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The Effects of Salts on the Solubilities of Benzene, Toluene, Ethylbenzene, and Propylbenzene in Water

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Salt effects on the solubilities of benzene, toluene, ethylbenzene, and propylbenzene were studied by making use of the solute vapor. The salting coefficients were determined at 25 °C, and the results were compared with the literature values and with those estimated by means of theoretical equations. The McDevit-Long equation did not give satisfactory predictions until the equation was multiplied by a factor of 0.4. The scaled particle theory gave a favorable agreement with the observations in most cases if suitable pair-potential parameters of solutes were used in the calculations.

The solubility of a nonelectrolyte (solute) in aqueous electrolyte solution has been found to depend on the concentration and on the type of electrolyte present in the solution. In a sufficiently dilute nonelectrolyte solution, the activity coefficient, f, in the salt solution of a given molar concentration, C, is given by:

$$\log f = \log(S_0/S) = k_s C, \qquad (1)$$

where S and S_0 denote the solubility of the nonelectrolyte in salt and salt-free solutions respectively, k_s being the salting coefficient.

In a previous paper, we reported a method of preparing aqueous solutions saturated with a solute such as benzene and the alkylbenzenes by means of a technique that made use of the solute vapor.[1] By means of this technique, the solubility equilibrium can be attained within quite a short time; moreover, we can determine the equilibrium solubility as a function of the vapor pressure of the solute. The present paper is an extension of the method to determining the salting coefficients of benzene, toluene, ethylbenzene, and propylbenzene. Many data on salt effects have been reported in the literature concerning benzene and, to less extent, toluene, but little is known about the alkylbenzenes of larger molecules. Almost all of the literature data have been obtained by putting "liquid" solute in direct contact with aqueous electrolyte solutions. Here we report salting coefficients determined by solubility measurements of the solute "vapor" in the presence of some typical electrolytes. The results obtained are compared below with the literature data and with those predicted by both the McDevit-Long equation and the scaled-particle theory.

Experimental

All the electrolytes and the nonelectrolytes used were of an analytical reagent grade. Deionized-redistilled water was used as a solvent. The concentrations of the electrolyte (stock) solutions were determined by either the argentometric or the gravimetric method.

The apparatus used and the procedures of the solubility measurements were the same as those described in the previous paper.[1] The apparatus was composed of two main parts: one was a separatory funnel (300 cm^3) in which an aqueous solution of from 100 to 200 cm^3 was placed, and the other was a pear-shaped flask (50 cm^3) in which a liquid solute of from 10 to 20 cm^3 was placed. We will call the former "solubility flask," and the latter, "solute reservoir." The solubility flask and the solute reservoir were connected to each other with Teflon and glass tubes. A Viton diaphragm pump was incorporated into the assembly. By means of the pump, the solute vapor was generated by bubbling air through the solute reservoir *via* a sintered glass ball and was then introduced into the solubility flask *via* another sintered ball. The solute vapor was thus circulated in a closed system. The total pressure inside the closed system was kept under atmospheric pressure. After the solubility equilibrium had been attained, an aliquot of the aqueous solution was taken out of the bottom of the solubility flask to determine the solute concentration by means of solvent extraction-spectrophotometry.

Results

The Time Required for Attaining the Solubility Equilibrium. An aqueous solution in the presence of an electrolyte has reached equilibrium with the solute vapor within 5 min at a circulation rate of 2 dm^3 min^{-1}. Some examples are shown in Fig. 1.

