CONTRIBUTION TO THE APPLICATION OF SCALED PARTICLE THEORY TO PREDICTION OF THE SALTING COEFFICIENT

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Dedicated to Prof. Dr E. Hála on the occasion of his 60th birthday.

The possibility of the extension of the scaled particle theory to nonelectrolytes moderately soluble in water and to aqueous electrolytes of various concentrations containing combinations of H^+, K^+, Na^+, NH_4^+, Mg^{2+}, OH^-, Cl^-, Br^-, and SO_4^{2-} ions was verified. Cyclohexanone, n-hexanol and benzene served as nonelectrolytes. The elaborated mathematical model was tested on the basis of experimental data published earlier.

The effect of aqueous electrolytes on the solubility of various nonelectrolytes was expressed by Setchenow[1] as

$$\log\left(c_1^0/c_1\right) = k_s c_{m,n}\,. \tag{1}$$

Previous attempts to express the dependence of the salting coefficient k_s on the characteristics of the particles in solution were based on the concepts of classical thermodynamics and electrostatic theory of the salt effect[2-4]. However, no satisfactory accord between prediction and experimental results was attained. Only the scaled particle theory[5-9] enabled to express a more precise formulation of Eq. (*1*) for prediction of the solubility of gases in nonpolar solvents. The generalization of this theory for the solubility of gases in water according to Pierotti and coworkers[10-12] and in aqueous electrolytes according to Shoor and Gubbins[13] made it possible for Masterton and coworkers[14,15] to elaborate a mathematical model for prediction of the effect of the sort and concentration of uni-univalent electrolytes on the solubility of moderately soluble gases.

The mentioned mathematical model[14,15] was generalized in the present work to describe the solubility of moderately soluble nonelectrolytes, whose concentration in the mixture is not negligible, in aqueous solutions of general electrolytes. For experimental verification of the generalized mathematical model, we used aqueous electrolytes containing various combinations of H^+, Na^+, K^+, NH_4^+, Mg^{2+}, OH^-, Cl^-, Br^-, and SO_4^{2-} ions. The nonelectrolytes were cyclohexanone, n-hexanol, and benzene. The experimental results of other authors were used too.

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THEORETICAL

The empirical Eq. (*1*) applies for approximate prediction of the solubility of sparingly soluble nonelectrolytes in aqueous solutions of salts. Its differential form

$$k_s = (d \log c_1/\mathrm{d}c_{m,n})_{c_{m,n}\to 0} \tag{2}$$

is more suitable for the calculation of the salting coefficient k_s (ref.[14]). The scaled particle theory[13,14] yields an expression for c_1:

$$-\log c_1 = \bar{g}_1^h/2\cdot 3kT + \bar{g}_1^s/2\cdot 3kT + \log\left(kT\sum_{j=1}^{4}\varrho_j\right) \tag{3}$$

which can be written shortly as

$$-\log c_1 = \alpha + \beta + \gamma\,. \tag{3a}$$

An equation for k_s follows from (*2*) and (*3*):

$$k_s = \left[\mathrm{d}(\bar{g}_1^h/2\cdot 3kT)/\mathrm{d}c_{m,n}\right]_{c_{m,n}\to 0} + \left[\mathrm{d}(\bar{g}_1^s/2\cdot 3kT)/\mathrm{d}c_{m,n}\right]_{c_{m,n}\to 0} + \\ + \left[\mathrm{d}(\log \sum \varrho_j/\mathrm{d}c_{m,n}\right]_{c_{m,n}\to 0} \tag{4}$$

or in a shorter form

$$k_s = k_\alpha + k_\beta + k_\gamma\,. \tag{5}$$

According to Masterton and coworkers[13,14], the terms α, β, and γ in (*3a*) can be expressed with the aid of parameters which characterize the properties of the nonelectrolyte, water, cation and anion in the resulting aqueous solution:

$$\alpha = \bar{g}_1^h/2\cdot 3kT = -\log(1 - \tau_3) + A\,, \tag{6}$$

where A is a function of τ_i ($i = 1, 2, 3$):

