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Solubility of Tetrabutylammonium Bromide in Benzene between 298.15 K and 323.15 K

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Tetrabutylammonium bromide, a weak organic salt, is used as a phase-transfer catalyst in a phase-transfer catalytic reaction producing the desired product, benzyl bromide in the organic phase. The solubility of tetrabutylammonium bromide in benzene (used as the organic phase solvent) is the possible dominant factor influencing benzyl bromide yield. In this study, the solubility of tetrabutylammonium bromide in benzene was measured in the temperature range between 298.15 K and 323.15 K, and a theoretical approach for the solid−liquid equilibrium of this binary mixture was proposed. The experimental data were then correlated with the Pitzer−Debye−Huckel equation, accounting for the ionic interaction, and with the UNIQUAC model, taking into account the ion−molecule and molecule−molecule interactions. An empirical parameter was introduced to represent the degree of partial dissociation of tetrabutylammonium bromide into ions in the solvent.

Introduction

The phase-transfer catalytic reactions always have the mild reaction conditions of room temperature and atmospheric pressure and have drawn very much attention from chemical industries. Tetrabutylammonium bromide (QBr) is a quaternary ammonium salt used as a phase-transfer catalyst in the benzyl chloride and sodium bromide reaction system described by Weng and Huang.[1] To progress this chemical reaction, benzyl chloride and sodium bromide were dissolved in a heterogeneous mixture of an organic solvent (benzene) and water, and the catalyst, tetrabutylammonium bromide, was added and distributed into the organic and aqueous phases. The desired reaction product, benzyl bromide, was produced in the organic phase, where QBr promotes the product generation. It would be reasonable to assume that the condition of the optimum solubility of QBr in the organic phase will produce the largest amount of benzyl bromide.

Recently, the solubilities of different salts in water or organic solvents have been reported in the literature, for instance, Kolker and de Pablo,[2] Pinho and Macedo,[3] Söhnel and Rieger,[4] Pitzer and Oakes,[5] and so forth. However, those published data concerning the solubility of salt mostly emphasized inorganic salts and reports for organic salts were seldom found. In this study, the solubility data of tetrabutylammonium bromide (QBr) in benzene were collected at different temperatures that would be helpful to design or operate this phase-transfer catalytic reaction system. The experimental data were then correlated with the modified Debye−Hückel model of Pitzer[6] for long distance ion−ion interaction and the UNIQUAC model[7] for short-distance ion−molecule and molecule−molecule interactions. Since tetrabutylammonium bromide is a weak salt and partially dissociates in solution, accurate determination of the dissociation constant is too difficult. To avoid this difficulty, the dissociation constant was represented as a parameter and determined by the correlation of experimental data for the present study.

Development of Solid−Liquid Equilibrium Equation for the Present System

The solubility of a solid in a solvent belongs to the problem of solid−liquid equilibrium. Attributed to the partial dissociation of a weak salt, an organic salt solution consists of cations, anions, solvent molecules, and nondissociated salt molecules.

The dissociation of an organic salt in a solvent is expressed by the following mechanism

$$\begin{array}{ccccccc} M_{\nu+}X_{\nu-(s)} & \leftrightarrow & \alpha\nu_{+}M^{z+}_{(solu)} & + & \alpha\nu_{-}X^{z-}_{(solu)} & + & (1-\alpha)M_{\nu+}X_{\nu-(solu)} \\ m & & \alpha\nu_{+}m & & \alpha\nu_{-}m & & (1-\alpha)m \end{array} \qquad (1)$$

where α is the degree of dissociation of the organic salt in a solvent, QBr in benzene in the present study.

In a saturated organic salt solution with a little excess of salt, the cations, anions, nondissociated salt molecules, pure solid salt, and solvent molecules should be in a state of equilibrium and all the chemical potentials of the above species should obey the equilibrium equation of equal chemical potential. Considering the equilibrium of a pure solid salt and its dissolved salt which would dissociate into ions, one should have the equation

$$\begin{aligned} \mu^{(s)}_{salt} &= \mu^{\circ(s)}_{salt} \\ &= \alpha(\nu_{+}\mu^{(l)}_{M^{z+}} + \nu_{-}\mu^{(l)}_{M^{z-}}) + (1-\alpha)\mu^{(l)}_{M_{\nu+}X_{\nu-}} \qquad (2) \end{aligned}$$

where ° stands for the pure salt.

