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Effects of Salts on the Solubility of Elemental Mercury in Water

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The effects of 11 salts, NaCl, $NaNO_3$, Na_2SO_4, NaBr, NaSCN, NaF, $NaClO_4$, KCl, $BaCl_2$, $(CH_3)_4NBr$, and $(C_2H_5)_4NBr$, on the solubility of elemental mercury in water have been studied at 25 °C. Salting coefficients were determined and compared with those predicted by both the McDevit-Long equation and the scaled particle theory (SPT). The McDevit-Long equation gave reasonably good predictions except for NaBr, $NaClO_4$, and NaSCN. SPT is also applicable to prediction of the salt effect when the energy parameter of mercury determined from the Henry law constant of aqueous solubility of mercury vapor is employed. Attempts to predict the effects of tetraalkylammonium salts by SPT failed.

Attention is being paid to the influence of salts on the activity coefficients of nonelectrolytes in aqueous solutions from both experimental and theoretical interest and many reports have appeared.[1)] However, few are concerned with elemental mercury as a nonelectrolyte except for the report by Glew and Hames, who restricted their study to conditions of 6.10 molal sodium chloride solution.[2)]

It has been pointed out that there is an essential difference between the solution properties for inert gases and nonpolar molecules in water and in organic solvents. A similar anomaly of elemental mercury in water solvent was suggested by Spencer and Voigt.[3)] They attributed this to the tendency of water molecules to form a structure around mercury atoms. The study of salt effects on the solubility of elemental mercury will help clarify the role of water.

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

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

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

In the present work, 11 salts showing no chemical reaction with elemental mercury were used. We have compared the values of observed k_S with those predicted from theoretical equations such as the McDevit-Long equation[4)] and the scaled particle theory (SPT),[5)] which have been accepted to give reasonably good predictions for inert gases and nonpolar nonelectrolyte.

Experimental

Electrolytes of analytical reagent grade were used except for a tetraethylammonium bromide of reagent grade. The salts were dissolved without further purification in redistilled water after drying at suitable temperatures. The concentrations of chloride, bromide, and thiocyanate salts were checked by the argentometric method. Purification of metallic mercury, the procedure of attaining saturated solubility of mercury vapor and measurements were the same as those described,[6)] the solubility apparatus being essentially the same as that previously used except for a slight modification to include two identical 300 cm³ solubility flasks instead of one flask. Mercury vapor was passed through a three-way stop-cock to each flask, and then combined with another three-way stop-cock attached to the outlet of each flask. One of the flasks was filled with pure water and the other with electrolyte solution. Saturated mercury solutions in both pure water and electrolyte solution can be obtained at the same time. It was confirmed by filling each flask with the same solution that concentrations of the saturated mercury solutions in the two flasks were identical with each other. A time of 30 min was found to be sufficient to attain the solubility equilibrium. The relative solubility of mercury in pure water and in the salt solution, S°/S, was measured directly by reading atomic-absorption peak-heights recorded on a chart for a set of samples withdrawn from the two solubility flasks. The value of S° was taken to be 63.9×10^{-6} g dm^{-3}.[6)] Preliminary experiments for some electrolyte solutions revealed that the values of S thus estimated are in reasonably good agreement with those measured by addition of standard mercury (II) solutions. Determination of the S°/S ratios was repeated at least three times for each electrolyte concentration at 25 °C. No data were obtained for iodide; use of I^- ion gave abnormal results probably due to some chemical reaction with elemental mercury.

Results and Discussion

Experimental Salting Coefficients. The solubility ratios, S°/S, of elemental mercury obtained at each electrolyte concentration and salting coefficients, k_S, for 11 salts determined by the least-squares method according to Eq. 1 are given in Table 1, together with correlation coefficients for log (S°/S) *vs.* C plots and intercepts of these plots at $C=0$. We see that the salt effects are well represented by Eq. 1 over the concentration range examined. The value of k_S for 6.10 mol dm^{-3} NaCl, 0.0413 at 25 °C, determined by Glew and Hames[2)] and expressed as reciprocal molality, is much lower than the present result. The apparent discrepancy can be attributed to the fact that a negative deviation from Eq. 1 occurs at such a high electrolyte concentration.