$$A = 3\tau_2\sigma_1[1 + \tau_1\sigma_1/\tau_2 + 3\tau_2\sigma_1/2(1 - \tau_3)]/2\cdot 3(1 - \tau_3) \tag{7}$$

and

$$\tau_i = (\pi/6)\sum_{j=1}^{4}\varrho_j\sigma_j^i \tag{8}$$

$$\beta = \bar{g}_1^s/2\cdot 3kT = -32\pi\sum_{j=1}^{4}\varrho_j\varepsilon_{1j}\sigma_{1j}^3/9(2\cdot 3kT) - 4\pi\varrho_2\mu_2^2\alpha_1/3(2\cdot 3kT)\,\sigma_{12}^3\,. \tag{9}$$

The term γ is defined by Eq. (*3*).

Expressions for the derivatives in Eq. (*4*) or (*5*) were derived[14] on the simplifying assumption that the aqueous solution contains a 1 : 1 electrolyte and the concentration of the nonelectrolyte is very low against that of water and both ions (hence ϱ_1 is much smaller than ϱ_2, ϱ_3, and ϱ_4). We shall derive in a similar manner general equations for k_α, k_β, and k_γ in (*5*) assuming that the solution contains an electrolyte of the general type A_mB_n and that the concentration of the nonelectrolyte in the solution is not negligible.*

By combining Eqs (*6*)–(*8*) and differentiating (for $c_{m,n} \to 0$) we obtain:

$$k_\alpha = [1/2{\cdot}3(1 - \tau_3)] \{(1 + 3\sigma_1) \tau' + \\ + [3\sigma_1^2/\tau_2^2(1 - \tau_3)] [(\tau_1'\tau_3 + \tau_3'\tau_1) \tau_2(1 - \tau_3) + \tau_1\tau_3(\tau_3'\tau_2 - (1 - \tau_3) \tau_2')] + \\ + [9\sigma_1^2/(1 - \tau_3)] [\tau_2\tau_3'(1 - \tau_3) + \tau_3^2\tau_3']\} . \qquad (10)$$

The number density of particles, $\varrho_j = Nc_j/1000$, in Eqs (*3*) and (*4*) is defined as follows[13,14]:

$$\varrho_1 = Nc_1/1000 , \qquad (11)$$

$$\varrho_2 = (Nd_2/M_2) . (1 - c_1\phi_1/1000 - c_{m,n}\phi_{m,n}/1000) , \qquad (12)$$

$$\varrho_3 = Nmc_{m,n}/1000 , \quad \varrho_4 = Nnc_{m,n}/1000 . \qquad (13), (14)$$

The symbol τ_i' denotes the first derivative $(d\tau_i/dc_{m,n})_{c_{m,n} \to 0}$ for which it follows from Eq. (*8*) that

$$\tau_i' = (\pi/6) \sum_{j=1}^{4} \varrho_j'\sigma_j^i . \qquad (15)$$

The analogous expression $(d\varrho_j/dc_{m,n})_{c_{m,n} \to 0} = \varrho_j'$ can be with the use of the modified Eq. (*1*)

$$\ln (\varrho_1/\varrho_1^0) = -2{\cdot}3k_sc_{m,n} \qquad (16)$$

written in the form[14]

$$\varrho_1' = -2{\cdot}3k_sc_1^0N/1000 , \qquad (17)$$

$$\varrho_2' = d_2(2{\cdot}3_1^0k_sc_1^0 - \phi_{m,n}) N/1000M_2 , \qquad (18)$$

$$\varrho_3' = mN/1000 , \quad \varrho_4' = nN/1000 . \qquad (19), (20)$$

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* The concentration of the electrolyte A_mB_n will be denoted as $c_{m,n}$; the saturated concentration of the nonelectrolyte in aqueous electrolyte as c_1 and the same in water as c_1^0.

