

# Effect of Different Salts on the Solubilities of Benzene and Diphenyl in *t*-Butyl Alcohol-Water Mixture and Hydrophobic Interaction

ZOU, Li-Zhuang\*<sup>a</sup>(邹立壮)    WANG, Xiao-Ling<sup>a</sup>(王晓玲)    ZHU, Shu-Quan<sup>a</sup>(朱书全)  
HAN, Bu-Xing<sup>b</sup>(韩布兴)    LIU, Rui-Lin<sup>b</sup>(刘瑞麟)    YAN, Hai-Ke<sup>b</sup>(阎海科)

<sup>a</sup>Department of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing 100083, China

<sup>b</sup>Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

The solubilities of benzene and diphenyl in mixed solvents of *t*-butyl alcohol (TBA) and water with different salts have been determined at  $T = 298.15, 303.15, 308.15$  and  $313.15$  K. The molar fraction of TBA [ $x(\text{TBA})$ ] in mixed solvent is 0.045, and the molality of the salts ( $m_s$ ) in mixed solvents are 0.000, 0.250, 0.500, 0.750 and 1.000 mol/kg, respectively. The standard Gibbs energies of solution of benzene and diphenyl in the mixed solvents have also been calculated based on the solubility data. The effects of different salts on the hydrophobic interaction (HI) for benzene-benzene pair in the systems were discussed.

**Keywords** hydrophobic interaction, solubility, benzene, diphenyl, *t*-butyl alcohol, Gibbs energy, salting effect

## Introduction

It is well known that electrolytes are able to change the structures and the physical and chemical properties of water and aqueous solutions. Thus, the variation of macroscopical thermodynamic property reflects the change in microscopic structure of solutions and the intermolecular interaction in the systems. The hydrophobic interaction (HI) not only plays an important role for studying and explaining many physical phenomena in aqueous solutions,<sup>1</sup> but also serves as an experimental probe for estimating the strength of solute-solute interaction which is related to the structure and property of sol-

vents.<sup>2</sup> Ben-Naim and Yaacobi have studied the effect of solutes on the HI for methane-methane pair in water,<sup>3</sup> and found that many solutes cause a strengthening effect on the HI, which results from the changing of water structure.

As a special mixed solvent, the properties of water-*t*-butyl alcohol (TBA) mixture have been investigated extensively.<sup>4-7</sup> All authors pointed out the existence of clathrate structure in water-rich region, which is formed in such a way that one TBA is surrounded by 17—22 water molecules, and the optimum composition of the mixtures to the forming clathrate is  $x(\text{TBA}) = 0.045$ . In order to study the effect of the solvent structure and the solute gathering state on the strength of HI, our previous papers<sup>8-11</sup> reported the HI for the aggregating process of methane-methane, benzene-benzene and methane-benzene in H<sub>2</sub>O-TBA mixed solvents. As a part of our systematic research on HI, in this paper, the effects of different salts on the solubilities of benzene and diphenyl in the water-TBA mixed solvents and the HI for the formation of benzene-benzene pair were studied.

## Experimental

### Material

Benzene, diphenyl and TBA are analytically pure

\* E-mail: zoulizhuang@263.net

Received March 21, 2001; revised August 14, 2001; accepted August 27, 2001.

Project supported by the National Natural Science Foundation of China (No. 29573144).

reagents purified by the method as described in the previous paper.<sup>10</sup> NaCl, KCl, RbCl, NH<sub>4</sub>Cl, KBr, AgNO<sub>3</sub> and CaCl<sub>2</sub> are analytically pure reagents. The water used was distilled twice and its conductivity was less than 10<sup>-4</sup> S/m.

#### *Preparation of the saturated solution*

Saturated solutions of benzene and diphenyl were obtained by following procedures: 15 mL of mixed solvents of different composition and a slight excess amount of benzene or diphenyl were added to different glass tubes. Then the tubes were sealed with a tight fitting ground stopper and parafilm, followed by equilibration in a shaking thermostat at 298.15, 303.15, 308.15 and 313.15 K (the fluctuation of temperature was  $\pm 0.01$  K). The equilibration time was 5–7 d depending on the temperature. During the experiments, the volume of benzene-rich phase was controlled to be very small so that the effect of TBA dissolved in benzene on the solvent concentration was negligible.