Solubility as a Function of the Solute-vapor Pressure. The aqueous phase in the solubility flask has come to be in equilibrium with the solute vapor, while in the solute reservoir the liquid solute has attained equilibrium with the vapor of water. From this point of view, the solute phase is no longer "pure"; hence, the vapor pressure of the solute inside the solubility flask differes from that of the pure solute. However, the solubilities of water in the liquid hy-

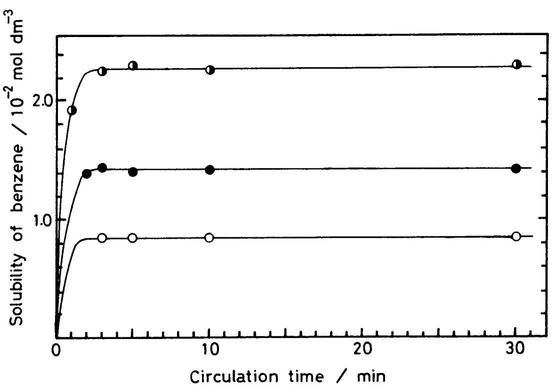

Fig. 1. Equilibrium solubility of benzene *vs.* circulation time.
Circulation rate: 2.0 dm^3/min. Pure water (○), 0.408 mol dm^{-3} $(C_2H_5)_4NBr$ (●), 0.991 mol dm^{-3} $(CH_3)_4NBr$ (◑). Temperature of aqueous solution: 35.0 (○), 25.0 °C (●, ◑). Temperature of solute reservoir: 15.0 (○), 11.8 (●), 19.0 °C (◑).

drocarbons employed here are as small as 3×10^{-3} in the mole fraction.[2] Suppose that Raoult's law is valid; then, the difference in vapor pressure between the pure and actual solutes is only 0.3% or so. We have thus considered it permissible to employ the vapor pressure of the pure solute for the present purpose, the vapor-pressure data of benzene and the alkylbenzenes being taken from previously published tabulations.[3]

In order to check whether or not the solubilities are linearly dependent on the solute-vapor pressure, preliminary experiments were made on the following solute-electrolyte combinations: benzene–tetraalkylammonium bromides, toluene–(NaCl, KCl, $BaCl_2$, and NaSCN). The solubility runs were carried out under conditions such that, at a constant temperature of the aqueous electrolyte solution, the temperature of the solute reservoir was raised nearly up to that of the aqueous solution. Some typical results are shown in Figs. 2 and 3 for a given electrolyte concentration and in Fig. 4 for a constant temperature of the aqueous electrolyte solution, 25 °C. Strictly speaking, the solute-vapor pressure inside the solubility flask may differ from that inside the solute reservoir because of such factors as solute-water and solute-electrolyte interactions in the aqueous phase and the difference in temperature between the solute reservoir and the solubility flask. However, as can be seen from Figs. 2, 3, and 4, a plot of the solubility *vs.* the vapor pressure of the pure solute appears as a straight line for each solute-electrolyte combination investigated, regardless of the salting-in or -out nature of the electrolyte.

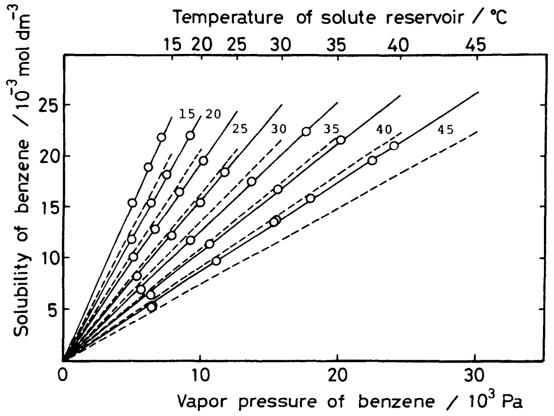

Fig. 2. Equilibrium solubility of benzene in $(CH_3)_4NBr$ aqueous solutions *vs.* vapor pressure. Pure water (dotted line), 0.496 mol dm^{-3} $(CH_3)_4NBr$ solution (solid line). The figure near each line indicates the temperature of aqueous solution.

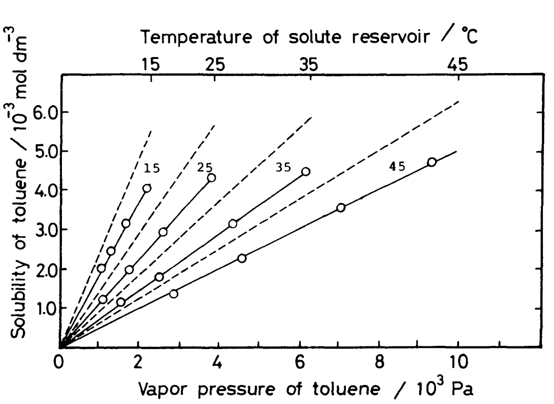

Fig. 3. Equilibrium solubility of toluene in NaCl aqueous solutions *vs.* vapor pressure.
Pure water (dotted line), 0.508 mol dm^{-3} NaCl solution (solid line). The figure near each line indicates the temperature of aqueous solution.

