components. The unusual S-shaped solubility curve of $Mg(IO_3)_2{\cdot}4H_2O$ in presence of iodic acid is to be noted. The marked increase of the solubility of the salt in high concentrations of iodic acid suggests possible complex polyiodate ions of magnesium in the solution. According to the configuration of the incomplete curves, it is also possible that some solid compound may form in the intermediate region. All the complexes studied were seeded with the compound $Ba(IO_3)_2{\cdot}I_2O_5$ reported above, and they were then stirred for long periods of time, 5-7 months, but no new solid phases appeared. The solutions containing more than 40% iodic acid were very viscous and difficult to sample. It was necessary to allow the mixture to settle for many days before the liquid could be filtered. According to the densities already noted some very dense solutions may be expected in the intervening region.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Activity Coefficient of Benzene in Aqueous Salt Solutions

BY W. F. MCDEVIT AND F. A. LONG

The effects of electrolytes on the solubility of benzene in aqueous solutions have been determined at 25°. The salting-out effect varies greatly among the various electrolytes and salting-in is observed for perchloric acid. A limiting law for the influence of electrolytes on the activity of non-polar solutes has been developed which relates the magnitude of the salt effect to the volume changes which occur when salt and water are mixed. This law can also be expressed in terms of Gibson's *Pe*, the "effective pressure" exerted by a salt in solution. Qualitatively the data for benzene agree well with the predicted salt effects.

Knowledge of the influence of electrolytes on the activity coefficient of benzene in aqueous solutions can be helpful from two standpoints in reaching a better understanding of the interactions between ions and neutral molecules. Since benzene is a compact non-polar molecule, this system can provide a basic example of the general phenomenon and the interpretation of the results should be less complex than for polar non-electrolytes. Furthermore, data on benzene are of value for comparison with the rather extensive data which already exist for various benzene derivatives.

This paper gives solubilities of benzene at 25° in water and in a number of electrolyte solutions. The resulting activity coefficients are discussed in terms of various theories of salt effects and more particularly in terms of other properties of the aqueous electrolyte solutions themselves. Comparison of the data for benzene with those for benzene derivatives will be considered in a later paper.

After these experiments were started, the authors learned of a similar investigation made at 30° for several electrolytes by Saylor, Whitten, Claiborne and Gross[1] using a different analytical procedure. It will be seen later that the data agree well for most of the electrolytes studied by both groups. Determinations of the solubility of benzene in a few electrolyte solutions have been also made by Schramm, Klapproth and Westheimer[2] and are in reasonable agreement with the present results.

Experimental

The benzene solubilities were determined by a variation of the Euler method in which a measured excess volume of benzene is added to the aqueous solution, and after equilibration, the volume of undissolved benzene is determined by measuring its length in a precision bore tube which leads from the top of the apparatus. The chief difference from the usual procedure is that the benzene phase is not dispersed into the aqueous, *i.e.*, equilibration is done across an unbroken phase boundary. Magnetic stirring of the aqueous phase makes it possible to attain equilibrium solubility in about 24 hours. The flask volume is approximately 500 ml.

All experiments were made at 25.00 ± 0.02°. The aqueous solutions were made up by weight from redistilled water and reagent grade electrolytes. The benzene was redistilled from reagent grade, thiophene-free material. On the basis of duplicate runs both with water and salt solutions we estimate that the solubilities are accurate to within 0.5%.

Results

The average value obtained for solubility of benzene in pure water is 1.77_5 moles per liter which agrees quite well with the values reported in the literature.[3]

Table I gives the results of the measurements in salt solutions. The listed values of f, the molar activity coefficient of benzene in the salt solution, are calculated from the relation

$$f = S_0/S$$

where S_0 and S are the molar solubilities of benzene in water and salt solution, respectively. (This definition assumes that f_0, the activity coefficient of benzene in saturated water solution, is unity which is entirely reasonable in view of the low solubility.) For completeness, data of Saylor, Whitten, Claiborne and Gross at 30° (re-calculated to molar concentration units) for salts which we have not studied are also included in Table I.[4] The last column of the table gives k_s, the limiting slope of $\log f$ *versus* salt molarity. Actually for all concentrations of the salt solutions studied by us, the data are well represented by the Setschenow equation

$$\log f = k_s C_S$$

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[1] J. H. Saylor, A. I. Whitten, Imogen Claiborne and P. M. Gross, THIS JOURNAL, **74**, 1778 (1952).