The quantity k_β in (*5*) can be calculated by combining Eqs (*4*), (*9*), (*11*)–(*14*), and (*16*)–(*20*) as follows:

$$k_\beta = -4\pi(N/3000)\,.\,2{\cdot}3kT\{\tfrac{8}{3}(m\varepsilon_{1m}\sigma_{1m}^3 + n\varepsilon_{1n}\sigma_{1n}^3) - \phi_{m,n}(d_2/M_2)\,.$$
$$(\tfrac{8}{3}\varepsilon_{12}\sigma_{12}^3 + \mu_2^2\alpha_1/\sigma_{12}^2) - 2{\cdot}3k_sc_1^0[\tfrac{8}{3}\varepsilon_1\sigma_1^3 - \phi_1(d_2/M_2)\,.\,(\tfrac{8}{3}\varepsilon_{12}\sigma_{12}^3 + \mu_2^2\alpha_1/\sigma_{12}^2)]\}\,. \quad (21)$$

The energetic parameters ε_j/k in this equation can be calculated for various cations and anions as[14,16]

$$\varepsilon_j/k = 2{\cdot}28\,.\,10^{-8}\alpha_j^{2/3}Z_j^{1/2}/\sigma_j^6\,. \quad (22)$$

The value of ε_2/k can be set[11,14] equal to 85·3. The values of ε_j/k were for a number of ions determined earlier (Table III). If they are unknown, they must be evaluated from the known solubility and dipole moment of water, μ_2.

The quantity k_γ in (*5*) can be calculated by combining Eqs (*4*), (*11*)–(*14*), and (*16*)–(*20*) as

$$k_\gamma = [m + n - \phi_{m,n} - d_2/M_2 - 2{\cdot}3k_sc_1^0(1 - \phi_1d_2/M_2)] :$$
$$: [2{\cdot}3c_1^0(1 - \phi_1d_2/M_2) + 1000d_2/M_2]\,. \quad (23)$$

By adding Eqs (*10*), (*21*), and (*23*) we obtain the salting coefficient k_s for the given system.

EXPERIMENTAL

The solubility of cyclohexanone, n-hexanol, and benzene in water and several aqueous electrolytes was measured at 25°C. These liquids were redistilled and their purity was checked by common methods. The concentration of electrolytes (NaCl, KCl, NaBr, NaOH, HCl, $MgCl_2$, $MgSO_4$, Na_2SO_4, $(NH_4)_2SO_4$) was in the range 0·1—2·0M. The content of benzene and cyclohexanone in equilibrated solutions was determined spectrophotometrically at 254 or 276 nm with the use of tabulated molar absorptivities. The accuracy of the determination, checked by measurement of standard solutions, was ±5%. The concentration of n-hexanol in equilibrated solutions was determined spectrophotometrically in the region 320—360 nm after reacting with $NaNO_2$ in acidic medium to give hexyl nitrite, which was extracted with n-heptane[25–27]. The accuracy of the determination, checked on standard solutions, was ±3%. We could not measure the solubility of cyclohexanone in a solution of NaOH owing probably to a slow irreversible condensation with the formation of cyclohexylidenecyclohexanone, whose absorption spectrum is different.

RESULTS AND DISCUSSION

The dependence of log (c_1^0/c_1) on the electrolyte concentration $c_{m,n}$ is shown in Figs 1–3 for cyclohexanone, n-hexanol, and benzene. It is seen that this dependence is linear in the whole range of $c_{m,n}$ values and satisfies Eq. (*1*).