The chemical potentials of the cation, anion, and salt molecule can be expressed as

$$\mu^{l}_{i} = \mu^{\theta}_{i} + RT\ln(\alpha\nu_{i}m\gamma_{i}) \qquad i = M^{z+},M^{z-} \qquad (3)$$

$$\mu^{l}_{M_{\nu+}X_{\nu-}} = \mu^{\theta}_{M_{\nu+}X_{\nu-}} + RT\ln((1-\alpha)m\gamma_{M_{\nu+}X_{\nu-}}) \qquad (4)$$

where θ denotes the standard state chemical potential of the cation, anion, or organic salt molecule. For the present system, the hypothetical fused salt and its dissociated ions

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at the system temperature and pressure with which we are concerned were chosen as the standard states of the present species. Substituting the above equations into eq 2, the equilibrium relation between the pure solid organic salt and the dissolved organic salt could be obtained. After further rearranging the related equations, we obtain

$$\mu^{\circ(s)}_{\text{salt}} = \{\alpha(\nu_+\mu^{\theta}_{M^{z+}} + \nu_-\mu^{\theta}_{M^{z-}}) + (1-\alpha)\mu^{\theta}_{M_{\nu+}X_{\nu-}}\} + \alpha RT\ln w + (1-\alpha)RT\ln[(1-\alpha)m\gamma_{M_{\nu+}X_{\nu-}}] \quad (5)$$

where

$$w = \alpha^{\nu}\nu_{\pm}^{\nu}m^{\nu}\gamma_{\pm}^{\nu}$$
$$\nu = \nu_+ + \nu_-$$
$$\gamma_{\pm}^{\nu} = \gamma_+^{\nu+}\gamma_-^{\nu-}$$
$$\nu_{\pm}^{\nu} = \nu_+^{\nu+}\nu_-^{\nu-} \quad (6)$$

The standard states of the species of the present system, the hypothetical fused salt and its dissociated ions at the system temperature and pressure, should obey an equation similar to eq 2. Here, it is assumed that the degree of dissociation of the dissolved tetrabutylammonium bromide in a solvent is equal to that of a fused salt. Although this assumption would not accurately represent the real case, however, it would simplify the later computation very much. Then we obtain

$$\mu^{\circ(f)}_{\text{salt}} = \alpha(\nu_+\mu^{\theta}_{M^{z+}} + \nu_-\mu^{\theta}_{M^{z-}}) + (1-\alpha)\mu^{\theta}_{M_{\nu+}X_{\nu-}} \quad (7)$$

Substituting eq 7 into eq 5, one obtains

$$\frac{\mu^{\circ(s)}_{\text{salt}} - \mu^{\circ(f)}_{\text{salt}}}{RT} = \alpha RT\ln(\alpha\nu_{\pm}m\gamma_{\pm})^{\nu} + (1-\alpha)RT\ln[(1-\alpha)m\gamma_{M_{\nu+}X_{\nu-}}] \quad (8)$$

where $\mu^{\circ(s)}_{\text{salt}} - \mu^{\circ(f)}_{\text{salt}}$ is the chemical potential difference between the fused state and the solid state at the system temperature and pressure. To compute this quantity, the following path is suggested

$$\begin{tikzcd}
\text{fused salt at temperature T} \arrow[r] \arrow[d] & \text{solid salt at temperature T} \\
\text{fused salt at melting point} \arrow[r] & \text{solid salt at melting point} \arrow[u]
\end{tikzcd}$$