[2] R. M. Schramm, W. Klapproth and F. H. Westheimer, *J. Phys. Colloid Chem.*, **55**, 843 (1951).

[3] (a) A. Seidell, "Solubilities of Organic Compounds," Third Edition, Vol. II, D. Van Nostrand Co., Inc., New York, N. Y.; (b) R. L. Bohon and W. F. Claussen, THIS JOURNAL, **73**, 1571 (1951).

[4] Saylor, *et al.*, also give data for sodium,, lithium, potassium and cesium chlorides and potassium bromide. The agreement with the results of the present study is good, in spite of the 5° temperature difference, except for the case of cesium chloride, where they observe a much lower value of k_s.

Table I

Activity Coefficients of Benzene in Salt Solutions, 25°

Starred salts are the Saylor, Whitten, Claiborne and Gross data at 30°

Salt	C_s	f	C_s	f	C_s	f	C_s		$\frac{\log f}{C_s} = k_s$
Na_2SO_4	0.137	1.196	0.256	1.372	0.543	1.975			0.548
$BaCl_2$	.134	1.110	.265	1.229	.669	1.635			.334
NaOH	.155	1.089	.444	1.307	1.110	1.925			.256
NaF*	.124	1.070	.254	1.160	0.508	1.340	0.677	1.494	.254
NaCl	.395	1.202	.986	1.560	1.867	2.242	3.945	5.638	.195
KCl	.263	1.106	.876	1.399					.166
NaBr	.393	1.155	.589	1.266	0.786	1.316			.155
LiCl	.435	1.150	1.088	1.425					.141
RbCl	.382	1.129	0.878	1.330					.140
KBr	.259	1.070	.928	1.294					.119
$NaNO_3$	.270	1.077	.457	1.137	.900	1.277			.119
$NaClO_4$	.145	1.037	.375	1.091	.762	1.203	0.904	1.256	.106
NH_4Cl	.205	1.055	.506	1.130	1.025	1.260			.103
NaI	.172	1.034	.431	1.094	1.232	1.320			.095
CsCl	.296	1.065	.574	1.117					.088
HCl	.203	1.025*	.421	1.050*	0.455	1.040*	1.000	1.118	.048
NH_4Br*	.251	1.020	.496	1.035	.737	1.075	0.983	1.109	.041
CsI			.682	0.992					−.006
$KO_2C_7H_5$*	.305	0.989	.337	1.000	.435	0.998	.504	0.993	−.006
$HClO_4$	.235	.979	.478	0.954	.782	.929			−.041
$(CH_3)_4NBr$*	.104	.940	.196	0.891	.332	.868	.469	0.920	−.24

where C_S is molarity of salt, and k_s a parameter dependent on the particular salt. For solutions of sodium chloride this linear relation holds very well up to salt concentrations of four molar.

Figure 1 is a plot of the data for all salts with the common anion, chloride ion, Fig. 2 is a similar plot for all of the sodium salts. For comparison purposes some examples of salting-in have been included in the figures. In addition experimental points have been given for representative cases in order to show the linear character of the plots. From the figures it is evident that for the univalent anions the salting-out decreases markedly in the order $OH^- > Cl^- > Br^- > NO_3^- > ClO_4^- > I^-$. For the alkali metal cations the order of decreasing salting-out is $Na^+ > K^+ > Li^+ = Rb^+ > Cs^+$. Quite similar orders of salt effects are observed with most non-electrolytes, whether polar or non-polar.[5] Finally it is seen that salts of large ions and also perchloric acid cause salting-in of benzene.