To calculate the salting coefficient according to Eqs (*5*), (*10*), (*21*), and (*23*), we used besides our experimental results also data published earlier (Table II). When using the scaled particle theory, it is necessary for the calculation of k_s to know the values

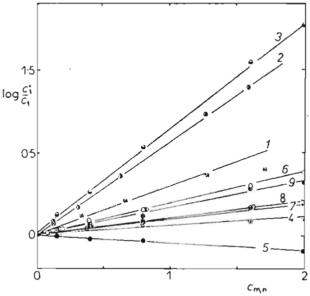
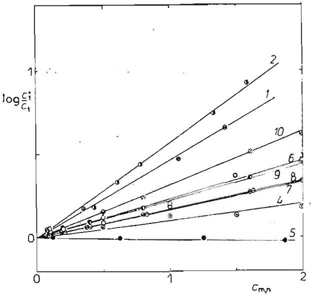


FIG. 1

Dependence of Solubility of Cyclohexanone on Electrolyte Concentration $c_{m,n}$ (mol/dm^3 *1* $MgCl_2$; *2* $MgSO_4$; *3* Na_2SO_4; *4* H_2SO_4) *5* HCl; *6* NaCl; *7* NaBr; *8* KBr; *9* KCl;



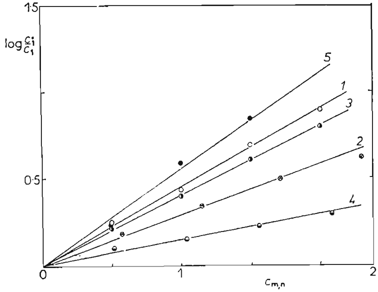


FIG. 2

Dependence of Solubility of n-Hexanol on Electrolyte Concentration

Curve numbers correspond to Fig. 1. Curve *10* NaOH.

FIG. 3

Dependence of Solubility of Benzene on Electrolyte Concentration

1 $MgSO_4$; *2* $MgCl_2$; *3* $(NH_4)_2SO_4$; *4* H_2SO_4; *5* Na_2SO_4.

of a number of quantities which characterize the behaviour of the solution components. The values used by us are given in Tables III – V. Of the nonelectrolytes for which the coefficient k_s was evaluated, the polarizability is known only for benzene[17]; for others its values were calculated from the bonding polarizabilities according to Denbigh[18] and Hirschfelder[19].

The values of σ_1 and ε_1/k for nonelectrolytes considered in this work are (except for benzene) not given in the literature. They were calculated from the corresponding experimental values of the salting coefficient k_s in 1 : 1 electrolytes by the optimalization method according to Marquardt so as to minimize the sum of squares of the deviations between calculated and experimental values of k_s. The results are:

Value	Benzene	Toluene	Ethyl acetate	Diethyl ether	n-Hexanol	Cyclohexanone
ε_1/k, K	212	117	117	139	133	320
σ_1, 10^{-8} cm	6·20	5·88	3·32	4·45	5·79	4·49

TABLE I

Comparison of Experimental (k_s^{exp}) and Calculated (k_s^{calc}) Values of k_s for Cyclohexanone, n-Hexanol and Benzene

Electrolyte	Cyclohexanone[a]			n-Hexanol[a]			Benzene[4,14]		
	k_s^{exp}	k_s^{calc}	Δ	k_s^{exp}	k_s^{calc}	Δ	k_s^{exp}	k_s^{calc}	Δ
NaCl	0·202	0·193	0·009	0·232	0·238	—0·006	0·198	0·203	—0·005
KCl	0·163	0·156	0·007	0·218	0·207	0·011	0·116	0·167	—0·001
LiCl	—	—	—	—	—	—	0·141	0·123	0·018
CsCl	—	—	—	—	—	—	0·088	0·068	0·020
NaBr	0·094	0·110	—0·016	0·166	0·208	—0·042	0·155	0·163	—0·008
KBr	0·102	0·096	0·006	0·168	0·176	—0·008	0·119	0·126	—0·007
NaJ	—	—	—	—	—	—	0·095	0·156	—0·061
NaF	—	—	—	—	—	—	0·254	0·217	0·037
NaOH	—	—	—	0·315	0·279	0·036	0·256	0·224	0·032
Na_2SO_4	0·645	0·629	0·016	—	—	—	0·557[a]	0·662	—0·102
$MgSO_4$	0·570	0·574	—0·004	0·568	0·698	—0·130	0·448[a]	0·669	—0·221
$MgCl_2$	0·285	0·309	—0·024	0·465	0·481	—0·016	0·290[a]	0·415	—0·125
$BaCl_2$	—	—	—	—	—	—	0·334	0·362	—0·028
$(NH_4)_2SO_4$	—	—	—	—	—	—	0·405[a]	0·458	—0·053

[a] Results of measurements of the present work.