Experimental Salting Coefficients. The salting coefficients were all determined at 25 °C. In the beginning of this study, the solubilities were measured under conditions where the temperatures of both the solubility flask and the solute reservoir were the same. However, somewhat poor reproducibilities were then oberved. This is probably due to the fact that, because it is difficult to keep both temperatures exactly the same, the solute vapor condenses temporarily inside the solubility flask. Therefore, the solubility in each electrolyte solution, S, was estimated as follows: the equilibrium solubility was first measured keeping the solute reservoir at a temperature just below 25 °C, while the temperature of the solubility flask was maintained at 25 °C, and then the equilibrium solubility was extrapolated to find S on the assumption that the solubility obeys Henry's law. The solubility in pure water, S_0, was also estimated in the same way. The values thus determined are, at 25 °C: $10^3\cdot S_0$ (in mol dm^{-3})=20.7 (benzene), 5.65 (toluene), 1.62 (ethylbenzene), 0.376 (propylbenzene). These values are in good agreement with those previously reported except for that of propylbenzene, which differs by *ca.* 10%.[1] In the present study, we will use as S_0 the values determined here. The salting coefficients, k_s, were determined by the least-squares method according to Eq. 1. The log (S_0/S) *vs.* C plots were almost proportional to the electrolyte concentrations up to 1 mol dm^{-3} for 1 : 1 electrolytes and 0.5 mol dm^{-3} for $BaCl_2$ and Na_2SO_4. The use of NaI as an electrolyte gave scattered plots and a poor reproducibility except in the case of benzene;

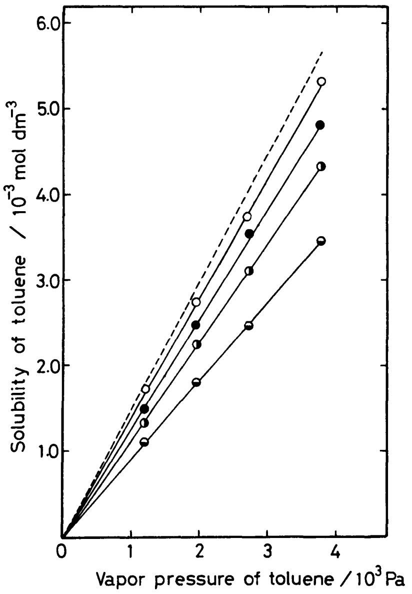

Fig. 4. Equilibrium solubility of toluene in KCl aqueous solutions *vs.* vapor pressure.
Pure water (dotted line), concentration of KCl: 0.101 (○), 0.253 (●), 0.505 (◑), 1.01 mol dm^{-3} (◒). The temperature of aqueous solution: 25.0 °C.

TABLE 1. SALTING COEFFICIENTS OF BENZENE, TOLUENE, ETHYLBENZENE, AND PROPYLBENZENE[a)]