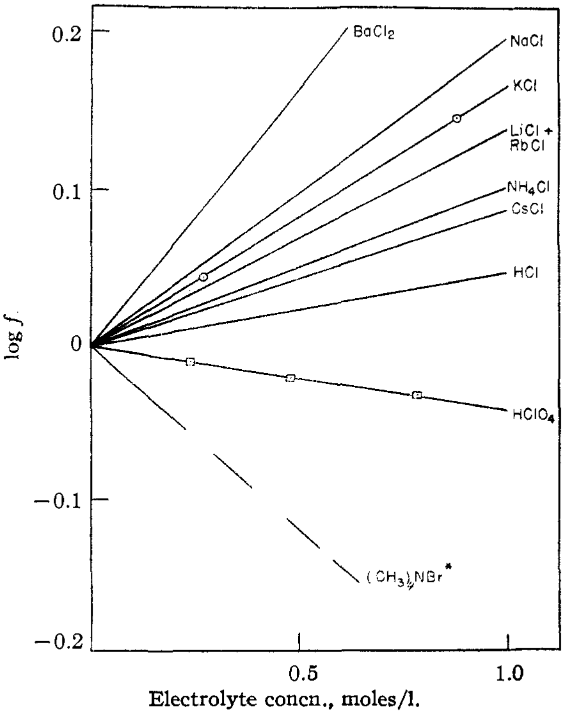

Fig. 1.—Effects of chloride salts on activity coefficient of benzene, 25°.

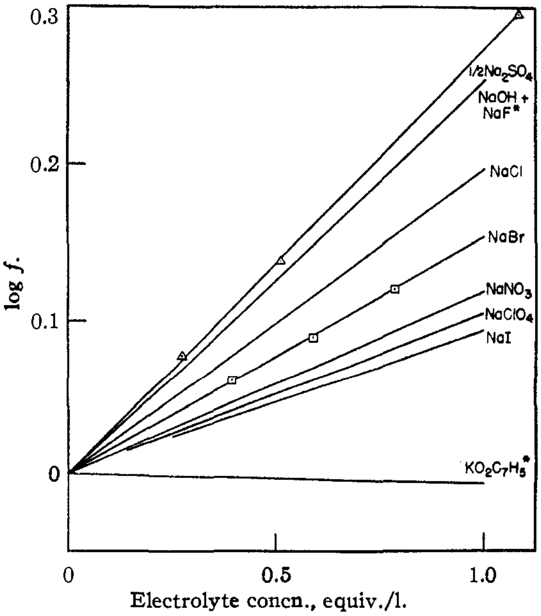

Fig. 2.—Effects of sodium salts on activity coefficient of benzene, 25°.

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[5] (a) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolyte Solutions," Reinhold Publishing Corp., New York, N. Y., Chap. 12; (b) F. A. Long, W. F. McDevit and Frances B. Dunkle. *J. Phys. Colloid Chem.*, **55**, 814 (1951).

In the case of benzene, as in fact with most other non-electrolytes, the observed salt effects are approximately additive with respect to the individual ions. Thus, the Δk's for chloride and bromide salts with a common cation are roughly the same. Similarly the Δk's from sodium to potassium and from sodium to hydrogen are both approximately constant. This additivity suggests that in dilute solution the effect of a given salt is the sum of individual contributions of the component ions.

Discussion

The outstanding feature of these results is the great diversity in the effects of different electrolytes. This marked variation has been observed whenever extensive studies of salt effect have been carried out. The fact that it exists for a substance which should be as relatively inert in water as benzene argues strongly against the notion that the diversity can be attributed primarily to specific interactions involving polar or other hydrophilic groups. It is much more likely that it arises primarily from differences in the behavior of the particular salt solutions toward the "cavity" created by the neutral molecule, and that polar groups, if present, simply have a modifying influence.

The problem of explaining salt effects is essentially the problem of calculating ΔF, the *non-ideal* free energy for transferring a molecule of benzene from pure water to the salt solution. Since at a given temperature the chemical potential of benzene is the same in all saturated solutions

$$kT \ln f = \Delta F$$

aside from a factor (which is quite small for these solutions), involved in the conversion from practical to rational units. For solutions so dilute with respect to benzene, ΔF should be independent of benzene concentration.