#### *Determination of solubility*

Working curves were obtained by measuring the absorbances of standard solutions of known molality, which were prepared by mixing the desired amount of solutes and solvents. The molality ranges of benzene and diphenyl standard solutions were  $5.0 \times 10^{-4}$ – $2.0 \times 10^{-3}$  mol/kg and  $8.0 \times 10^{-6}$ – $5.0 \times 10^{-5}$  mol/kg, respectively. The absorbances *vs.* molality curves are linear in the above molality ranges. The absorbances for the saturated solutions of benzene and diphenyl in different mixed solvents were measured by a UV-752 spectrophotometer (produced by Shanghai Third Analytical Instrument Factory) after proper dilution with their respective solvents at 254 and 247 nm wavelength, respectively, and their solubilities can be determined by the working curves. In order to eliminate the influence of temperature change, all the experimental operations were carried out in a box in which the temperature was the same as that of the shaking thermostat. The experiments showed that the molar absorbance coefficients and the wavelengths of the maximum absorbance of benzene and diphenyl were not affected by TBA and different salts on the above experimental conditions.

#### *Determination of TBA concentration in benzene-rich phase*

The refractive index for the solution of benzene-rich phase was measured by a WZS-1 refractive index meter (produced by Shanghai Instrument Factory) at the same temperature as the shaking thermostat, and the concentration of TBA in benzene-rich phase was determined by the working curve. The experiment showed that the content of water in benzene-rich phase was very small when the mole fraction of TBA in H<sub>2</sub>O-TBA mixed solvents was less than 0.07.

## Results and discussion

#### *Vapor pressures of benzene and diphenyl*

In water-rich region, for benzene-water-TBA-salt system, benzene-rich phase can be treated approximately as binary solution of TBA and benzene because the contents of the salts and water are negligible. The activity coefficient of benzene ( $\gamma_1$ ) in benzene-rich phase can be calculated by the Eq. (1).<sup>12</sup>

$$\ln \gamma_1 = -\ln(x_1 + A_{12}x_2) + x_2[A_{12}/(x_1 + A_{12}x_2) - A_{21}/(A_{21}x_1 + x_2)] = \ln[p/(p^* \cdot x_1)] \quad (1)$$

$$\text{and } A_{12} = V_1/V_2 \exp[-(\lambda_{12} - \lambda_{11})/(RT)] \quad (2)$$

$$A_{21} = V_1/V_2 \exp[-(\lambda_{12} - \lambda_{22})/(RT)] \quad (3)$$

where  $A_{12}$  and  $A_{21}$  are the adjustable parameters;  $p$  stands for partial pressure of benzene at equilibrium condition;  $p^*$  is vapor pressure of pure benzene;  $V_1$  and  $V_2$  are mole volumes of pure benzene and TBA, respectively;  $\lambda_{11}$ ,  $\lambda_{12}$  and  $\lambda_{22}$  stand for the energies of molecular interaction of benzene-benzene, benzene-TBA, and TBA-TBA, respectively;  $x_1$  and  $x_2$  denote mole fractions of benzene and TBA in the benzene-rich phase, respectively. On the basis of the dependence of  $p$  on  $x_1$  at 298.15 K,<sup>13</sup> the differences of energies of molecular interaction are calculated as:  $\lambda_{12} - \lambda_{11} = 499.37$  J/mol and  $\lambda_{12} - \lambda_{22} = 5201.30$  J/mol. The effect of temperature on  $\lambda$  may be neglected.<sup>12</sup> Thus, by combining Eqs. (1)–(3), with the calculated values of  $\lambda_{12} - \lambda_{11}$  and  $\lambda_{12} - \lambda_{22}$ , the vapor pressure of benzene for benzene-

TBA solution can be calculated. In water-rich region of the mixed solvent, experiments show that the effect of salts on the concentration of TBA in benzene-rich phase is very small, hence the effect of salts on the vapor pressure of benzene may be neglected. At 298.15, 303.15, 308.15 and 313.15 K the partial pressure of benzene calculated are 11585, 14378, 17036, and 21387 Pa, respectively.