Salting Coefficients Calculated by the McDevit-Long Equation. Several theories have been given to explain the salt effects on the solubility of nonelectrolyte such as hydration, electrostatic, van der Waals force, internal pressure and scaled particle. The last two theories give a good prediction of the trend of the observed k_S value. Based on the internal pressure concept, McDevit and Long derived the equation[4)]

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

where $\bar{V}_1^\circ$ is the molar volume of the liquid nonelec-

Table 1. Solubility ratios and salting coefficients of elemental mercury in aqueous salt solutions
(Values in parentheses are those calculated using the energy parameter of elemental mercury, $\varepsilon_1/\kappa=851$ K given in Ref. 13.)

Salt	Concentration C/mol dm^{-3}	Solubility ratio $S°/S$[a)]	log ($S°/S$) at $C=0$ (γ)[b)]	Salting coefficient			
				Observed		Calculated	
				k_S	k_S^*[c)]	k_S[d)]	k_S^*[e)]
NaCl	0.250	1.050					
	0.501	1.105	0.0025	0.0788	0.0872	0.071	0.0789
	0.752	1.154	(0.999)				(0.0187)
	1.00	1.204					
$NaNO_3$	0.250	1.037					
	0.500	1.074	−0.0002	0.0616	0.0652	0.047	0.0732
	0.753	1.106	(0.996)				(0.0088)
	1.00	1.156					
Na_2SO_4	0.125	1.104					
	0.250	1.216	0.0053	0.308	0.319	0.221	0.152
	0.375	1.314	(0.999)				(0.023)
	0.501	1.447					
NaBr	0.253	1.023					
	0.506	1.038	0.0063	0.0173	0.0227	0.060	0.0577
	0.750	1.046	(0.988)				(−0.0166)
	1.01	1.055					
NaSCN	0.266	0.977					
	0.531	0.964	0.0008	−0.0345	−0.0338	0.060	0.0436
	0.797	0.944	(0.987)				(0.0129)
	1.062	0.917					
NaF	0.250	1.102					
	0.500	1.207	0.0029	0.157	0.174	0.110	0.0732
	0.750	1.321	(0.999)				0.0129
$NaClO_4$	0.250	1.093					
	0.500	1.172	0.0098	0.117	0.114	0.035	0.0899
	0.750	1.252	(0.999)				(0.0363)
	1.00	1.338					
KCl	0.250	1.046					
	0.500	1.095	0.0018	0.0703	0.0743	0.055	0.0667
	0.750	0.120	(0.987)				(0.0023)
	1.00	1.188					
$BaCl_2$	0.250	1.080					
	0.500	1.148	0.0039	0.115	0.121	0.170	0.109
	0.750	1.233	(0.999)				(−0.0687)
$(CH_3)_4NBr$	0.250	0.968					
	0.500	0.923	0.0051	−0.0779	−0.112	−0.090	0.579
	0.750	0.886	(0.999)				(0.567)
	1.00	0.845					
$(C_2H_5)_4NBr$	0.250	0.933					
	0.500	0.870	−0.0022	−0.116	−0.176	−0.121	0.753
	0.746	0.812	(0.999)				(0.770)
	0.995	0.766					

a) $S°$ and S denote pure water and salt solution, respectively. b) Correlation coefficient. c) Defined by $k_S^*=k_S+(0.036-\phi_0\times10^{-3})/2.30$, where ϕ_0 is the apparent molal volume of the salt. d) Calculated by the McDevit-Long equation. e) Calculated by the scaled particle theory.