Electrolyte	Observed		Calculated	
	This work	Literature	M-L[b)]	SPT[c)]
Benzene				
NaCl	0.188	0.195[d)]	0.436(0.174)	0.199
$NaNO_3$	0.113	0.119[d)]	0.314(0.126)	0.207
NaBr	0.156	0.155[d)]	0.367(0.147)	0.170
NaSCN	0.048		0.168(0.067)	0.150
NaF	0.249	0.254[d)]	0.681(0.272)	0.197
$NaClO_4$	0.115	0.109[d)]	0.262(0.105)	0.244
KCl	0.157	0.166[d)]	0.349(0.140)	0.176
NaI	0.099	0.095[d)]	0.279(0.112)	0.166
$BaCl_2$	0.310	0.334[d)]	1.030(0.412)	0.266
Na_2SO_4	0.514	0.548[d)]	1.365(0.546)	0.512
$(CH_3)_4NBr$	−0.15	−0.15[e)]	−0.54(−0.22)	1.700
$(C_2H_5)_4NBr$	−0.29	−0.25[e)]	−0.80(−0.32)	2.189
Toluene				
NaCl	0.242	0.267[f)]	0.518(0.207)	0.248
$NaNO_3$	0.154		0.373(0.149)	0.258
NaBr	0.190		0.435(0.174)	0.218
NaSCN	0.066		0.199(0.080)	0.200
NaF	0.336		0.807(0.323)	0.244
$NaClO_4$	0.139		0.311(0.124)	0.299
KCl	0.214	0.205[f)]	0.414(0.166)	0.222
$BaCl_2$	0.414		1.221(0.489)	0.392
Na_2SO_4	0.684	0.651[f)]	1.619(0.648)	0.636
Ethylbenzene				
NaCl	0.280		0.601(0.240)	0.286
$NaNO_3$	0.165		0.432(0.173)	0.300
NaBr	0.232		0.504(0.202)	0.256
NaSCN	0.079		0.231(0.092)	0.238
NaF	0.438		0.937(0.375)	0.281
$NaClO_4$	0.142		0.360(0.144)	0.345
KCl	0.250		0.480(0.192)	0.259
$BaCl_2$	0.457		1.417(0.567)	0.491
Na_2SO_4	0.693		1.878(0.751)	0.737
Propylbenzene				
NaCl	0.281		0.708(0.283)	0.323
$NaNO_3$	0.153		0.510(0.204)	0.339
NaBr	0.233		0.595(0.238)	0.292
NaSCN	0.069		0.272(0.109)	0.275
NaF	0.373		1.104(0.442)	0.315
$NaClO_4$	0.131		0.425(0.170)	0.389
KCl	0.256		0.566(0.227)	0.294
$BaCl_2$	0.467		1.671(0.668)	0.582
Na_2SO_4	0.748		2.214(0.886)	0.834

a) Observed and calculated at 25 °C. b) McDevit-Long equation (multiplied by a factor of 0.4). c) Scaled-particle theory. d) Ref. 4. e) Ref. 7. f) Z. Sir, L. Strnadova, and V. Rad, *Collect. Czech. Chem. Commun.*, **45**, 679(1980).

therefore, the results for the other solutes were omitted. The observed k_s values are listed in Table 1, together with the literature values. The present results are in good agreement with the literature. Comparisons for ethylbenzene and propylbenzene cannot be made, since no data are available for these solutes in the literature at the present time.

Salting Coefficients Calculated by Means of the McDevit-Long Equation. Based on the internal pressure theory (IPT), McDevit and Long have derived this equation[4)]:

$$k_s = \overline{V}_1^{\circ}(V_s - \overline{V}_s^{\circ})/2.3\,\beta_0 RT, \qquad (2)$$

where $\overline{V}_1^{\circ}$ is the partial molar volume of the solute at an infinite dilution, V_s is the molar volume of the pure electrolyte, $\overline{V}_s^{\circ}$ is the partial molar volume of the electrolyte at an infinite dilution, and β_0 is the compressibility of pure water. At 25 °C, $\overline{V}_1^{\circ}$ (in $cm^3\,mol^{-1}$)=89.4 (benzene), 106 (toluene), 123 (ethylbenzene), and 145 (propylbenzene).[5)] All the other parameters were taken from the literature.[4,6–8)] The values of k_s calculated by means of Eq. 2 are given in Table 1.