The vapor pressure of diphenyl can be calculated by Eq. (4),<sup>14</sup> which can be used in the temperature range from 288.20 K to 313.70 K, and it may be assumed that the partial pressure of diphenyl is independent of the total pressure.

$$\log p = 14.407 - 4262/T \quad (4)$$

where  $T$  is absolute temperature.

#### Effects of salts on the solubilities of benzene and diphenyl

The solubilities ( $S$ ) of benzene and diphenyl in various mixtures of water-salt-TBA [ $x(\text{TBA}) = 0.045$ ] at 298.15, 303.15, 308.15 and 313.15 K are presented in Tables 1 and 2, respectively. It can be seen from Table 1 that the solubility of benzene in the mixed solvent decreases with increasing molalities ( $m_s$ ) of the salts except for  $\text{AgNO}_3$ . The order of salting out effect for 1-1 electrolytes is  $\text{NaCl} > \text{KCl} > \text{RbCl} > \text{NH}_4\text{Cl} > \text{KBr}$ .

**Table 1** Solubilities ( $S$ ) of benzene in  $\text{H}_2\text{O}$ -TBA [ $x(\text{TBA}) = 0.045$ ]-salt mixture at different temperatures and molalities of salts ( $m_s$ )

Salts	$m_s$ (mol/kg)	$S \times 10^2$ (mol/kg)			
		298.15 K	303.15 K	308.15 K	313.15 K
NaCl	0.000	2.50	2.92	3.36	4.02
	0.250	1.94	2.20	2.47	2.90
	0.500	1.74	1.96	2.17	2.41
	0.750	1.61	1.80	1.89	2.06
	1.000	1.53	1.61	1.72	1.83
KCl	0.250	2.01	2.28	2.54	2.96
	0.500	1.85	2.04	2.24	2.53
	0.750	1.75	1.92	2.03	2.18
	1.000	1.61	1.70	1.80	1.98
RbCl	0.500	1.86	2.09	2.29	2.61
$\text{NH}_4\text{Cl}$	0.250	2.07	2.30	2.57	3.01
	0.500	1.90	2.13	2.35	2.64

continued

Salts	$m_s$ (mol/kg)	$S \times 10^2$ (mol/kg)			
		298.15 K	303.15 K	308.15 K	313.15 K
KBr	0.750	1.76	1.97	2.14	2.29
	1.000	1.69	1.77	1.90	2.12
	0.250	2.09	2.43	2.72	3.18
	0.500	1.92	2.16	2.43	2.81
	0.750	1.80	2.02	2.20	2.44
$\text{CaCl}_2$	1.000	1.72	1.83	2.02	2.27
	0.500	1.39	1.58	1.76	1.98
$\text{AgNO}_3$	0.250	2.50			
	0.500	5.70			
	0.750	7.76			
	1.000	10.3			

**Table 2** Solubilities ( $S$ ) of diphenyl in  $\text{H}_2\text{O}$ -TBA [ $x(\text{TBA}) = 0.045$ ]-salt mixture at different temperatures and molalities of salts ( $m_s$ )

Salts	$m_s$ (mol/kg)	$S \times 10^4$ (mol/kg)			
		298.15 K	303.15 K	308.15 K	313.15 K
NaCl	0.000	3.69	5.84	8.65	12.3
	0.250	4.36	6.76	9.55	13.3
	0.500	5.56	8.32	11.1	15.0
	0.750	6.75	9.81	12.5	17.0
	1.000	7.99	11.8	15.8	20.1
KCl	0.250	4.14	6.45	9.35	13.0
	0.500	5.39	8.02	10.8	14.5
	0.750	6.40	9.24	12.1	16.5
	1.000	7.33	11.2	14.9	19.1
RbCl	0.500	5.12	7.91	10.3	13.8
$\text{NH}_4\text{Cl}$	0.250	3.82	6.00	8.79	12.3
	0.500	4.33	6.63	9.39	12.7
	0.750	4.77	7.41	10.1	13.7
	1.000	5.49	8.21	11.5	14.8
	KBr	0.250	3.99	6.23	9.08
0.500		4.88	7.31	10.0	13.6
0.750		5.80	8.56	11.6	15.3
1.000		6.86	10.2	13.2	17.2
$\text{CaCl}_2$		0.500	6.89	10.6	14.0
	$\text{AgNO}_3$	0.250	9.34		
0.500		15.2			
0.750		20.6			
	1.000	26.2			