The most widely known theories on salt effect are those of Debye and McAulay[6] and Debye[7] according to which f depends primarily upon ionic charge and radius and the molar dielectric decrement of the neutral solute in water. The first theory predicts a linear limiting dependence of $\log f$ on salt concentration and the latter a linear dependence of $1/F$ on salt concentration. A more recent theory by Kirkwood[8] which can also be applied to this problem takes the volume and shape of the neutral molecule into account and similarly predicts a linear dependence of $\log f$ on salt concentration. All of these theories treat the solvent as a continuous dielectric and consider only departures from ideality arising from electrostatic interactions involving the ionic charges.

In Table II the values of k_s predicted by these theories for a few arbitrarily selected salts are compared with the experimental results. The molar volume of benzene in the solutions was assumed to be the same as its pure liquid volume and, for the Debye theories, the dielectric decrement of benzene was crudely estimated by considering that it acts as a simple diluent of negligible static polarization. Ionic radii were taken from Pauling.[9]

TABLE II

COMPARISON OF BENZENE SALT EFFECTS WITH DEBYE AND KIRKWOOD THEORIES

Salt	k_s (obsd.)	k_s (calcd.) Debye	k_s (calcd.) Kirkwood
NaF	0.254	0.130	0.133
NaCl	.195	.126	.125
LiCl	.141	.127	.143
NH_4Cl	.103	.123	.109
NaI	.095	.122	.120
CsCl	.088	.121	.105
$(CH_3)_4NBr$	−0.24	.110	.093

These theories clearly predict the general order of magnitude of the effects, but fail to predict the marked specific effects of different salts. Furthermore, no possible adjustment of the theoretical parameters can account for the cases where there is salting in. These serious shortcomings undoubtedly arise from over-simplification of the models, particularly in their failure to take into account the unique and complex nature of water as a solvent. On the other hand any attempt to introduce a more detailed molecular model immediately leads to inordinate mathematical difficulties just as in most other aspects of the theory of aqueous solutions.

The general trend toward salting-in by larger ions is undoubtedly due, in part, to dispersion forces between ions and neutral solute and solvent molecules[10] and to effects arising from the displacement of water molecules against their own cohesive forces. However, no simple treatment can make the first of these factors account for the results in any detail, particularly, for example, the relatively low salting-out by lithium and hydrogen ions and the exceptionally high salting-out by hydroxide ions.

Fortunately it is more feasible to relate the observed variations in the effects of different salts to other observable properties of the particular salt solutions. In fact if one assumes that the only role of the non-polar solute is simply to occupy volume and thus to modify the ion–water interactions in this simple fashion, one can derive a limiting expression for the free energy of transfer of non-polar solute from water to the salt solution and from this predict values of k_s, the limiting slope of $\log f$ *versus* salt concentrations.

Employing a procedure similar to that used by Hildebrand and Scott[11] for determining the influence of volume changes on the free energy of mixing liquids, one can show that the excess work which must be done against ion–solvent forces to introduce a volume, V_i, into the salt solution is proportional to the volume change ΔV^m which occurs on mixing

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(6) P. Debye and J. McAulay, *Physik. Z.*, **26**, 22 (1925).

(7) P. Debye, *Z. physik. Chem.*, **130**, 56 (1927).

(8) J. G. Kirkwood, Chap. 12, E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corp., New York, N. Y., 1943; *Chem. Revs.*, **24**, 233 (1939).

(9) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y.

(10) (a) J. O'M. Bockris, J. Bowler-Reed and J. A. Kitchener, *Trans. Faraday Soc.*, **47**, 184 (1951); (b) W. F. McDevit and F. A. Long, presented at 118th Semi-annual Meeting, Amer. Chem. Soc., Chicago, Ill., Sept., 1950.

(11) J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes," 3rd edition, Reinhold Publishing Corp., New York, N. Y., 1950, p. 137.

