.....	25; 30	D	HNO ₃ , HClO ₄ ; NaNO ₃ , NaClO ₄ ; KNO ₃	bd	(135)
Nitramide.....	25	D	NaCl; KCl		(126)
<i>m</i> -Nitroaniline.....	25	S	LiCl; NaCl, KCl, KBr, KI, K ₂ SO ₄	acd	(92)
<i>p</i> -Nitroaniline.....	25	S	LiCl; NaCl; KCl, KBr, KI, K ₂ SO ₄	acd	(92)
<i>o</i> -Nitrobenzaldehyde.....	25	S	HCl, HNO ₃ ; NaCl, NaNO ₃ ; KCl, KNO ₃	abd	(62)
<i>m</i> -Nitrobenzaldehyde.....	25	S	HCl; KCl	bd	(62)
Nitrobenzene.....	18	S	KNO ₃ ; aniline nitrate; salts of organic acids	bcd	(43)
	30	S	HCl; NaF, NaCl; KCl, KBr, KC ₇ H ₅ O ₂ ; CsCl; NH ₄ Cl; (CH ₃) ₄ NBr	ad	(151)
<i>o</i> -Nitrobenzoic acid..	25; 35	S	NaCl; NaNO ₃	abd	(77)
	25	S	NaCl, NaNO ₃ , Na ₂ SO ₄ ; MgSO ₄ ; BaCl ₂ , Ba(NO ₃) ₂	abd	(145)
	50	S + D	NaCl; MgSO ₄	bd	(164)
	25	S	HCl	bd	(86)
<i>m</i> -Nitrobenzoic acid.	50	S + D	NaCl; MgSO ₄	bd	(164)
	25	S	NaCl; KCl, KBr, KNO ₃	abd	(78)
	25	S	HCl	bd	(86)
<i>p</i> -Nitrobenzoic acid.	50	S + D	NaCl; MgSO ₄	bd	(164)
<i>p</i> -Nitrophenol.....	25	S	LiCl; NaCl; KCl, KBr, KI, K ₂ SO ₄	acd	(92)
Nitrous acid.....	25	VP	HNO ₃ ; KNO ₃	abd	(3)
Oxalic acid.....	25	S	HCl; NaCl; KCl; NH ₄ Cl	abe	(73)
	25	S	HCl, H ₂ SO ₄	be	(86)

TABLE A-2—Continued

NONELECTROLYTE	T	METHOD	SALTS	NOTES*	REFER- ENCES
Phenol.....	25	D	K ₂ SO ₄ ; Ba(NO ₃) ₂	ae	(150)
	20	D	LiCl; NaCl; KCl	abd	(133)
	25	S	Na ₂ SO ₄	abe	(29)
	25	D	NaCl, NaBr, NaNO ₃ , Na ₂ SO ₄ ; KCl, KBr, KNO ₃ , K ₂ SO ₄	abd	(40)
	25	D	LiCl; NaCl, NaBr, Na ₂ SO ₄ ; KCl, KBr, K ₂ SO ₄ ; MgCl ₂ ; CaCl ₂ ; SrCl ₂ ; BaCl ₂	bcd	(74)
	25	D	LiCl; NaCl; MgCl ₂ ; CaCl ₂ ; SrCl ₂ ; BaCl ₂	abe	(73)
	25-60	S	NaCl, NaNO ₃ ; KCl, KNO ₃	be	(123)
	Phenylacetic acid...	50-85	S	NaCl, NaNO ₃ ; KCl, KNO ₃	be
25		S	HCl	bd	(86)
<i>p</i> -Phenylenediamine	25	S	LiCl; NaCl; KCl, KBr, KI, K ₂ SO ₄	ace	(92)
Phenylthiourea.....	25	S	NaNO ₃ ; KNO ₃	abd	(14)
	20	S	LiNO ₃ ; NaNO ₃ , Na ₂ SO ₄ , Na ₂ CO ₃ ; KNO ₃ , KC ₂ H ₃ O ₂ , K ₂ SO ₄ ; NH ₄ NO ₃ , (NH ₄) ₂ SO ₄ ; MgSO ₄ ; Ba(NO ₃) ₂	abd	(148)
	20	S	NaCl, NaI, NaNO ₂ , NaClO ₃ , NaClO ₄ ; KCl, KBr, KI, KNO ₂ , KClO ₃ ; RbNO ₃ ; CsNO ₃ ; BaCl ₂ ; AlCl ₃	abd	(11)
<i>o</i> -Phthalic acid.....	25; 35	S	HCl; LiCl; NaCl, NaNO ₃ , Na ₂ SO ₄ ; KF, KCl, KBr, KI, KNO ₃ , KClO ₃ , KBrO ₃ , KIO ₃ , KC ₂ H ₃ O ₂ , K ₂ SO ₄ ; RbCl; CsCl; NH ₄ Cl; MgCl ₂ ; CaCl ₂ ; BaCl ₂ ; Hg(CN) ₂	abd	(144)
			NaC ₆ H ₅ SO ₃ , NaC ₇ H ₇ SO ₃ , NaC ₈ H ₉ SO ₃	abd	(52)
	25	S	NaCl; KCl, KBr; MgCl ₂	abd	(73)
	25	S	HCl, HNO ₃	bd	(86)
	25	S	LiCl, Li ₂ SO ₄ ; NaCl, NaNO ₃ , Na ₂ SO ₄ ; NH ₄ Cl	ad	(97)
Quinone.....	12-24	S	HCl, H ₂ SO ₄ ; LiCl; NaCl, Na ₂ SO ₄ ; KCl, KBr; RbCl; CsCl; MgSO ₄ ; CaCl ₂ ; BaCl ₂	abd	(102)
			(NH ₄) ₂ SO ₄	bd	(103)
	18	S	KI; NH ₄ Cl; CH ₃ NH ₃ Cl; C ₂ H ₅ NH ₃ Cl; C ₄ H ₉ NH ₃ Cl; (CH ₃) ₃ (C ₂ H ₅)NCl; (C ₂ H ₅) ₄ NCl	abd	(104)
	24	S	KCl, KBr, KI, KNO ₃ , KSCN, K ₂ SO ₄	bce	(92)