The solubility of diphenyl increases with increasing the molalities ( $m_s$ ) of the salts, as can be seen from the data in Table 2. That is, the effects of all the salts on

the solubility of diphenyl in the mixed solvents of water-TBA [ $x(\text{TBA}) = 0.045$ ] are salting in and the order of salting in for the 1-1 electrolytes is  $\text{AgNO}_3 > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{KBr} > \text{NH}_4\text{Cl}$ .

Figs. 1 and 2 show clearly that the solubilities of both benzene and diphenyl in aqueous solution of NaCl at 298.15 K decrease with the molality of NaCl. As discussed above, the solubility of benzene in the  $\text{H}_2\text{O}$ -TBA-salt [ $x(\text{TBA}) = 0.045$ ] mixture decreases with  $m_s$  (except  $\text{AgNO}_3$ , which will be discussed later), while that of diphenyl increases with the molalities of the salts. Thus, TBA in the solution results in the different effects of the salts on the solubilities of the two solutes, which is discussed in the following.

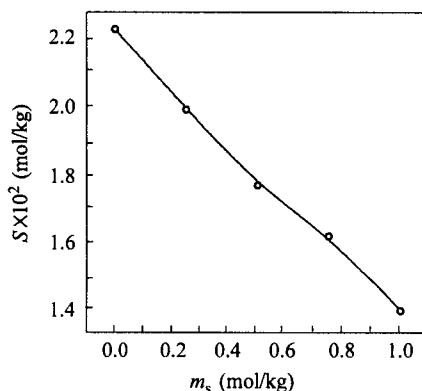


Fig. 1 Dependence of the solubility of benzene in water on the molality of NaCl at 298.15 K.

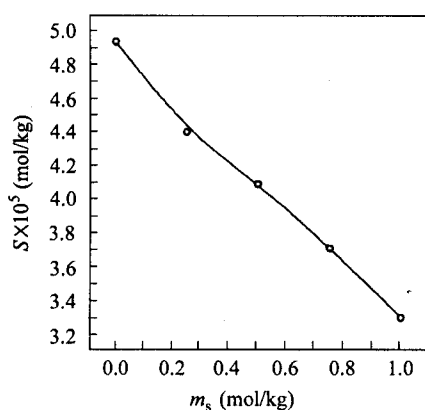
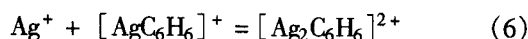
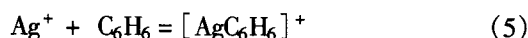


Fig. 2 Dependence of the solubility of diphenyl in water on the molality of NaCl at 2978.15 K.

As mentioned above, in water-rich region of TBA-water solution, there exists clathrate structure formed in such a way that one TBA molecule is surrounded by a number of water molecules. Addition of a salt to water-TBA solution affects the solubility of the solute in several

ways. Firstly, the ions of the salt interact with water molecules (hydration), which reduces the solubility because some of the water molecules are controlled by ions, and the stronger the interaction between the ion and water, the lower the solubility of benzene or diphenyl is. Secondly, some of the  $\text{H}_2\text{O}$ -TBA clusters are broken by strong water-ion interaction and the solubility is increased because more free TBA molecules exist in the solution. Evidently, the more the free TBA, the larger the solubility of benzene or diphenyl is because both of them are soluble in TBA. Thirdly, the ions interact with the solute, which also increases the solubility. The salt effect depends on which of the three factors is dominant. For diphenyl, the solubility is salting in because it has a larger size and the second or third factor discussed above is dominant. The solubility of benzene is salting out because its size is relatively small, and the first factor is dominant. In other words, the interaction between benzene and ion or TBA is weaker than that between diphenyl and ion or TBA.