TABLE II

Comparison of Experimental and Calculated Values of k_s for Toluene, Ethyl Acetate, and Diethyl Ether

Electrolyte	Toluene[20]			Ethyl acetate[21,a]			Diethyl ether[21,a]		
	k_s^{exp}	k_s^{calc}	Δ	k_s^{exp}	k_s^{calc}	Δ	k_s^{exp}	k_s^{calc}	Δ
NaCl	0·267	0·256	0·011	0·172	0·167	0·005	0·238	0·246	—0·008
KCl	0·205	0·225	—0·020	0·151	0·156	—0·005	0·223	0·227	0·006
LiCl	0·191	0·181	0·010	—	—	—	0·176	0·180	—0·004
CsCl	—	—	—	0·154	0·137	0·017	—	—	—
RbCl	—	—	—	0·160	0·137	0·023	—	—	—
NaBr	—	—	—	0·123	0·141	—0·018	—	—	—
KBr	—	—	—	0·111	0·133	—0·022	—	—	—
CsBr	—	—	—	0·097	0·107	—0·010	—	—	—
RbBr	—	—	—	0·117	0·113	0·004	—	—	—
NaOH	—	—	—	—	—	—	0·292	0·288	0·004
Na_2SO_4	0·651	0·724	—0·073	0·579	0·462	0·117	0·480	0·604	—0·124
K_2SO_4	0·675	0·585	0·090	0·484	0·437	0·047	—	—	—
Li_2SO_4	0·591	0·483	0·108	—	—	—	—	—	—
$(NH_4)_2SO_4$	0·414	0·538	—0·124	—	—	—	—	—	—
$MgSO_4$	—	—	—	0·508	0·422	0·086	—	—	—
$CuSO_4$	—	—	—	0·448	0·317	0·131	—	—	—
$CuCl_2$	—	—	—	0·309	0·234	0·075	—	—	—

[a] The ionic strength was replaced by the concentration.

TABLE III

Values of α and σ for Ions Used in the Calculation of k_s (ref.[22])

Ion	$\alpha \cdot 10^{24}$ cm^3	$\sigma \cdot 10^8$ cm	Ion	$\alpha \cdot 10^{24}$ cm^3	$\sigma \cdot 10^8$ cm
Li^+	0·075	1·20	J^-	6·28	4·39
Na^+	0·21	1·90	OH^-	1·89[a]	2·90[c]
K^+	0·87	2·66	NH_4^+	1·77[b]	2·90[c]
Rb^+	1·81	2·96	Mg^{2+}	0·12	1·30
Cs^+	2·79	3·38	Ba^{2+}	1·69	2·70
Cu^{2+}	1·81	1·92	Ca^{2+}	0·53	1·98
F^-	0·99	2·72	Zn^{2+}	0·11	1·48
Cl^-	3·02	3·62	SO_4^{2-}	5·824	4·72[d]
Br^-	4·17	3·90			

[a] Ref.[23]; [b] ref.[16]; [c] ref.[23]; [d] calculated value.

The calculation of k_s on the values of $\alpha_2 = 2{\cdot}75 \,.\, 10^{-8}$ cm^3, $\varepsilon_2/k = 85{\cdot}3$ K, $\mu = 1{\cdot}84 \,.\, 10^{-18}$ (ref.[14]) were used for water.