TABLE A-2—*Concluded*

NONELECTROLYTE	T	METHOD	SALTS	NOTES*	REFER- ENCES
Salicylic acid.....	°C.		See <i>o</i> -hydroxybenzoic acid		
Succinic acid.....	25	S	LiCl; NaCl; KCl, KBr, KI	abe	(72)
	12-24	S	LiCl; NaCl, NaI; KCl, KBr, KI; RbCl; CsCl	abe	(102)
	25	S	HCl, HNO ₃ , H ₂ SO ₄	be	(86)
Sucrose.....	-3	FP	CuSO ₄	ace	(165)
	-2	FP	LiCl; NaCl, NaBr, NaNO ₃ ; KCl, KBr, KI, KNO ₃ , K ₂ SO ₄ ; MgCl ₂ , Mg(NO ₃) ₂ ; BaBr ₂ , Ba(NO ₃) ₂ ; CuSO ₄	ae	(143)
Sulfur dioxide.....	25; 35	S	NaCl, NaBr, NaSCN, Na ₂ SO ₄ ; KCl, KBr, KI, KNO ₃ , KSCN, K ₂ SO ₄ ; NH ₄ Cl, NH ₄ Br, NH ₄ NO ₃ , NH ₄ SCN, (NH ₄) ₂ SO ₄ ; CdCl ₂ , CdBr ₂ , CdI ₂ , CdSO ₄	abde	(49)
	10-90	S	Na ₂ SO ₄ ; KCl	abe	(79)
Tartaric acid.....	25	S	NaCl; KCl	abe	(73)
	25	S	HCl, H ₂ SO ₄	be	(86)
<i>o</i> -Toluic acid.....	25	S	NaCl, NaNO ₃ , Na ₂ SO ₄ ; MgSO ₄ ; BaCl ₂ , Ba(NO ₃) ₂	abd	(145)
Trimethylamine.....	25	D	LiCl; NaCl, NaBr, NaI, Na ₂ SO ₄ ; KCl, KBr, KI, K ₂ SO ₄ ; SrCl ₂ ; BaCl ₂	bcde	(74)

* See this page for definition of abbreviations.

the following abbreviations: S, solubility; D, distribution; VP, vapor pressure; FP, freezing point. The lists of the salts studied (given in the fourth column) are complete except that in some cases salts of the larger organic anions have not been listed in detail. The symbols used in the fifth column have the following meanings:

- The studies involved electrolyte concentrations below 1 molar.
- The studies involved electrolyte concentrations of 1 molar or higher.
- Only one electrolyte concentration was studied.
- The concentration of the nonelectrolyte was below about 0.2 molar.
- The concentration of the nonelectrolyte was above 0.2 molar.

Additional references

The following paragraphs contain references to salt effect studies which were of an extensive or survey nature.⁶

⁶ All of the data in this appendix are for aqueous solutions. Actually, several studies have

Gross (65) gives activity coefficients of several nonelectrolytes in 0.5 molal potassium chloride and compares the data with the dipole moments of the molecules.

Knox and Richards (86) give the solubility of several weak acids in high concentrations of hydrochloric, nitric, sulfuric, or acetic acid.

Larsson (93) gives the effect of salts of one or two aliphatic acids on several weak organic acids.

Lindenberg and Lemaignen (100, 101) give the salt effect of sodium chloride on solutions of three ketones.

Neuberg (124, 125) gives the salting-in effects of such salts of organic acids as benzoic, salicylic, and benzenesulfonic for a number of nonelectrolytes, both polar and nonpolar. (See also references 16, 34, 52, and 98.)

been made of systems with nonaqueous or mixed solvents. See, for example, references 13, 36, 170, and 179.