As mentioned above, the solubility of benzene increases with the molality of  $\text{AgNO}_3$ , while other salts studied reduce the solubility. This phenomenon can be explained by the fact that  $\text{Ag}^+$  can form a  $\pi$ -electron complex with benzene in the aqueous solution<sup>15</sup> [Eqs. (5) and (6)],



It is evident that Eqs. (5) and (6) can increase the solubility. In other words, the third factor discussed above becomes dominant. Formation of  $\text{Ag}^+$ -diphenyl  $\pi$ -electron complexes can also enhance the solubility of diphenyl.

Based on the discussions above, the order  $\text{NaCl} > \text{KCl} > \text{RbCl}$  of the salting out effect for benzene is understandable because that is the order of hydration of the cations. The order  $\text{NaCl} > \text{KCl} > \text{RbCl}$  of salting in for diphenyl can be understood.

#### *Effect of $x(\text{TBA})$ on the solubilities*

The solubilities of benzene and diphenyl in both water-TBA and water-TBA-NaCl mixtures were determined at 298.15 and 303.15 K, in which the molality

of NaCl is fixed at 1 mol/kg and the mole fraction of TBA are 0.000, 0.010, 0.020, 0.030, 0.040, 0.045 and 0.060, respectively. The results are shown in Figs. 3 and 4, respectively.

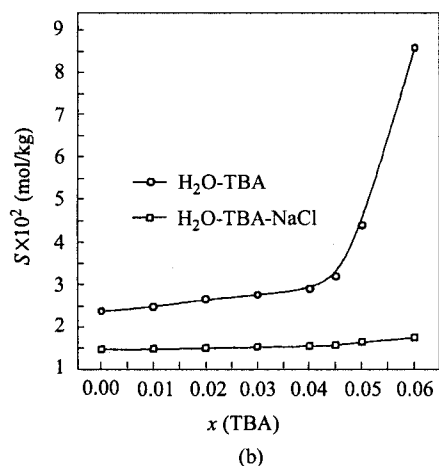
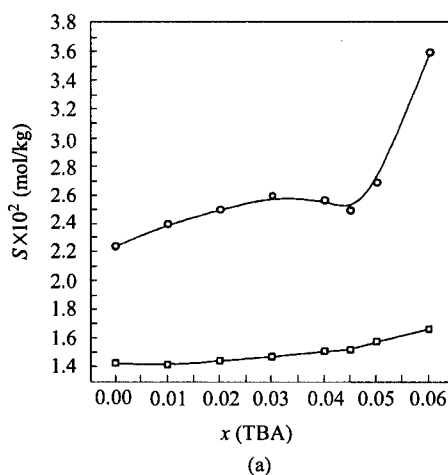


Fig. 3 Dependence of the solubilities of benzene in two mixtures on  $x(\text{TBA})$  at 298.15 K (a) and 303.15 K (b).

As can be seen from Fig. 3, the solubilities of benzene in water-TBA mixtures are higher than those in water-TBA-NaCl system. In other words, the effect of NaCl on the solubility of benzene is salting out under the experimental conditions. The solubility of benzene in  $\text{H}_2\text{O}$ -TBA solution increases very slowly for  $x(\text{TBA}) < 0.045$ , and increases sharply for  $x(\text{TBA}) > 0.045$ . The explanation for this result is similar as that in the previous paper.<sup>10</sup> The solubility of benzene in water-TBA-NaCl mixture is nearly constant in the whole experimental  $x(\text{TBA})$  range. This must be due to the salting

out effect.

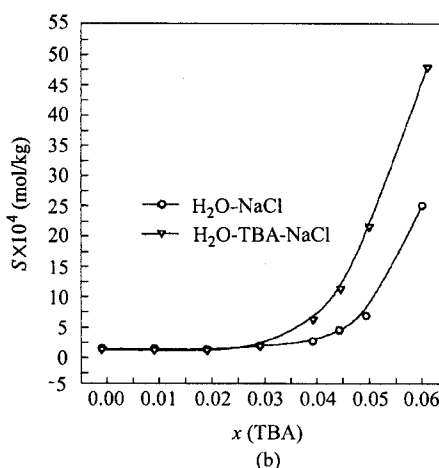
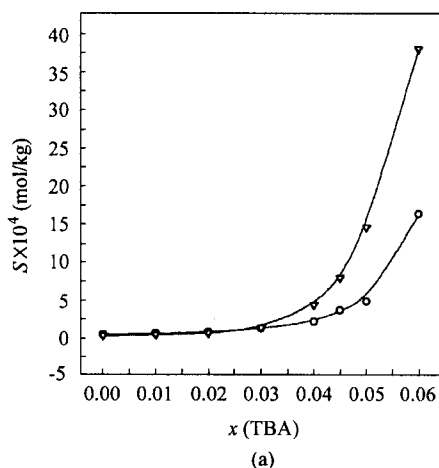