trolyte, V_S the molar volume of pure (liquid) electrolyte, $\bar{V}_S^\circ$ the partial molar volume of the salt at infinite dilution, and β_0 the compressibility of pure water. The factor $(V_S-\bar{V}_S^\circ)$ in Eq. 2 indicates electrostriction of the solvent caused by the salt, which is related to modification of the water structure by the salt added. The values of k_S calculated by using Eq. 2 are given in Table 1. The molar volume of liquid mercury 14.8 cm^3 was obtained by dividing atomic weight by density at 25 °C. The value of β_0 was taken to be 45.6×10^{-6} bar^{-1}.[4)] All the V_S data were taken from the work of Lundén,[7)] and the values for $\bar{V}_S^\circ$, the sum of partial molar volumes of individual cation and anion, from that of Millero.[8]

The calculated k_s values are in reasonably good agreement with the observed values except for NaBr, NaSCN, and $NaClO_4$. In the McDevit-Long equation, the parameter concerned with nonelectrolyte is only its molar volume, hence the characteristic properties of nonelectrolyte such as nonelectrolyte-solvent and nonelectrolyte-electrolyte interactions are not taken into consideration. This probably causes the discrepancies observed for these three salts. The observed k_s values indicate that the increased interactions of mercury atoms with Br^- or SCN^- ions play an important role for NaBr or NaSCN salt and that the decreased interactions of mercury atoms with surrounding water molecules should be considered for $NaClO_4$ salt.

Salting Coefficients Calculated by the Scaled Particle Theory. In the SPT, which has been successfully applied to predict the solubility of nonelectrolyte in various solvents,[5] two steps are involved: (1) the creation of a cavity in the solvent of a suitable size to accommodate a nonelectrolyte molecule, and (2) the introduction of a nonelectrolyte into the cavity, the nonelectrolyte molecule interacting with the solvent and electrolyte species through repulsive, dispersion, and inductive forces. The SPT allows computations of the free energies involved in (1) and (2). The theory would reflect the characteristic properties of nonelectrolyte in its solubility in electrolyte solution more adequately than the McDevit-Long equation.

TABLE 2. PARAMETERS USED FOR CALCULATI NG SALTING COEFFICIENTS BY SCALED PARTICLE THEORY

Elemental Mercury: $\sigma=0.290$ nm,[a] $\alpha=5.05\times10^{-24}$ cm (molecule)$^{-1}$,[b] $\varepsilon/\kappa=851$[a], or 283 K[c]

Ion	σ / nm	$10^{24}\ \alpha$ / $cm^3\ mol^{-1}$	$\bar{V}_{ion}$[d] / $cm^3\ mol^{-1}$
Na^+	0.190[e]	0.21[f]	−6.21
K^+	0.266[e]	0.87[f]	4.02
Ba^{2+}	0.270[e]	1.73[g]	−22.47
$(CH_3)_4N^+$	0.694[h]	8.4[i]	84.57
$(C_2H_5)_4N^+$	0.800[h]	16.4[i]	144.12
F^-	0.272[e]	1.03[g]	3.84
Cl^-	0.362[e]	3.02[f]	22.83
Br^-	0.390[e]	4.17[f]	29.71
NO_3^-	0.406[j]	4.36[g]	34.00
SO_4^-	0.440[j]	5.83[g]	23.98
ClO_4^-	0.452[j]	5.24[g]	49.12
SCN^-	0.428[j]	7.56[k]	40.7

a) Ref. 13. b) Ref. 12. c) Estimated in this work. d) Ref. 8. e) Pauling crystal ionic radius.[18] f) Ref. 10. g) Calculated from mole refraction data cited in Ref. 20. h) Ref. 19. i) Ref. 21. j) Estimated from Hepler's equation.[15] k) Estimated in this work by measuring mole refraction.

