Solubility of Toluene in Aqueous Salt Solutions

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Salting out effects of 12 inorganic salts on the solubility of toluene in water are determined at 25°C, and the validity of a predicting method is discussed based on these experimental data. Salts studied are NaCl, KCl, NH_4Cl, $BaCl_2$, $CaCl_2$, LiCl, Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, Li_2SO_4, $ZnSO_4$, and $CuSO_4$.

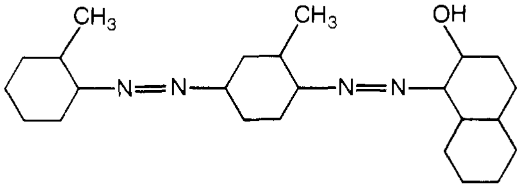
Salt effects on the solubilities of nonelectrolytes in water have been investigated theoretically as well as experimentally by many workers, and a number of correlating or predicting methods have been described in the literature (*6–10*). A majority of these experiments was devoted to the solubilities of gases in liquids. Salt effects on the solubility of liquid nonelectrolytes in water are also of industrial importance in liquid-liquid contact operations such as in extraction processes.

In the present work, an experimental investigation of the solubilities of toluene in 12 aqueous salt solutions was made at 25°C. The equilibrium data were obtained by employing a method similar to that described by Sobotka and Kahn (*11*).

Experimental

The experimental apparatus and procedure used in this work were similar to those of Sobotka and Kahn (*11*). To make the measurements more accurate, the apparatus used consisted of a 1-liter dissolution flask and a 2-ml microburet. The scale was calibrated in advance by use of mercury. The dissolution flask was immersed in a water bath controlled thermostatically at 25.00° ± 0.01°C. To avoid condensation of toluene from the gas phase, the temperature of the gas phase in the dissolution flask was kept 1°C higher than that of the liquid phase. The dissolution flask and the microburet were connected tightly.

Experimental procedures were as follows. Solute toluene stained with Sudan IV



[effect of addition of Sudan IV on solubility is discussed by Sobotka and Kahn (*11*)], a water-insoluble lipoid-soluble dye, was added dropwise from the microburet to aqueous salt solution retained in the dissolution flask (the concentration of Sudan IV in toluene was 0.1 wt %). The aqueous salt solution was violently stirred by a magnetic stirring device. During the period before equilibrium state was reached, the added toluene was dissolved, and the Sudan IV was precipitated and floated on the surface in the form of dark brown solid particles. When the aqueous salt solution was saturated with toluene, the excess amount of toluene appeared as immiscible red liquid droplets suspended in the aqueous solution. To ensure complete saturation, time allowed for equilibration was about 24 hr. The last reading to the microburet scale before appearance of the droplets was used for the calculation of the solubility. The advantage of this method is the visibility of the end point of saturation with the dyed toluene. In this method the accuracy of solubility measurements was chiefly restricted by the titration technique, and the estimated accuracy of solubilities was less than 0.008 ml/1000 ml of solution.

Salts studied in this work were NaCl, KCl, NH_4Cl, $BaCl_2$, $CaCl_2$, LiCl, Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, Li_2SO_4, $ZnSO_4$, and $CuSO_4$. Toluene, all of the salts, and the Sudan IV used in this work were of reagent grade and were used without further purification. The salt concentration was determined either gravimetrically with an Ostwald-type pycnometer or by evaporation to dryness.

Results and Discussion

The accuracy and reliability of the measuring apparatus and procedure were verified by comparing the observed solubilities of toluene and benzene in pure water at 25°C with those in the literature where available. The average values of the measured solubilities of toluene and benzene in water were 0.5633 and 2.0403 ml/1000 ml of H_2O, respectively. The value for toluene agreed well with those listed in Landolt-Börnstein Tabellen (*5*). For benzene, however, the solubilities reported by other investigators (*1, 3*) are not consistent with each other. The value determined in this work was intermediate between these values. As the result, the experimental method and procedure can be considered to be satisfactory. The observed solubilities of toluene in the aqueous salt solutions are given in Table I. In Figures 1 and 2, the logarithm of the ratio of the solubility in water to that in aqueous salt solution is plotted as a function of ionic strength for each salt. As can be seen in these figures, the solubility data can be correlated well by the following Setscenow equation:

$$\log \frac{S_w}{S} = K_s \cdot C \qquad (1)$$

It is evident from Figures 1 and 2 that for anions the salting out effect decreases markedly in the order $SO_4^{2-} > Cl^-$, and for the cations the order of decreasing salting out is $Na^+ > K^+ > Li^+ > Cu^{2+} > Ca^{2+} > Zn^{2+} > Ba^{2+} > NH_4^+$. This result is consistent with the order for the solubilities of benzene in aqueous salt solutions reported by McDevit and Long (*9*).