Fig. 4 Dependence of the solubilities of diphenyl in two mixtures on  $x(\text{TBA})$  at 298.15 K (a) and 303.15 K (b).

The effect of NaCl on the solubility of diphenyl is different from that of benzene, as can be known by comparing Figs. 3 and 4. The solubility of diphenyl in water-TBA-NaCl is lower than that in water-TBA when  $x(\text{TBA})$  is lower than 0.03. When  $x(\text{TBA})$  is higher than 0.03, however, the solubility of diphenyl in water-TBA-NaCl is higher. The reason is that the effect of NaCl on the number of free TBA molecules is very limited when  $x(\text{TBA}) < 0.03$  because water is excessive in the system (the number of cluster of TBA- $\text{H}_2\text{O}$  is very less), and thus the effect of the first factor discussed above is dominant. At higher  $x(\text{TBA})$  [ $x(\text{TBA}) > 0.03$ ], because a number of clusters of TBA- $\text{H}_2\text{O}$  are broken by NaCl, the free TBA molecules in water-TBA-NaCl are more than those in water-TBA, and the second and third

factors discussed above are dominant.

### Standard Gibbs energy of solution

According to thermodynamic principles, the chemical potential of a solute indifferent phases is equal under equilibrium condition. In this work, for benzene  $\mu_B$  (vapor phase) =  $\mu_B$  (benzene-rich phase) =  $\mu_B$  (water-rich phase), and for diphenyl  $\mu_D$  (vapor phase) =  $\mu_D$  (water-rich phase) =  $\mu_D$  (solid phase). When a solute from the ideal gases to the ideal dilute solution, its standard Gibbs energy of solution can be calculated by Eq. (7).

$$\Delta G_s^0(g \rightarrow \text{sln}) = RT[\ln(p/p^0) - \ln(m/m^0)] \quad (7)$$

where  $p$  is the partial pressure of solute in vapor phase;  $p^0$  denotes the standard pressure (101325 Pa);  $m^0$  and  $m$  stand for the molality of a solute at the standard state (1 mol/kg) and in a solution under the experimental conditions. In this work, it is assumed that the water-rich phases are ideal dilute solutions and the vapor phases are ideal gases for the two solutes. Therefore, the standard Gibbs energies of solution of benzene and diphenyl can be calculated from Eq. (7) and the results are given in Tables 3 and 4.

**Table 3** Standard Gibbs free energies of solution ( $\Delta\mu_s$ ) of benzene in H<sub>2</sub>O-TBA [ $x$  (TBA = 0.045)]-salt mixture at different temperatures and molalities ( $m_s$ )

Salts	$m_s$ (mol/kg)	$\Delta\mu_s$ (kJ/mol)			
		298.15 K	305.15 K	308.15 K	313.15 K
NaCl	0.000	3766	3981	4126	4314
	0.250	4402	4702	4910	5153
	0.500	4665	4993	5248	5630
	0.750	4856	5208	5598	6048
	1.000	4981	5487	5848	6344
KCl	0.250	4307	4605	4843	5101
	0.500	4518	4884	5160	5504
	0.750	4674	5039	5425	5893
RbCl	1.000	4858	5351	5723	6145
	0.500	4496	4832	5102	5439
NH <sub>4</sub> Cl	0.250	4242	4583	4813	5057
	0.500	4454	4779	5046	5395
	0.750	4635	4975	5279	5765
	1.000	4741	5249	5582	5964
KBr	0.250	4214	4448	4668	4910
	0.500	4424	4739	4953	5234
	0.750	4586	4920	5215	5597
CaCl <sub>2</sub>	1.000	4694	5161	5430	5788
	0.500	5227	5537	5785	6141