Table IV

Values of $\phi_{m,n}$ for Electrolytes for which k_s was Calculated

Electrolyte	$\phi_{m,n}$ cm^3	Ref.[a]	Electrolyte	$\phi_{m,n}$ cm^3	Ref.[a]
LiCl	18·5	23	Na_2SO_4	23·63	23
NaCl	18·55	23	$MgSO_4$	6·85	calc.
KCl	28·85	23	K_2SO_4	39·35	calc.
RbCl	34·00	23	Li_2SO_4	21·94	calc.
CsCl	41·32	23	$ZnSO_4$	4·65	calc.
NaBr	25·27	23	$CuSO_4$	5·94	calc.
KBr	35·67	23	$(NH_4)_2SO_4$	59·22	calc.
NaJ	36·45	23	H_2SO_4	35·46	calc.
CsJ	59·32	23	$CaCl_2$	24·24	23
NaF	—0·20	calc.	$BaCl_2$	28·43	23
NaOH	—2·52	23	$MgCl_2$	20·17	calc.
HCl	19·03	23	$CuCl_2$	15·32	calc.

[a] Data according to ref.[23] were recalculated for an electrolyte concentration of 1 mol/dm^3.

TABLE V

Values of α, ϕ_1, and c_1^0 for Nonelectrolytes Used in the Calculation of k_s

Nonelectrolyte	$\alpha \,.\, 10^{24}$ cm^3	Ref.	ϕ_1 cm^3	c_1^0 mol/dm^3	Ref.
Benzene	9·89	17	78·3	0·024	24
Toluene	12·26	[a]	106·4	0·0053	20
Cyclohexanone	11·54	[a]	98·6	1·010	[b]
n-Hexanol	11·51	[a]	122·4	0·061	[b]
Ethyl Acetate	8·48	[a]	93·95	0·922	24
Diethyl Ether	9·82	[a]	95·88	0·900	24

[a] Calculated from bonding polarizabilities according to ref.[18]; [b] experimental results of the present work.

Values of ϕ_1 were calculated from c_1^0 and measured densities of saturated aqueous solutions.

To calculate the value of k_s in the case of SO_4^{2-} ions, we used the value of $\sigma_4 = 4{\cdot}72 \,.\, 10^{-8}$ cm, which was found from the experimental k_s values for $C_6H_5CH_3$—SO_4^{2-}—H_2O systems[20]. The calculation of this value from estimated atomic diameters and bond lengths[23] gave $4{\cdot}51 \,.\, 10^{-8}$ cm. The agreement of both values is satisfactory and they are in accord with the data obtained by other method[28]. The values of ε_1/k and σ_1 found for benzene differ much from those given in the literature[19] (440 and $5{\cdot}27 \,.\, 10^{-8}$). The found value of $\varepsilon_1/k = 212$ is very close to 214, which was calculated from Eq. (*21*) in ref.[14] and gave the best agreement between theory and experiment.

The correlation of the experimental and calculated values of k_s for all studied nonelectrolytes and 1 : 1 electrolytes (Fig. 4) shows that the dependence of k_s on the electrolyte concentration is well described by the generalization of the original expression according to Eq. (*3*) in ref.[14] for nonelectrolytes well soluble in water with the use of Eqs (*5*), (*10*), (*21*), and (*23*). The error expressed by the mean quadratic deviation between the measured and calculated k_s values is $\sigma_k = 0{\cdot}02$. From the equation $c_1 = c_1^0 \exp(-2{\cdot}3k_s c_{m,n})$ the relative error in the determination of the nonelectrolyte concentration can be calculated as

$$\varepsilon(c_1) = \pm 2{\cdot}3\sigma k_s c_{m,n} \,. \qquad (24)$$

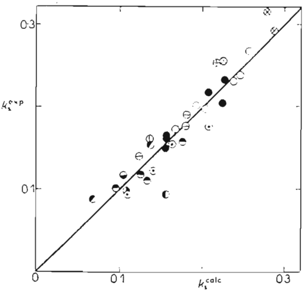


FIG. 4

Comparison of Experimental (k_s^{exp}) and Calculated (k_s^{calc}) Salting Coefficients for 1 : 1 Electrolytes

○ NaCl; ● KCl; ⊖ LiCl; ◐ CsCl; ⊙ NaBr; ◒KBr; ◐ NaI; ⊕ NaF; ⊗ NaOH; ⦶ RbCl; ◑ CsBr; ◒ RbBr. Relevant data are given in Tables I and II.