On the basis of SPT considerations given by Shoor and Guggins,[9] Masterton and Lee[10] have presented useful equations which enable one to estimate the salting coefficient k_s^*, defined by

$$k_s^* = \lim_{C\to 0}\frac{1}{C}\log\frac{X_o}{X}, \tag{3}$$

where X_O and X denote the mole fraction solubility of nonelectrolyte in pure water and an electrolyte solution of molarity of C, respectively. The salting coefficient can be written as follows:

$$k_s^* = k_\alpha + k_\beta + k_\gamma, \tag{4}$$

where k_α and k_β are related to steps (1) and (2), respectively, and k_γ refers to the number densities of species present in the solvent. The expressions k_α, k_β, and k_γ are given by Eqs. 32, 19, and 11, respectively, in Ref. 10. These equations are expressed as functions of hard sphere diameter, σ, the energy parameter, ε/κ, polarizability, α, and apparent molal volume of salt at infinite dilution, ϕ_O. Subscripts 1, 2, 3, and 4 refer, respectively, to nonelectrolyte, water, cation, and anion. The hard sphere diameter is taken as twice that of the crystal ionic radius. Values of σ are given in Table 2, references being specified in the footnote. For water molecules, the following parameters are employed: $\sigma_2=0.275$ nm, $\varepsilon_2/\kappa=85.3$ K, and the dipole moment$=6.14\times10^{-30}$ C m. When values corresponding to ϕ_O, $(\sigma_1, \sigma_3, \sigma_4)$, $(\alpha_1, \alpha_3, \alpha_4)$, and ε_1/κ are known, the value of k_S for a given nonelectrolyte-salt pair can be calculated. The value of ϕ_O is taken as the sum of the partial molal volume, $\bar{V}_{ion}$, of cation and anion, that is $\phi_O=\bar{V}_3+\bar{V}_4$. Since the expression for k_s^* defined by Eq. 3 differs from the conventional k_S appearing in Eq. 1, the observed k_S is converted into k_s^* by means of the relation[11]

$$k_s^* = k_S + (0.036 - \phi_o \times 10^{-3})/2.30. \tag{5}$$

In calculating k_s^* by the SPT, it is important to choose adequate parameters, since the calculated k_s^* value varies to a great extent with them. First, let us discuss the parameters for elemental mercury as a nonelectrolyte. The value 5.05×10^{-24} cm^3/molecule can be taken for α_1,[12] but it is difficult to select proper σ_1 and ε_1/κ values. We adopt here the value of 0.290 nm for the hard sphere diameter of mercury atom.[13] Calculations were first made using $\varepsilon_1/\kappa=851$ K but the results (Table 1) are unsatisfactory. An attempt was made to estimate the ε_1/κ value according to the derivation made by Pierotti,[14] who gave a relation between Henry's law constant, k_H, and the free energy changes in steps (1) and (2). Using $\sigma_1=0.290$ nm and $K_H=422$ atm at 25 °C,[6] we estimated the value ε_1/κ of elemental mercury to be 283 K, which is much smaller than the value obtained from viscosity data. The parameters used in the present calculation by the SPT are given in Table 2. The values of both observed and calculated k_s^* are given in Table 1.

If we employ the energy parameter derived from Henry's constant, the SPT is applicable, at least to an extent that the McDevit-Long equation can predict, to the salt effect on the elemental mercury solubility in water. Similarly to the McDevit-Long equation, the SPT approach gives poor agreement for NaBr and NaSCN salts. No reasonable interpretation can been given. The results of the SPT calculations for salt effects are sensitive to the ionic diameter of the electrolyte. It is difficult to estimate ionic diameters of polyatomic ions, since no accurate crystal ionic radii are known. In the present calculations, ionic radii adopted for polyatomic ions except for tetraalkylammonium ions are those estimated using Hepler's semiempirical equation.[15] It is not clear whether the equation can be properly extended to these ions. Masterton *et al.* tried to estimate the best ionic radii for SPT calculation which give the best fit to the observed salting coefficients.[11] In contrast with the McDevit-Long equation, the SPT gives great discrepancies between observed and calculated k_s^* for $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$ salts. This can not be overcome even if diameters for tetraalkylammonium cations proposed by Masterton *et al.* are used. The failure of the SPT for tetraalkylammonium salts certainly does not lie solely with uncertainty of their ionic diameters, but should be ascribed to their abnormal physico-chemical properties for which the SPT does not account. The anomalous behavior exhibited by tetraalkylammonium ions has been revealed by many experimental observations and theoretical considerations.[16,17]

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