Salting Coefficients Calculated by Means of the Scaled-particle Theory. In order to predict the salting coefficients, equations have been derived based on the scaled-particle theory (SPT) by Masterton and Lee[9)] and, more recently, by Miyajima *et al.*[10)] We have calculated the salting coefficients according to the latter authors, since their equations are more definite and are more widely applicable. In the present calculations, however, we neglected the self-interaction coefficient, k_2, in the equation given by Miyajima *et al.* since, in the present case, plots of $\log(S_0/S)$ *vs.* the electrolyte concentrations are almost linear through the zero intercept. Equations leading to k_0 are expressed as functions of the hard-sphere diameter, σ; the energy parameter, ε/κ; the polarizability, α; and the apparent molar volume of salt at an infinite dilution, ϕ_0. We adopted the same values of σ and ε/κ for water as those used in Ref. 10, and the same values of σ, α, and ϕ_0 for electrolytes as those used in Ref. 1, the parameter for I^- being taken from Ref. 9. The values of ε/κ for the electrolytes have been evaluated by means of Mavroyannis-Stephen equation:

$$\varepsilon/\kappa=2.28\times10^{-8}\alpha^{3/2}Z^{1/2}\sigma^{-6}, \tag{3}$$

where Z is the total number of electrons of species. The necessary information on the parameters used for solutes is tabulated in Table 2.

TABLE 2. PARAMETERS USED FOR SOLUTES IN CALCULATING SALTING COEFFICIENTS BY SCALED-PARTICLE THEORY

Solute	$10^{24}\times\alpha$[a]	$10^8\times\sigma$[b]	ε/κ[c]
	$cm^3\,mol^{-1}$	cm	K
Benzene	10.43	5.46	188
Toluene	12.26	5.93	159
Ethylbenzene	14.09	6.31	145
Propylbenzene	16.03	6.67	135

a) Estimated from molar refractivity. b) Evaluated by Eq. 4 in the text. c) Evaluated by Eq. 3 in the text.

Discussion

Table 1 shows that the absolute values of the salting coefficient as calculated by means of the McDevit-Long equation are generally larger than those observed and that, if the equation is multiplied by a factor of 0.4, the calculations give the closest prediction. The various k_s values observed for a number of hydrocarbons available in the literature enable us to compare the data with those estimated by the use of Eq. 2. The results are summarized in Table 3, from which it is noticable that most ratios, k_s(obsd)/k_s(calcd), are in the range of from 0.3 to 0.4. The McDevit-Long equation implies that the k_s is linearly dependent on the molar volume of the solute at a given electrolyte. Such plots are shown in Fig. 5 using the data obtained in the present study. The k_s appears for each electrolyte to be approximately proportional up to the molar volume corresponding to

TABLE 3. COMPARISON OF SALTING COEFFICIENTS REPORTED IN THE LITERATURE WITH THOSE CALCULATED BY MCDEVIT-LONG EQUATION

Solute	Molar volume	Electrolyte	k_s		Ratio[a]
	$cm^3\,mol^{-1}$		obsd	calcd	
Benzene	89	NaCl	0.175[b]	0.434	0.4
Chlorobenzene	101.8	NaCl	0.2090[c]	0.497	0.42
		NaBr	0.1292[c]	0.418	0.31
		Na_2SO_4	0.5808[c]	1.56	0.37
Pentane	115.2	NaCl	0.221[c]	0.562	0.39
p-Dichlorobenzene	117.8	NaCl	0.2448[c]	0.575	0.43
		NaBr	0.1744[c]	0.483	0.36
		Na_2SO_4	0.2925[c]	1.799	0.16
Naphthalene	125	NaCl	0.213[b]	0.610	0.35
		NaCl	0.260[c]	0.610	0.43
		NaBr	0.169[c]	0.513	0.33
		Na_2SO_4	0.716[c]	1.909	0.38
Hexane	130.6	NaCl	0.276[c]	0.638	0.43
		NaBr	0.161[c]	0.536	0.30
		KCl	0.244[c]	0.510	0.48
		Na_2SO_4	0.788[c]	1.99	0.40
Biphenyl	149	NaCl	0.276[c]	0.727	0.38
		NaBr	0.209[c]	0.611	0.34
		KCl	0.255[c]	0.582	0.44
		Na_2SO_4	0.846[c]	2.28	0.37
Fluorene	153	NaCl	0.267[b]	0.747	0.36
Anthracene	160	NaCl	0.238[b]	0.781	0.30
Phenanthrene	160	NaCl	0.275[b]	0.781	0.35
		NaCl	0.287[c]	0.781	0.37
		NaBr	0.211[c]	0.656	0.32
		KCl	0.279[c]	0.625	0.45
		Na_2SO_4	0.784[c]	2.44	0.32
Pyrene	172	NaCl	0.286[b]	0.839	0.34
Fluoranthene	175	NaCl	0.339[b]	0.854	0.40
Chrysene	194	NaCl	0.336[b]	0.947	0.35
Benz[*a*]anthracene	194	NaCl	0.354[b]	0.947	0.37

