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Solubility of CH_4 in the mixed solvent *t*-butyl alcohol and water ☆

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Abstract

The solubility of CH_4 in water + *t*-butyl alcohol (TBA) mixtures has been measured at 283.15, 288.15, 293.15 and 298.15 K respectively and at pressures of up to 5 MPa. The solubility varies slowly with the composition of the solvent in the water-rich region and maxima and minima are observed in solubility versus solvent concentration curves at the lower temperatures. Anomalous behaviour of the solubility observed can be explained by the existence of a clathrate-like structure, which has been suggested by other authors. The standard thermodynamic functions are also closely related to the clathrate sturcture. The shapes of the solubility isotherms at different pressures are nearly the same, which shows that the dissolved gas and pressure do not significantly affect the structure of the solvent mixtures.

Keywords: Methane; Solubility; TBA; Water

1. Introduction

The solubility of gas in liquid is a topic of special interest to scientists. This can be traced to the requirements originating in rather diverse fields of the pure and applied sciences. Examples of the areas to which gas solubility in liquids is

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Table 1
Solubilities of CH_4 in TBA–water mixtures at 283.15, 288.15, 293.15 and 298.15 K

283.15 K		288.15 K		293.15 K		298.15 K	
P/MPa	$x_2 \times 10^4$	P/MPa	$x_2 \times 10^4$	P/MPa	$x_2 \times 10^4$	P/MPa	$x_2 \times 10^4$
$x_{TBA} = 0.000$							
1.150	3.439	1.129	3.247	1.217	2.764	1.173	2.955
2.109	6.702	2.198	6.256	2.279	5.085	1.865	4.633
3.113	9.658	3.108	8.431	3.126	8.038	2.576	6.330
4.163	12.80	4.113	11.04	4.142	10.85	3.389	7.816
5.182	15.33	5.087	13.04	5.086	12.16	4.341	9.866
						5.016	11.19
$x_{TBA} = 0.010$							
1.188	4.158	1.215	3.747	1.212	3.326	1.117	2.845
2.236	7.561	2.202	6.654	2.231	5.885	2.166	5.141
3.253	10.63	3.211	9.163	3.231	8.329	3.182	7.520
4.274	13.25	4.211	11.91	4.253	10.92	4.160	9.644
5.163	15.25	5.135	13.78	5.182	12.54	5.043	11.60
$x_{TBA} = 0.020$							
1.219	3.736	1.165	3.649	1.169	3.387	1.161	3.014
2.167	7.248	2.149	6.405	2.148	5.840	2.160	5.302
3.129	10.39	3.133	9.234	3.100	8.180	3.133	7.723
4.219	13.95	4.155	11.78	4.109	10.47	4.098	9.757
5.071	17.51	5.101	14.01	5.099	12.66	5.083	11.90
$x_{TBA} = 0.030$							
1.105	3.779	1.084	3.317	1.162	3.342	1.189	3.188
2.102	6.690	2.046	6.011	2.048	5.491	2.093	5.218
3.046	9.579	3.128	9.123	3.039	8.148	3.050	7.676
4.095	13.43	4.131	11.68	4.106	10.63	4.168	10.05
5.032	15.38	5.005	13.79	5.023	12.66	5.112	11.99
$x_{TBA} = 0.045$							
1.178	3.925	1.191	3.797	1.163	3.451	1.167	3.309
2.067	6.694	2.050	6.319	2.121	5.958	2.110	5.873
3.070	9.333	3.090	9.236	3.119	8.714	2.989	8.228
4.051	12.53	4.107	11.97	4.038	11.02	4.022	10.78
5.111	14.48	5.124	13.92	4.913	13.11	5.119	13.70
$x_{TBA} = 0.060$							
1.139	3.997	1.169	3.865	1.182	3.930	1.142	3.851
2.091	6.893	2.045	6.610	2.031	6.611	1.985	6.684
3.085	9.821	3.032	9.036	3.001	9.388	2.989	9.408
4.095	12.94	4.202	11.62	3.851	12.13	3.985	12.65
5.010	14.99	4.851	13.58	4.809	14.93	4.778	14.68
$x_{TBA} = 0.080$							
1.142	5.483	1.092	5.311	1.093	5.395	1.140	5.781
2.052	9.614	1.981	9.496	1.762	8.564	1.942	9.594
2.936	13.27	3.004	13.70	3.009	14.74	2.985	14.73
3.658	17.05	3.892	18.20	3.835	18.22	3.849	18.74
4.581	20.69	4.596	21.02	4.594	20.88	4.589	22.06

Table 1 (continued)