Van Krevelen and Hoftijzer (*12*) and Onda et al. (*10*) proposed a method to predict the magnitude of the salting out effect based on the modified Setschenow equation:

$$\log \frac{S_w}{S} = K_s' \cdot I \qquad (2)$$

where I is the ionic strength defined by

$$I = \frac{1}{2}(Z_c^2 C_c + Z_a^2 C_a) \qquad (3)$$

They regarded the parameter K_s' as the sum of constants which are characteristic of each constituent chemical species as follows:

$$K_s' = x_n + x_c + x_a \qquad (4)$$

x_c and x_a are assumed to be independent of temperature, and x_n is dependent.

It is only natural to think that a similar treatment to that mentioned above could be extended to develop predictions

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Table I. Solubilities of Toluene in Various Aqueous Salt Solutions at 25°C

Salt	I	S	K_S'	Salt	I	S	K_S'
NaCl	0.5011	0.410	0.2669	$CaCl_2$	1.5207	0.343	0.1338
	0.9991	0.298			1.5222	0.363	
	1.4933	0.223			2.9919	0.221	
	1.9933	0.169			4.4766	0.143	
KCl	0.5070	0.446	0.2047		4.5366	0.139	
	1.0009	0.345		$BaCl_2$	0.8583	0.463	0.0928
	1.4969	0.276			1.6215	0.395	
	1.9932	0.223			3.1122	0.292	
NH_4Cl	0.5089	0.529	0.0550	LiCl	0.5359	0.426	0.1909
	0.9805	0.496			0.9631	0.350	
	1.0603	0.492			1.4600	0.286	
	1.4968	0.467			2.2649	0.220	
Na_2SO_4	0.7482	0.387	0.2168	$(NH_4)_2SO_4$	1.4211	0.351	0.1384
	1.4976	0.270			3.0741	0.218	
	2.2632	0.183			4.6506	0.133	
	3.0003	0.124			6.0717	0.078	
K_2SO_4	0.3024	0.505	0.2246	$CuSO_4$	0.3536	0.504	0.1449
	0.5874	0.415			0.7296	0.444	
	0.8943	0.355			1.1600	0.380	
	1.1973	0.293			1.5544	0.335	
	1.5033	0.266			2.0148	0.288	
	1.5063	0.265		Li_2SO_4	0.8424	0.434	0.1975
$ZnSO_4$	0.8144	0.431	0.1293		1.2992	0.360	
	1.9800	0.307			2.3324	0.242	
	2.0272	0.309			3.5608	0.166	
	3.6908	0.192			3.9776	0.150	
	6.2956	0.086					