a) k_s(obsd)/k_s(calcd). b) Taken from W. E. May, S. P. Wasik, and D. H. Freeman, *Anal. Chem.*, **50**, 997 (1978). c) Taken from M. Aquan-Yuen, D. Mackay, and W. Y. Shiu, *J. Chem. Eng. Data*, **24**, 30 (1979).

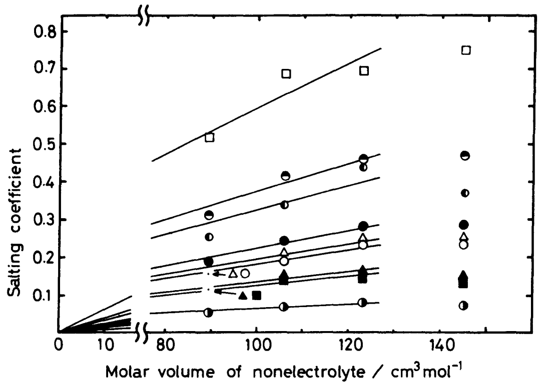

Fig. 5. Salting coefficient *vs.* molar volume of solute. Electrolyte: Na_2SO_4 (□), $BaCl_2$ (⊖), NaF (◐), NaCl (●), KCl (△), NaBr (○), $NaNO_3$ (▲) $NaClO_4$ (■), NaSCN (◑).

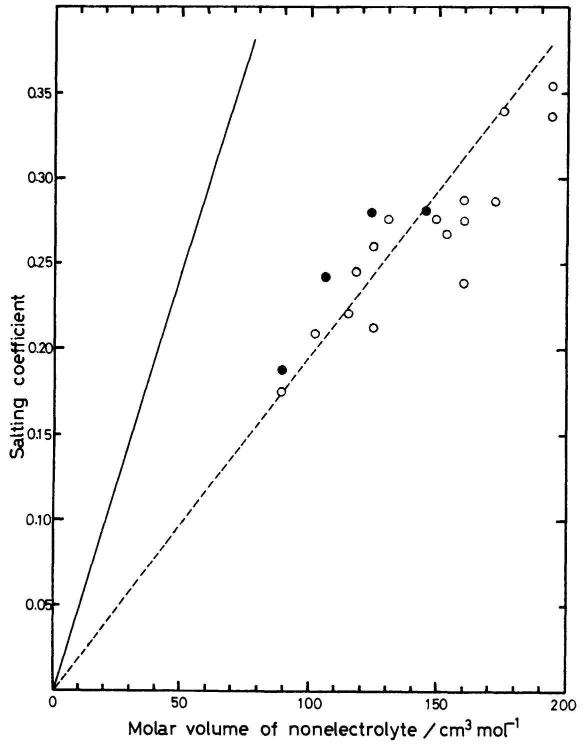

Fig. 6. Salting coefficient for NaCl *vs.* molar volume of solute.
This work (●), literature values (○).

ethylbenzene, but exhibits a poor proportionality in the vicinity of propylbenzene. According to the data shown in Table 3, the values of k_s observed for NaCl are plotted against the molar volume of each solute. The results are shown in Fig. 6, where the solid line and the dotted line indicate, respectively, the molar volume dependence of k_s expected from Eq. 2 and that of k_s multiplied the equation by a factor of 0.4. The plots in Fig. 6, though they seem to scatter around the dotted line, when inspected in more detail display a gently downward curve with an increase in the molar volume rather than a straight line.