(liquid) salt and water.[12] Consider a Taylor's expansion of the free energy of the solution around V_0 where

$$V_0 = n_w V_w + n_s V_s$$

where n_w and n_s are moles of water and salt, V_w is the molar volume of water and V_s is the liquid volume of pure salt per mole, a quantity which will be discussed below. This can be written

$$\begin{aligned} A(V_0 + \Delta V^m) &= A(V_0) + (\mathrm{d}A/\mathrm{d}V)_{T,V=V_0}\Delta V^m + {}^1/_2(\mathrm{d}^2A/\mathrm{d}V^2)(\Delta V^m)^2 + \ldots \\ &= A(V_0) - P\Delta V^m - \frac{1}{2\beta V}(\Delta V^m)^2 + \ldots \end{aligned}$$

where $A(V_0)$ is the Helmholtz free energy of mixing at constant volume and β is the compressibility of the solution. Then when there is an extra volume change, V_i, due to the introduction of a neutral solute

$$A[V_0 + (\Delta V^m + V_i)] = A(V_0) - P(\Delta V^m + V_i) - \frac{1}{2\beta V}(\Delta V^m + V_i)^2 + \ldots$$

For the case where V_i becomes infinitesimal

$$\lim_{V_i \to 0} \frac{\mathrm{d}A}{\mathrm{d}V_i} = -P - \frac{1}{\beta V}\Delta V^m + \ldots$$

$$\text{or } \frac{\mathrm{d}F}{\mathrm{d}V_i} = -\frac{1}{\beta V}\Delta V^m + \ldots$$

where the remaining terms are of order $(\Delta V^m)^2$ and higher.

The limiting dependence of this last equation on salt concentration will be

$$\lim_{\substack{V_i \to 0 \\ C_s \to 0}} \frac{d^2F}{\mathrm{d}C_s\mathrm{d}V_i} = \frac{(V_s - \bar{V}_s^0)}{\beta_0}$$

where $\bar{V}_s^0$ is the partial molar volume of salt at infinite dilution and β_0 is the compressibility of water. If we introduce formally the relationships

$$V_i = n_i V_i^0 \text{ and } \mathrm{d}F/\mathrm{d}n_i = RT \ln f$$

the result is obtained[13]

$$\text{(1a)} \quad \lim_{\substack{C_s \to 0 \\ n_i \to 0}} \frac{\mathrm{d}\log f}{\mathrm{d}C_s} = \frac{\bar{V}_i^0(V_s - \bar{V}_s^0)}{2.3\beta_0 RT} = k_s$$

where C_s is the molar concentration of salt.

A physical interpretation of Equation 1a follows from the fact that the contraction in total volume, $V_s - \bar{V}_s^0$, which takes place (generally) on mixing salt and water, can be interpreted as a compression of the solvent. This compression makes it more difficult to insert the volume, V_i, of the neutral solute and results, experimentally, in salting-out. In other words the expression is simply an explicit formulation of the long-recognized concept that when salt is added to an aqueous solution of a non-electrolyte the increase in internal pressure resulting from ion–solvent interaction "squeezes out" the non-electrolyte molecules.[14]

An equivalent but more direct application of this same idea can be made by utilizing Gibson's development[15] of an expression for the "effective pressure," P_e, exerted by a salt in solution, since the extra work necessary to introduce the non-polar solute should be simply $P_e V_i$. Gibson introduces P_e as a parameter in the Tait equation for liquid compressibility, arriving at the expression

$$\text{(2)} \quad \beta^P V^P = \frac{0.4343\, x_1 A}{B + P + P_e} - \frac{x_2 \mathrm{d}V}{M_2 \mathrm{d}P}$$

where β^P and V^P are, respectively, the compressibility and specific volume of the solution at pressure P, x_1 and x_2 the weight fractions of the solvent and salt and B and C are parameters characteristic of the solvent. The second term on the right of Equation 2 is small at moderate pressures and concentrations and is frequently ignored. Gibson then derives the relation

$$\text{(3)} \quad V_s^P - \bar{V}_s^P = \frac{434.3A}{B + P + P_e}\frac{\mathrm{d}P_e}{\mathrm{d}m}$$

where m is the molality of the salt and $\bar{V}_s^P$ is the partial molal volume at the pressure P. At atmospheric pressure the term on the left is identical with the volume difference which enters into Equation 1a. Furthermore, if one converts to molar concentrations, multiplies through by V_i and takes limits as before, these expressions yield a limiting law formally identical with that obtained earlier

$$\text{(1b)} \quad \lim_{\substack{C_s \to 0 \\ n_i \to 0}} \frac{\mathrm{d}\ln f}{\mathrm{d}C_s} = \lim_{C_s \to 0} \frac{\bar{V}_i^0}{RT}\frac{\mathrm{d}P_e}{\mathrm{d}C_s} = \frac{\bar{V}_i^0(V_s - \bar{V}_s^0)}{RT\beta_0}$$