Following the above computation path, the equation given below is obtained

$$\mu^{\circ(s)}_{\text{salt}} - \mu^{\circ(f)}_{\text{salt}} = -\int_{T}^{T_m} s^{\circ(f)}_{\text{salt}}\,dT + 0 - \int_{T_m}^{T} s^{\circ(s)}_{\text{salt}}\,dT \quad (9)$$

where T_m is the melting point of the organic salt and $s^{\circ(s)}_{\text{salt}}$ and $s^{\circ(f)}_{\text{salt}}$ are the entropies of the solid organic salt and the hypothetical fused organic salt at the system temperature and pressure, respectively. The difference between $s^{\circ(s)}_{\text{salt}}$ and $s^{\circ(f)}_{\text{salt}}$ can also be estimated through the same computation path given above. The final form is

$$s^{\circ(s)}_{\text{salt}} - s^{\circ(f)}_{\text{salt}} = \int_{T}^{T_m}\frac{c_p^f}{T}\,dT - \frac{\Delta H_m^f}{T_m} + \int_{T_m}^{T}\frac{c_p^s}{T}\,dT \quad (10)$$

where c_p^f and c_p^s are the specific heats of the fused and solid organic salts at constant pressure, respectively, and ΔH_m^f is the enthalpy change of the organic salt from the solid state to the fused state. For tetrabutylammonium bromide, the melting temperature is 374.65 K and the enthalpy of fusion is 18 204.80 $J\cdot g^{-1}\cdot mol^{-1}$.

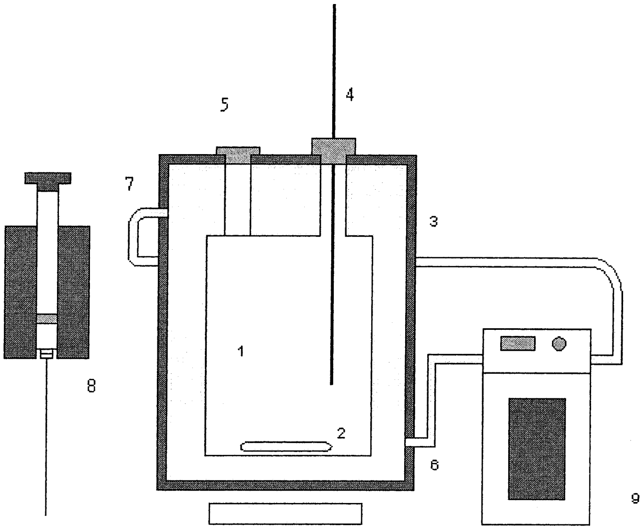

Figure 1. Apparatus for the solid−liquid equilibrium experiment: 1, cell; 2, magnetic stirrer; 3, insulation; 4, thermometer; 5, septum; 6, entry of thermostated water; 7, exit of thermostated water; 8, thermostated syringe; 9, circulating thermostated cell.

Substituting eq 10 into eq 9, performing integration, and assuming $C_p^f \approx C_p^s$, we finally obtain the solubility model of the partially dissociated tetrabutylammonium bromide in benzene as

$$\frac{\mu^{\circ(s)}_{\text{salt}} - \mu^{\circ(f)}_{\text{salt}}}{RT} = \frac{\Delta H_m^f}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) = 2\alpha\ln(\alpha\nu_{\pm}m\gamma_{\pm}) + (1-\alpha)\ln[(1-\alpha)m\gamma_{\text{QBr}}] \quad (11)$$

where γ_{QBr} is the activity coefficient of a nondissociated QBr molecule and α is the degree of dissociation of QBr in benzene. As it was recognized that most of the weak electrolytes like weak acids and bases, the weakness (degree of dissociation) is possibly determined by the conductivity or pH measurements. Unfortunately, there is difficulty in conducting such measurements to obtain an accurate degree of dissociation for the present QBr salt in benzene mixture. However, to simplify the correlation computations, the dissociation constant was represented by an empirical parameter dependent on system temperature and expressed in the following form

$$\alpha = \exp(a/T) \quad (12)$$

where a is considered as a new parameter and determined in the future computation. It is interesting and worthy of mention that the parameter a in our computation is nearly a constant value of 263.4 for the present system.