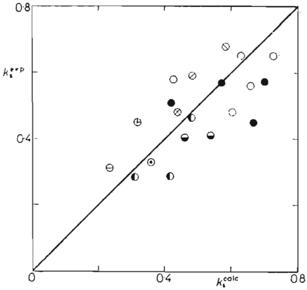


FIG. 5

Similar Comparison as in Fig. 4 for 2 : 1, 1 : 2, and 2 : 2 Electrolytes

○ Na_2SO_4; ● $MgSO_4$; point with cross axis from left to right $CuSO_4$; ⊙ $BaCl_2$; ⊖ $CuCl_2$; ◒ $(NH_4)_2SO_4$; ◐ $MgCl_2$; ⊗ K_2SO_4; point with cross axis from right to left Li_2SO_4.

This means that for $c_{m,n} = 1$ the mean relative deviation between the experimental and calculated values of k_s is $\pm 5\%$ for 1 : 1 electrolytes.

The values of k_s calculated for salts containing polyvalent ions are mostly not in good agreement with the experimental ones. The prediction of k_s values is satisfactory only for the systems cyclohexanone or n-hexanol–$MgCl_2$ and benzene–$BaCl_2$ or $(NH_4)_2SO_4$. A comparison of experimental and calculated values of k_s is shown in Fig. 5. The standard deviation is in this case $\sigma_k = 0{\cdot}1$ corresponding to the mean relative deviation between experimental and calculated k_s values $\pm 23\%$.

The described method enables to predict the value of the salting coefficient although some quantities necessary for the calculation according to the scaled particle theory are not known. It is sufficient if there are available the solubility data for the given nonelectrolyte in solutions of several electrolytes, for which the necessary values are known. For example, it is possible to calculate the salting coefficient for esthers in aqueous alkali metal hydroxides, which cannot be experimentally determined, although the corresponding values of σ_1 and ε_1/k are not known. These can be estimated by an optimalization calculation from experimental k_s values in solutions of other 1 : 1 electrolytes.

CONCLUSIONS

The scaled particle theory was applied to nonelectrolytes moderately soluble in water and electrolytes of the types 1 : 1, 2 : 1, 1 : 2, and 2 : 2. It was shown that the derived equations can be used for the calculation of the salting coefficient for 1 : 1 electrolytes with an accuracy of $\pm 5\%$, whereas for other electrolyte types this agreement is less favourable ($\pm 23\%$).

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LIST OF SYMBOLS

c_j	concentration of *j*-th particle in solution
$c_{m,n}$	concentration of electrolyte A_mB_n in solution
d_2, M_2	specific and molar masses of water
$\bar{g}^h$	change of partial molar free energy of nonelectrolyte during formation of sufficiently large cavity in aqueous electrolyte to accomodate a nonelectrolyte molecule
$\bar{g}_1^s$	change of partial molar free energy of nonelectrolyte during penetration of its molecule into a formed cavity
k	Boltzmann's constant
k_s	salting coefficient
N	Avogadro's constant
c_1	solubility of nonelectrolyte in aqueous electrolyte
c_1^0	solubility of nonelectrolyte in water
T	absolute temperature
Z_j	total number of electrons in the ion
α_j	polarizability of *j*-th particle
ε_j/k	energetic parameter of *j*-th according to Lennard-Jones (6—12) (ref.[12,13,16,19])
$\phi_{m,n}$	apparent molar volume of electrolyte at infinite dilution
ϕ_1	apparent molar volume of nonelectrolyte at infinite dilution
μ_2	dipole moment of water
ϱ_j	number of *j*-th particles in unit volume of solution (number density)
σ_j	diameter of *j*-th particle

Subscripts

$j = 1$—4 refers to: 1 — nonelectrolyte, 2 — water, 3 — cation, 4 — anion; m and n denote numbers of cations and anions in an electrolyte molecule A_mB_n

Concentrations are in mol/dm^3. The symbols are the same as in ref.[14].