The quantity V_s, the volume occupied by the salt as a liquid, which enters in Equation 1 has frequently been used in discussing properties of electrolyte solutions[16] and estimated values are tabulated for a number of salts.[17] However, V_s clearly cannot be determined directly from experiment; hence when the necessary compressibility data are available, it is preferable to employ values of $\mathrm{d}P_e/\mathrm{d}C_s$ directly in equation 1a (which is equivalent to the use of Equation 3 as a definition of V_s).

Values of k_s calculated from Equation 1 are compared with observed values in Table III. The second column gives values of $\mathrm{d}P_e/\mathrm{d}C_s$ calculated from Gibson's data on the compressibility of salt solutions. For the salts indicated by an asterisk in Table III compression data were not available and k_s was calculated from Equation 1a using the values of V_s listed by Lunden. These values and the corresponding ΔV values are given in the third and fourth columns; for completeness these quantities, calculated from equation 3, are also given for the other salts. In all cases values of $\bar{V}_s^0$ were taken from Harned and Owen and Lunden. The value of β_0 was taken as 45.6 × 10^{-6} reciprocal bars and that of V_i^0 as 89.4 cc., the value for pure benzene. It should be noted that for all the cases where $\mathrm{d}P_e/\mathrm{d}C_s$ values were employed the alternative method employing Lunden's V_s values can also be used. Comparison of the values calculated from the two methods indicated satisfactory agreement except for lithium and ammonium chlorides.

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[12] An alternate procedure, which leads to the same final results for ΔF, is to calculate the work for a stepwise process for addition of salt and non-electrolyte to water, at constant $V = V_0$ followed by an expansion to atmospheric pressure.

[13] A small factor for conversion from rational to practical units has been omitted since it is not important to the present discussion.

[14] (a) H. Euler, *Z. physik. Chem.*, **31**, 360 (1899); (b) G. Geffcken, *ibid.*, **49**, 257 (1904); (c) G. Tammann, *Z. anorg. allgem. Chem.*, **158**, 25 (1926).

[15] R. E. Gibson, THIS JOURNAL, **56**, 4, 865 (1934); **57**, 284 (1935); *Am. J. Sci.*, **35**, 49 (1938).

[16] H. S. Harned and B. B. Owen, reference 5a, Chap. 8.

[17] B. Lundén, *Z. physik. Chem.*, **192**, 345 (1943).

TABLE III

COMPARISON OF OBSERVED AND CALCULATED SALT EFFECTS

For starred salts, V_s data are from Lunden; for other salts, calculations involve dP_e/dC_s

Salt	$\frac{dP_e}{dC_s}$, $\frac{\text{bar l.}}{\text{mole}}$	V_s, ml./mole	$(V_s - \bar{V}_s^0)$ ml./mole	k_s Calcd.	k_s Obs.
Na_2SO_4	850	(50.5)	(39.1)	1.33	0.549
NaOH	540	(18)	(24.5)	0.85	.256
NaF ‡	...	17	19.5	.67	.254
NaCl	270	(29)	(12.5)	.42	.195
NaBr	225	(34)	(10.5)	.35	.155
$NaNO_3$	200[a]	(36)	(9)	.31	.119
$NaClO_4$ ‡	...	49	7.5	.26	.106
NaI	175	(43)	(8.0)	.27	.095
$BaCl_2$	645	(53)	(29.5)	1.01	.334
NaCl	270	(29)	(12.5)	0.42	.198
KCl	220	(36.5)	(10)	.34	.166
LiCl	200	(26)	(9)	.31	.141
RbCl ‡	...	41	9	.31	.140
NH_4Cl	95[a]	(40.5)	(4)	.15	.103
CsCl	165[a]	(46.5)	(7.5)	.26	.088
HCl ‡	...	20.5	2.5	.09	.048
$HClO_4$ ‡	...	42	− 1.5	−.05	−.041
$(CH_3)_4NBr$ ‡	...	98.5	−15.6	−.54	−.24

[a] From Gibson's data assuming additive effects for individual ions.