283.15 K		288.15 K		293.15 K		298.15 K	
P/MPa	$x_2 \times 10^4$	P/MPa	$x_2 \times 10^4$	P/MPa	$x_2 \times 10^4$	P/MPa	$x_2 \times 10^4$
$x_{TBA} = 0.100$							
1.086	6.763	1.114	7.167	1.051	7.063	1.139	7.732
1.906	11.42	1.901	12.25	1.911	12.80	2.008	14.16
2.935	18.88	2.900	18.88	2.987	19.28	3.028	20.58
3.787	22.30	3.808	24.43	3.759	23.58	4.000	26.12
4.383	27.21	4.420	27.75	4.412	28.23	5.024	33.16
$x_{TBA} = 0.150$							
1.033	13.26	1.124	14.61	1.073	13.79	1.125	14.56
1.920	22.84	1.974	25.23	1.961	25.12	1.966	25.28
3.021	37.73	3.091	38.66	2.996	37.61	3.046	38.13
4.024	50.03	4.092	51.47	4.053	51.13	4.056	52.33
4.887	61.98	4.976	61.91	4.981	63.00	4.922	63.47
$x_{TBA} = 0.300$							
1.124	42.75	1.066	40.72	1.099	41.45	1.076	40.10
2.026	78.73	1.967	75.18	1.938	72.67	1.986	74.66
3.045	116.9	3.037	115.4	3.030	113.5	3.083	114.0
3.991	152.7	4.052	153.9	3.973	147.1	4.093	152.2
4.900	189.4	4.918	185.2	4.923	183.6	4.942	189.4
$x_{TBA} = 0.600$							
1.139	129.6	1.055	118.9	0.973	107.0	1.242	134.6
1.973	225.0	1.879	211.6	1.899	207.6	2.013	218.4
2.976	341.4	3.003	337.7	3.009	331.3	3.083	331.6
4.083	463.1	4.027	448.1	4.002	435.9	4.044	422.7
4.786	541.2	4.851	535.2	4.843	528.5	4.888	522.3

important are chemical technology, geochemistry, environmental science, and biomedical technology. Thus it is not surprising that many papers have been published on this subject.

In this paper the solubility of CH_4 in water and t-butyl alcohol (TBA) mixture has been systematically determined and studied. Attention has been given to the effects of temperature, pressure and solvent composition on the solubility, especially in the water-rich region of the mixture.

2. Experimental

The experimental apparatus and procedure employed in this study have previously been described in detail [1,2].

The purity of CH_4 supplied by Beijing Analytical Instrument Factory was 99.95%. The TBA, originally AR grade, was first dehydrated using CaO for 24 h, and was then pruified by distillation with a large reflux ratio. The index of refraction of the treated TBA at 298.15 K is 1.385, which is the same as the value in the handbook [3]; The water used was twice distilled and its conductivity was less than 10^{-6} Ω^{-1} cm^{-1}.

3. Results and discussion

3.1. Solubility

The solubility of CH_4 in TBA–water mixtures was determined at 283.15, 288.15, 293.15 and 298.15 K and at pressures up to 5 MPa over the whole range of the mixture compositions. The results are listed in Table 1. At constant temperature and fixed solvent composition $\ln(f_2/x_2)$ is a linear function of P_2. Thus the Henry's law constants and partial molar volumes of CH_4 in the liquids can be obtained using the equation [4]

$$\ln(f_2/x_2) = \ln H + \bar{V}_2 P_2/RT \tag{1}$$

where P_2 and f_2 stand for partial pressure and fugacity of CH_4; x_2 is the mole fraction of CH_4 in the liquid phase; H is Henry's law constant and $\bar{V}_2$ is the partial molar volume of the dissolved gas, both in the limit of zero pressure.

The application of Eq. (1) requires knowledge of the solvent vapour pressures which had been measured earlier [5]. The fugacity of the gas in the vapour phase is calculated using the equation and the virial coefficients in the literature [6]. The Henry's law constants (H) and the partial molar volumes calculated from Eq. (1) and the data in Table 1 are listed in Table 2.

The data in Table 1 show that the solubility of CH_4 in the mixed solvents increases with pressure at all temperatures and solvent compositions.

By combination of Eq. (1) and the corresponding data in Table 2 the solubility under any condition can be calculated. The dependence of solubility on temperature and solvent composition at different pressures is nearly the same. Fig. 1 shows the solubility versus x_{TBA} curves at 0.101325 MPa. Only the water-rich region is shown in the figure because the anomalous phenomenon appears in this composition range. From Fig. 1 the following conclusions can be drawn.

(1) The solubility changes very slowly with the mole fraction of TBA (x_{TBA}) when x_{TBA} is less than about 0.05. At the lower temperatures maxima and minima were observed.

(2) The solubility increases dramatically with TBA when x_{TBA} exceeds about 0.05.

The anomalous behaviour of the solubility can be explained by a clathrate structure model of the binary solvent, which has been proposed by other authors and is discussed below.