Experimental Work

Chemicals. The organic salt, tetrabutylammonium bromide, and benzene were GR grade and purchased from Merck Co. with purity higher than 99.5%. All chemicals were used without further purification.

Experimental Apparatus and Procedure. The experimental apparatus is similar to that used by Pinho and Macedo[3] as shown in Figure 1. The volume of the jacketed

Table 1. Experimental and Literature Data of Solubility[a] of KCl in Water

T/K	S(exp)	S(ref 9)
293.15	34.1	34.0
303.15	37.0	37.0
313.15	40.1	40.0
323.15	42.5	42.6

[a] The units of the solubility, S, are g of KCl/100 g of water.

glass cell is about 60 cm^3. The circulating thermostat (Model RTE 221) with an uncertainty of ±0.1 K for experiments in the temperature range from 263.15 K to 473.15 K was a product of Neslab Company. The temperature in the cell was read with a thermometer (Amarell Co.) with an uncertainty of ±0.1 K. An electronic balance of Ohaus Analytical Plus Co. (Model AP 110S) with an uncertainty of 0.1 mg was used for weighing the mass of salt.

During experiments, the thermostat was controlled at the desired temperature. The jacketed glass cell was charged with solvent and a little excess of dried QBr above the estimated solubility, and the mixture was stirred with a magnetic stirrer for about 2 h to attain the solid−liquid equilibrium. Then the stirrer was turned off and the mixture was allowed to settle for 2 h so that the nondissolved tetrabutylammonium bromide would precipitate on the bottom of the cell. A long syringe was pierced through the cap of the cell and dipped in the cell for more than 10 min so that the phase equilibrium in the neighborhood of the syringe would be maintained. About 5 cm^3 of sample was then taken from the mixture about 0.7 cm above the nondissolved QBr solid layer. At the early stage of the experiments, three test samples were taken separately from 0.7, 1.4, and 2.0 cm above the nondissolved QBr solid layer for refractory measurement. The identical refractory measurements of all samples ensure that the concentration gradient effect in the liquid phase is negligible and that the sampling position, 0.7 cm above the nondissolved QBr solid, is proper. The samples were weighed and the values were recorded, and then the samples were dried in an oven for more than three weeks. The correct mass of QBr was determined until the mass difference between two consecutive dried QBr samples (about a four-day interval) was less than 0.1 mg. Then the solubility of QBr in benzene was calculated from the recorded weights.

To ensure the reliability of the present experimental technique, the measurements of the solubility of potassium chloride in water were conducted at 293.15 K, 303.15 K, 313.15 K, and 323.15 K and the measured data were compared with those from the literature. Good agreement was obviously shown in Table 1.

Experimental Results and Correlation

At the beginning of this study, the liquid−liquid equilibrium experiment of the water + benzene + QBr mixture had been conducted to determine the optimum solubility of QBr in benzene that would produce the largest amount of benzyl bromide. However, during the experiment, it was observed that QBr strikingly affected the liquid−liquid equilibrium in a way that the quantity of the organic phase was decreasing and even disappeared if QBr was added continuously. Thus, it is impossible to determine the optimum solubility of QBr in this heterogeneous mixture by liquid−liquid equilibrium considerations. Therefore, the solubility of QBr in benzene became the first priority of experimental work on this research subject.

The experimental solubilities of QBr in benzene at different temperatures were given in Table 2, and a plot of the solubility of QBr versus temperature was given in Figure 2. It is obvious that the solubility increases rapidly with increasing temperature.

Table 2. Experimental and Calculated Solubility of QBr in Benzene

T/K	m/mol·kg^{-1}	$\Delta m \times 10^3 m$/mol·kg^{-1}
298.15	0.62	1.21
303.15	1.33	-9.33
306.15	1.79	16.4
311.15	2.72	-16.0
313.15	3.22	2.79
316.15	4.06	3.79
318.15	4.57	2.45
323.15	6.03	4.46
	AAD	0.0191
	RMSD[a]	0.0241

[a] RMSD = $[\sum_i^i(\Delta m_i)^2/k]^{1/2}$, where k is the total number of data points and Δm is the experimental value − calculated value.