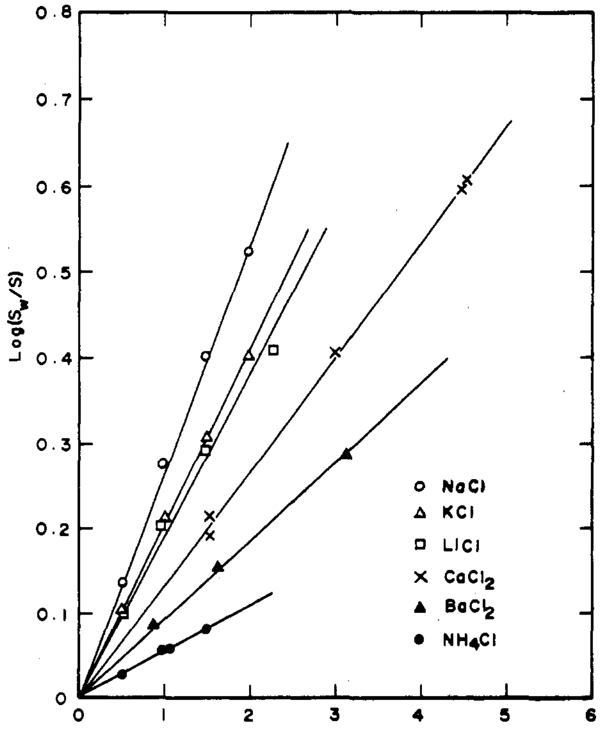

Figure 1. Solubilities of toluene in aqueous salt solutions

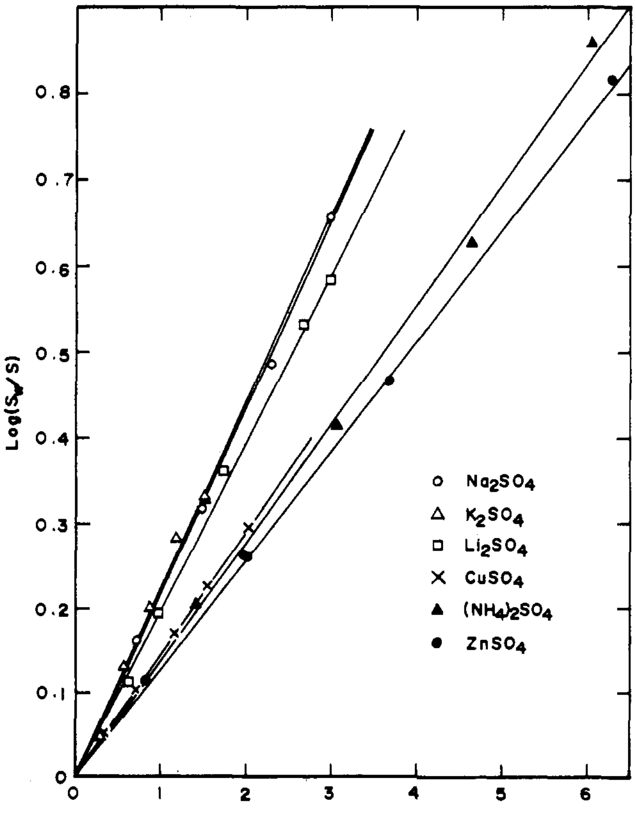

Figure 2. Solubilities of toluene in aqueous salt solutions

Table II. Calculated Results: *x*

Species	x	Species	x
Toluene	0.0248	Ba	−0.0896
Na	0.0208	Zn	−0.0856
K	−0.0026	Cu	−0.0698
Li	−0.0237	Cl	0.1812
NH_4	−0.1006	SO_4	0.1900
Ca	−0.0722		

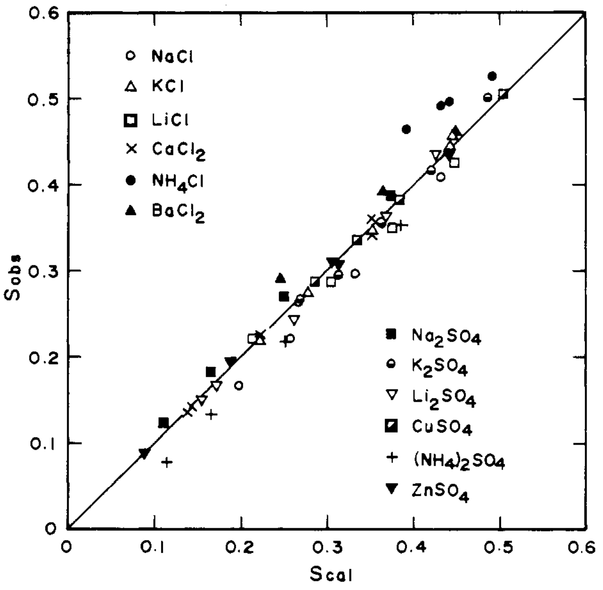

Figure 3. Comparison of observed and calculated results

for the systems described in this paper. Recently, Bidner and Santiago (*2*) measured the solubilities of *n*-butyl formate in various aqueous salt solutions and presented a comparable predicting method based on solubility data on these measurements as well as for other solutes. However, a majority of the nonelectrolytes discussed were rather soluble in water, and the data cannot be correlated well by the Setschenow equation over the concentration range considered. Therefore, so long as Equation 2 is used as the basis, it might be concluded that the predicting method has an accuracy restriction.

In the present work we have applied Equations 2–4 to the systems studied here, as well as those by Long and McDevit (*6*) and Kothari and Sharma (*4*). The values of x were estimated by the least-squares method similar to that in the previous paper (*10*) where details of the numerical procedure can be found. However, in the present investigation the Fletcher-Powell method was used instead of the Gauss-Seidell method to solve the simultaneous regression equations. The calculated results of x_n, x_c, and x_a are given in Table II.

In Figure 3 we have compared solubilities calculated by using Equation 2 and those x values against observed data. Large deviations are observed for NH_4Cl, but the agreement between the calculated and observed results is very good for the other salts. The correlation for the salting out effect by van Krevelen and Hoftijzer (*12*) appears to be applicable not only for gases but also to some extent for liquids.

Nomenclature

C_i = concentration of species i, mol/l.
I = ionic strength defined in Equation 3, mol/l.
K_s, K_s' = salting out parameter, l./mol
S = solubility of toluene, ml/1000 ml solution
x = empirical constant, l./mol
Z = ionic valency

Subscripts

a = anion
c = cation
n = nonelectrolyte
s = salt
w = water

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