**Table 4** Standard Gibbs free energies of solution ( $\Delta\mu_s$ ) of diphenyl in H<sub>2</sub>O-TBA [ $x$  (TBA = 0.045)]-salt mixture at different temperatures and molalities ( $m_s$ )

Salts	$m_s$ (mol/kg)	$-\Delta\mu_s$ (kJ/mol)			
		298.15 K	305.15 K	308.15 K	313.15 K
NaCl	0.000	8335	8266	8048	7777
	0.250	8753	8656	8316	7994
	0.500	9353	9159	8699	8305
	0.750	9835	9573	8998	8679
	1.000	10251	10030	9606	9068
KCl	0.250	8624	8517	8263	7938
	0.500	9276	9065	8623	8212
	0.750	9703	9423	8915	8549
	1.000	10038	9906	9456	8926
RbCl	0.500	9150	9029	8505	8088
NH <sub>4</sub> Cl	0.250	8422	8334	8103	7792
	0.500	8731	8584	8272	7867
	0.750	8976	8865	8468	8071
	1.000	9324	9124	8784	8271
KBr	0.250	8530	8428	8188	7859
	0.500	9023	8832	8445	8046
	0.750	9456	9230	8820	8357
CaCl <sub>2</sub>	1.000	9875	9667	9150	8657
	0.500	9884	9776	9305	8738

The results show that the  $\Delta G_s^0$  of benzene increases with both  $m_s$  and temperature. The  $-\Delta G_s^0$  of diphenyl increases with  $m_s$  and decreases with increasing the temperature. The values of  $\Delta G_s^0$  of benzene are positive, while those of diphenyl are negative. It means that diphenyl is more soluble in the water-TBA-salt mixtures than benzene if their partial pressures are the same.

### Hydrophobic Interaction

The Gibbs energy changes for the process of bringing two benzene molecules from infinite separation to a distance  $R$  at specified temperature and standard pressure can be separated into two terms.<sup>16</sup>

$$\Delta G = \Delta G(d) + \Delta G(\text{HI}) \quad (8)$$

where  $\Delta G(d)$  stands for the direct benzene-benzene pair potential, *i. e.* the work required to carry out the same process as described above in vacuum;  $\Delta G(\text{HI})$  is the indirect part of the Gibbs energy change, which displays the properties of the solvent in which the process is carried out. If the solvent is water or an aqueous solution,

$\Delta G(\text{HI})$  is referred to as hydrophobic interaction (HI) part. For the dimerizing process of two apolar molecules, according to Ben-Naim's thermodynamic cycle, the  $\Delta G(\text{HI})$  can be calculated using following equation:

$$\Delta G(\text{HI}) = \Delta G_s(2) - \Delta G_s(1) \quad (9)$$

where  $\Delta G_s(1)$  and  $\Delta G_s(2)$  are the standard Gibbs energies of solution for a solute in the non-aggregating and aggregating states, respectively. Because the solubility of solute in the aggregating state can not be measured, it was replaced with that of a standard compound of which the structure is very similar to that of the aggregating state. Therefore, the HI to be obtained by this method is the conditional HI. For benzene, if the aggregating state is similar to diphenyl molecule structure, the simulated dimerizing process can be expressed as



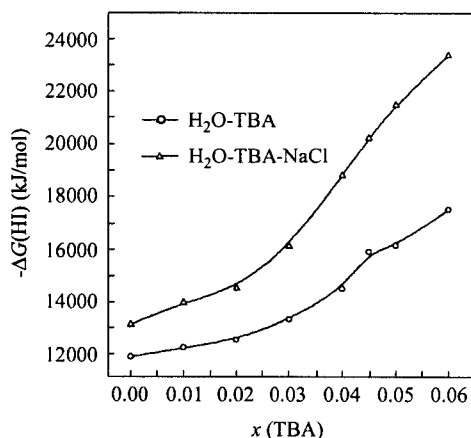
Based on the  $\Delta G_s$  of benzene and diphenyl, the  $\Delta G(\text{HI})$  for benzene-benzene pair can be calculated by formula (10), and the results are given in Table 5.