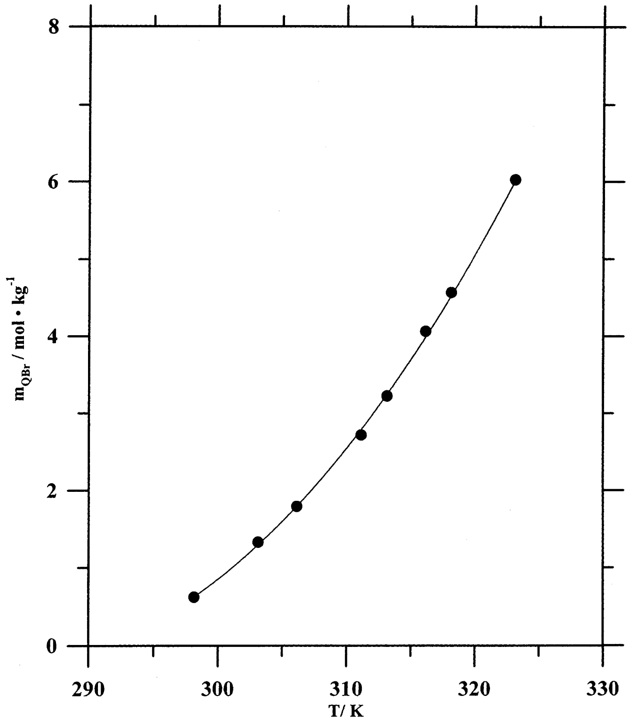

Figure 2. Solubility of QBr in benzene at various temperatures: ●, experimental; —, calculated (UNIQUAC + PDH).

The experimental solubility data of QBr in benzene were used for model correlation based on eq 13. As mentioned earlier, there are existing ion−ion, ion−molecule, and molecule-molecule interactions in the solution which need to be considered for the estimations of the mean activity coefficient of dissociated QBr and the activity coefficient of the QBr molecule. To take into account the ion−ion long distance interaction, the model employed here is the Pitzer−Debye−Hückel equation[6] while the ion−molecule and molecule−molecule interactions were described by the modified UNIQUAC equation.[7] Both the PDH equation and the UNIQUAC equation are given in the Appendix, and the volumetric and surface parameters of the combinatorial part of the model are given in Table 4 for reference.

The objective function for determining the most suitable parameters was defined as

$$Q = \sum_{j=1}^{N}\left\{\left[\frac{\Delta H_{\mathrm{m}}^{\mathrm{f}}}{T_{\mathrm{m}}}\left(\frac{1}{T_{\mathrm{m}}} - \frac{1}{T}\right)\right]^{\mathrm{exp}} - \left[\frac{\Delta H_{\mathrm{m}}^{\mathrm{f}}}{T_{\mathrm{m}}}\left(\frac{1}{T_{\mathrm{m}}} - \frac{1}{T}\right)\right]^{\mathrm{cal}}\right\}^2 \quad (13)$$

Table 3. UNIQUAC Model Parameters for the QBr + Benzene Binary Mixture

parameter[a]	value
A_{12}	-1121.82
A_{21}	-1052.98
A_{13}	-1121.82
A_{31}	-1052.98
A_{14}	121.63
A_{41}	-1445.10
A_{24}	-6.42
A_{42}	117.92
A_{34}	-6.42
A_{43}	117.92

[a] Note: 1, 2, 3, and 4 stand for QBr, Br^-, Q^+, and benzene.

Table 4. UNIQUAC Group Size Parameters[a]

group	r_k	q_k
NCH_2	0.9597	0.632
CH_2	0.6744	0.540
CH_3	0.9011	0.848
Br^-	1.2520	1.163
ACH	0.5313	0.400

[a] All data are from ref 10 except those for Br^- from ref 11.