The McDevit-Long equation gives satisfactory predictions of k_s for such solutes as H_2, N_2, O_2, CH_4, C_2H_4, and rare gases.[9,11] On the other hand, as was originally pointed out by McDevit and Long, the equation gives a k_s value for benzene consistently too high by a factor of from 2 to 3.[4] Deno and Spink also suggested that the equation must be multiplied by a factor of 0.3 to improve the agreement with the observed and the calculated k_s values of benzene.[7] It is noteworthy that the McDevit-Long equation predicts a high k_s not only for benzene, but also for such hydrocarbons as are shown in Table 3. The IPT explains the salt effect in terms of the electrostriction, $V_s-\bar{V}_s^\circ$ of the solvent caused by salt, and it does not take into account any interactions which may be possible between solute and solvent and between solute and electrolyte. The solute-solvent interaction should be an important factor, especially in the case of aromatic hydrocarbon solutes. Masterton *et al.* have emphasized that the solute-electrolyte interaction, especially with anions, plays a major role in the salting-in of some aromatic hydrocarbons.[12] We can see from Table 3 that the k_s(obsd)/k_s(calcd) ratio is definitely smaller for Br^- than for Cl^-. However, the solute-electrolyte interaction seems to be less important than the solute-solvent interaction, since the k_s(obsd)/k_s(calcd) ratios for various hydrocarbons are almost consistently in the range from 0.3 to 0.4. An empirical factor of from 0.3 to 0.4 cannot be explained quantitatively at present.

The SPT involves two steps: (1) the creation of a cavity in the solvent of a suitable size to accommodate a solute molecule, and (2) the interaction of a solute molecule with the solvent and electrolyte species. The theory would, therefore, reflect the characteristic interactions between solute and solvent and between solute and electrolyte. It is important in calculating k_s by means of SPT to select the most suitable values of σ and ε/κ for the solute in question. Lennard-Jones 6—12 pair potential parameters have been reported except for propylbenzene, but they differ from report to report.[13] At first we adopted the pair-potential parameters evaluated by the use of the following equations:

$$\sigma=(2.3454+0.2972\ \omega)\ (T_c/P_c)^{1/3}, \tag{4}$$

$$\varepsilon/\kappa=(0.8082-0.4504\ \omega)\ T_c, \tag{5}$$

where $\omega=-1+3\theta/7(1-\theta)\times\log P_c$, $\theta=T_b/T_c$ and where T_c, T_b, and P_c are the critical temperature, the boiling temperature, and the critical pressure of the solute respectively. These equations have been explained as being successful for nonpolar molecules.[14] We have taken the alkylbenzenes used in this study to be nearly nonpolar, with quite small dipole moments. The values of ε/κ estimated from Eq. 5 are: ε/κ (in K)=398 (benzene), 406 (toluene), 412 (ethylbenzene), and 415 (propylbenzene). The calculated k_s values, however, led to consistently lower results compared with the observations. Masterton and Lee found that Eq. 3 gave an appropriate ε/κ value in predicting the k_s of benzene.[9] Wilcox and Schrier also recommended the use of the ε/κ estimated from Eq. 3 in calculating the k_s values of polar solutes such as alcohols.[15] For the solutes considered in this work, the values of ε/κ have been determined by Eq. 3 using the corresponding σ values estimated from Eq. 4. These parameters are shown in Table 2. The calculated k_s values are in reasonable agreements with the observations, as will be seen from Table 1, except for $NaNO_3$, NaSCN, $NaClO_4$ and tetraalkylammonium salts. The considerable discrepancies relating to NO_3^-, SCN^-, and ClO_4^- may be attributable to the uncertainty as to the true σ values for these polyatomic anions. In the case of tetraalkylammonium salts, however, the failure of SPT is inherent.

The present method to determine k_s, which makes use of solute vapor, has a potential usefulness when an anionic or cationic electrolyte is subject to being extracted into the liquid solute phase accompanying a counter ion; hence, it is difficult to determine k_s in the presence of a liquid solute.

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