**Table 5**  $-\Delta G(\text{HI})$  for the benzene-benzene pair in  $\text{H}_2\text{O}$ -TBA [ $x(\text{TBA}) = 0.045$ ]-salt mixture at different temperatures and molalities of salts ( $m_s$ )

Salts	$m$ (mol/kg)	$-\Delta G(\text{HI})/(\text{J/mol})$			
		298.15 K	305.15 K	308.15 K	313.15 K
NaCl	0.000	15868	16228	16300	16405
	0.250	17558	18040	18135	18300
	0.500	18684	19145	19194	19565
	0.750	19548	19990	20194	20725
	1.000	20213	21004	21303	21757
KCl	0.250	17238	17727	17950	18140
	0.500	18312	18835	18942	19219
	0.750	18997	19500	19765	20336
	1.000	19753	20609	20902	21217
RbCl	0.500	18142	18694	18709	18966
$\text{NH}_4\text{Cl}$	0.250	16907	17501	17729	17906
	0.500	17639	18141	18364	18657
	0.750	18247	18816	19026	19602
	1.000	18805	19623	19947	20201
KBr	0.250	16957	17323	17524	17679
	0.500	17880	18039	18352	18515
	0.750	18628	19069	19251	19550
	1.000	19263	19989	20011	20233
$\text{CaCl}_2$	0.500	20338	20850	20875	21020

The results show that the  $\Delta G(\text{HI})$  are negative under the experimental conditions, and the absolute values increase with the molality of the salts and temperature. The order of salt effect of different salts on HI is the same as that on the solubility of benzene. In other words, the effect of different salts on the strength of HI for benzene-benzene pair in water-rich region of  $\text{H}_2\text{O}$ -TBA mixed solvents was dominated by the first factor discussed above, and the stronger the interaction between the ions of salt and water, the stronger the HI displaying in the dimerizing process of benzene molecules is.

$\Delta G(\text{HI})$  gives the information about the strength of solute-solute interaction which is related to the structure and property of solvent. Generally,  $-\Delta G(\text{HI})$  increases with lowering of water structure. In water-rich region of water-TBA mixture, the "ice-like" structure of water is broken to some extent because water can form clathrate structure with TBA as mentioned above. Thus  $-\Delta G(\text{HI})$  increases with  $x(\text{TBA})$  as shown in Fig. 5. When a salt is added into the water-TBA system, the "ice-like" structure of water is further broken by forming hydrated ions and  $-\Delta G(\text{HI})$  increases with increasing  $m_s$  and the interaction between the salt and water. Thus, in water-rich region  $-\Delta G(\text{HI})$  in different mixtures should be increased in the order  $-\Delta G(\text{HI})$  (in water-salt-TBA)  $>$   $-\Delta G(\text{HI})$  (in water-TBA)  $>$   $-\Delta G(\text{HI})$  (in water). *i. e.* the indirect interaction of benzene-benzene in water-salt-TBA mixtures is most favourable to forming the dimer for benzene molecules. The conclusion is consistent with results calculated based on experimental solubility data, as shown in Fig. 5.



**Fig. 5** Dependence of  $\Delta G(\text{HI})$  for benzene-benzene pair in two mixtures on  $x(\text{TBA})$  at 298.15 K.

It should be pointed out that the  $\Delta G(\text{HI})$  in this work is for the process of moving two benzene molecules from infinite separation to a conformation like diphenyl. It is not the largest value for the various possible aggregation forms. For example, the  $\Delta G(\text{HI})$  for the two benzene molecules which are parallel may be more negative, because it will be more favourable to reduce benzene contact with water and make the aggregating state more stable. The negative value of  $\Delta G(\text{HI})$  implies that the indirect part of the Gibbs energy is favorable to the aggregation of benzene molecules in the aqueous solution, and the tendency for aggregation of benzene molecules increases with decreasing the structure of water. In other words, the salts and TBA are favorable to the aggregation of benzene under the experimental conditions of this work.

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(E0103212 LI, L. T.; FAN, Y. Y.)