To find the minimum objective function is a complicated problem, since too many parameters are involved. To make the computation converge more easily, the number of interaction parameters was reduced by adopting the assumption proposed by Chen et al.[8] that the interaction parameters of cation−molecule and anion−molecule were identical. The estimated interaction parameters for the present system are given in Table 3. The deviation between the experimental and the calculated values and the average absolute deviation (AAD) are given in Table 2. The correlation result is also drawn in Figure 2. The numerical values in the figure showed that the correlation is satisfactory.

It should be mentioned that special care must be taken for handling the concentration, since molality and mole fraction were used in the present computation. For instance, the activity coefficient was multiplied by molality and the equation shown in the Appendix was in mole fraction. The molality and mole fraction were calculated according to the individual definitions. Thus, the molecular weights and the masses of tetrabutylammonium (solute) and benzene (solvent) were required at the beginning of the computations.

Conclusion

In this study, the solubility of the organic salt tetrabutylammonium bromide in benzene was measured at different temperatures from 298.15 K to 323.15 K. The experimental data showed that the solubility increased with increasing temperature. Since tetrabutylammonium bromide is partially dissociated, the interparticle interaction is more complicated than those of the totally dissociated inorganic salts. A theoretical approach was proposed to analyze the solid−liquid equilibrium of QBr in benzene. This approach has general application to other organic salt systems. Since the degree of dissociation is too difficult to measure, it was viewed as a parameter and estimated by the experimental solubility data. The experimental data were correlated with the PDH equation,[6] taking into account the ionic interaction, and the UNIQUAC model,[7] taking into account the ion−molecule and molecule−molecule interactions. The correlation is satisfactory with the average absolute deviation of 0.0191 mol of QBr/kg of benzene.

Appendix

The Pitzer−Debye−Hückel equation is expressed as

$$\ln \gamma_{\pm} = -\sqrt{\frac{1000}{M_s}}A_{\phi}\left[\frac{2|z_+z_-|}{\rho}\ln(1+\rho\sqrt{I_x}) + \frac{|z_+z_-|\sqrt{I_x}-2I_x^{1.5}}{1+\rho\sqrt{I_x}}\right]$$

$$A_{\phi} = \frac{1}{3}\left(\frac{e}{\sqrt{DkT}}\right)^3\sqrt{\frac{2\pi d_0 N_A}{1000}}$$

$$I_x = {}^1/_2\sum_i x_i z_i^2$$

$$\rho = 14.9$$

where M_s is the molecular weight of the solvent, I_x is the ionic strength in mole fraction, A_ϕ is a parameter of the PDH equation, and d_0 is the density of the solvent.

The UNIQUAC model is expressed as

$$G^E = G^E(\text{combinatorial}) + G^E(\text{residual})$$

$$\frac{G_c^E}{RT} = \sum_{i=1}^{n} x_i \ln\frac{\Phi_i}{x_i} + \frac{z}{2}\sum_{i=1}^{n} q_i x_i \ln\frac{\theta_i}{\Phi_i}$$

$$\frac{G_r^E}{RT} = -\sum_{i=1}^{n} q_i' x_i \ln\left(\sum_{j=1}^{n}\theta_j'\tau_{ji}\right)$$

$$\ln \gamma_i = \ln\frac{\Phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_{j=1}^{n}x_j l_j - q_i'\ln\left(\sum_{j=1}^{n}\theta_j'\tau_{ji}\right) + q_i' - q_i'\sum_{j=1}^{n}\frac{\theta_j'\tau_{ij}}{\sum_{k=1}^{n}\theta_k'\tau_{kj}}$$

where

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$$

$$\Phi_i = \frac{r_i}{\sum_{j=1}^{n} x_i r_i}$$

$$\theta_i = \frac{x_i q_i}{\sum_{j=1}^{n} x_j q_j}$$

$$\theta_i' = \frac{x_i q_i'}{\sum_{j=1}^{n} x_j q_j'}$$

$$\tau_{ij} = \exp(-A_{ij}/T), \quad \tau_{ii} = \tau_{jj} = 1$$

where q_i is the structure area parameter of pure component i; q_i' is the modified structure area parameter of pure component i; r_i is the volume parameter of pure component

i; z is the coordinate number; and A_{ij} is the adjustable interaction parameter between components i and j.

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