The most significant point in Table III is that the order of the calculated values of k_s is closely the same as that of the observed values for both the anion and cation series, further, the ratios of the observed and calculated values are roughly constant throughout. One inversion appears in each series and when the series are mixed two other inversions enter, but in all cases these occur only when the effects of the salts are very nearly the same. The limiting law correctly predicts the high salting-out of sodium sulfate and sodium hydroxide and the markedly low salting-out for lithium and hydrogen chlorides. Likewise Equation 1 correctly predicts salting-in for perchloric acid and tetramethylammonium bromide. In a qualitative sense, then, the limiting law is quite satisfactory and the basic assumption that the salt effects on non-polar solutes are primarily determined by the properties of the salt solutions themselves seems well substantiated.

From graphs of the available data it is found that P_e is linear in molar salt concentration up to comparatively high values of the latter and, as noted earlier, log f is also linear in salt molarity. This consistency, along with the similarity in the specific effects of different salts, lends further verification to the physical interpretation placed on the parameter P_e.

Quantitatively, the predicted values of k_s are consistently too high by a factor of from two to three. This discrepancy can be attributed to the assumption, implicit in the development of Eq. 1, that the volume occupied by the non-electrolyte is continuous rather than made up of discrete molecules. Hence the derivation ignores the fact that the closeness of approach of a neutral molecule to an ion is limited by the finite radius of the latter as well as by the ion radius. To take this into account, however, one must know explicitly the function for the mutual potential energy between ion and neutral molecule in the solvent. The present treatment yields no such information, but the potential undoubtedly falls rapidly with distance of separation and use of an approximate potential function shows that the observed discrepancy is in the expected direction and can be roughly accounted for.

Specifically we assume that the ions and non-electrolyte are spheres and that the potential between them is of the form K'/r^4, where r is the distance of separation of their centers. (This is the form of the leading term in Kirkwood's expression[8] for ion-cavity repulsion). This leads to an expression

$$\lim_{C_s \to 0} \frac{d \log f}{dC_s} = \frac{K}{a + b}$$

where a and b are the radii of the ion and neutral molecule, respectively, and K includes K' and universal constants. Now if the limiting law is assumed to be correct for the case of very small non-electrolyte molecules, K/a can be evaluated

$$\frac{K}{a} = \frac{(V_s - \bar{V}_s^0)\bar{V}_1^0}{2.3RT\beta_0}$$

Then for the case of a non-electrolyte molecule with finite radius

$$\lim_{C_s \to 0} \frac{d \log f}{dC_s} = \frac{(V_s - \bar{V}_s^0)\bar{V}_1^0}{2.3RT\beta_0} \frac{a}{a + b}$$

and we conclude that the magnitude of the effect should be smaller than that predicted by Eq. 1 by the factor $a/(a + b)$, the ratio of the ion radius to the sum of the ion and non-electrolyte radii. For the present case the radius of the benzene molecule is at least equal to the effective radii of the ions considered and therefore the calculated salt effect should be too large by at least a factor of two, which is about what is observed. Actually the value of the factor is strongly dependent on the particular selection of a potential function, but for any reasonable choice it will be less than one and thus in the right direction to explain the high predictions of Eq. 1.

A detailed application of the limiting law to salt effects on other non-electrolytes, both polar and non-polar will be made in a subsequent paper. However, it is worth mentioning that for most other non-polar solutes the observed order of salt effects is very closely that predicted by Eq. 1. In fact, for non-polar molecules smaller than benzene the numerical correspondence between observed and calculated values of k_s is in closer agreement than for benzene, a fact which is in accord with the foregoing discussion.

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