Baumgartner and Atkinson [7] measured the ultrasonic velocity in aqueous TBA solutions at 283.15 and 298.15 K. The system shows a maximum of the sound velocity in water-rich region. Sakurai [8] measured the partial molar volumes of TBA in water at various temperatures and found minima in the water-rich region,

Table 2
Henry's law constants and the partial mole volume of CH_4 in TBA–water mixtures

T/K	x_{TBA}	H/MPa	$\bar{V}_2/(\mathrm{ml\ mol^{-1}})$	x_{TBA}	H/MPa	$\bar{V}_2/(\mathrm{ml\ mol^{-1}})$
283.15	0.000	2878	12.4	0.080	2062	−11.7
	0.010	2693	52.2	0.100	1437	−5.6
	0.020	2696	1.0	0.150	771.3	−25.1
	0.030	2909	10.4	0.300	261.3	−51.9
	0.045	2866	40.7	0.600	87.3	−43.4
	0.060	2760	43.3			
288.15	0.000	3335	24.6	0.080	2029	−6.1
	0.010	3092	38.0	0.100	1531	−31.6
	0.020	3093	29.9	0.150	764.3	−20.5
	0.030	3193	14.0	0.300	260.2	−37.5
	0.045	2986	45.0	0.600	87.9	−32.7
	0.060	2796	93.8			
293.15	0.000	3578	28.1	0.080	1977	6.0
	0.010	3377	49.9	0.100	1453	4.1
	0.020	3344	49.3	0.150	776.1	−32.1
	0.030	3412	30.5	0.300	264.3	−34.8
	0.045	3256	26.6	0.600	90.8	−39.3
	0.060	2848	2.1			
298.15	0.000	3955	26.0	0.080	1951	−7.7
	0.010	3767	30.3	0.100	1419	−7.1
	0.020	3728	26.4	0.150	778.3	−40.1
	0.030	3654	33.8	0.300	270.3	−52.1
	0.045	3436	8.5	0.600	91.6	−31.5
	0.060	2901	17.3			

with deeper dips at lower temperatures. Li et al. [9] determined the partial molar volumes of dimethyl sulphoxide and acetone in TBA–water mixtures at 278.15 288.15 and 298.15 K. Minima were observed on the partial molar volume curves (partial molar volume against x_{TBA}) at all the three temperatures at about $x_{TBA} = 0.03$. Iwasaki and Fujiyama [10] studied the light-scattering spectra of the binary mixture at 297.15 K at various concentrations.

An anomalous phenomenon was also found in the water-rich region. Wang et al. [5] studied the vapour pressure of the binary system at 283.15, 288.15, 293.15, 298.15 and 303.15 K. Maxima and minima were observed in the vapour pressure versus composition curves at the lower temperatures. Based on their experimental results, all the above authors pointed out the existence of a clathrate structure which is formed in such a way that one TBA is surrounded by 17–22 water molecules.

Formation and dissociation of the clathrate structure, according to thermodynamic principles, should be in equilibrium under specified conditions and the quantity of the clathrate depends mainly on the composition and temperature.

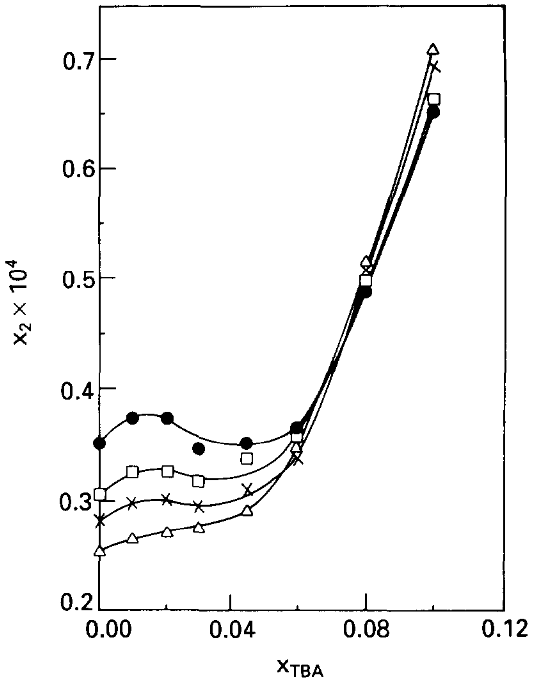

Fig. 1. Solubilities of CH_4 in TBA–water mixtures at 0.101325 MPa: ●, 283.15 K; □, 288.15 K; ×, 293.15 K; △, 298.15 K.

Based on this, it can be deduced that the anomalous variation of the solubility with x_{TBA} is a result of the combination of the following factors:

(1) the formation of the clathrate structure decreases the solubility because it is not easy for the gas to enter the clathrate;

(2) the gas solubility increases with free TBA concentration because the solubility of the gas in pure TBA is much higher than in water;

(3) clathrate structure is enhanced when the temperature is lowered.

In the concentration range $x_{TBA} < 0.045$, the solubility varies slowly with TBA concentration. The reason is probably that both free TBA and the clathrate increase with x_{TBA} and factors (1) and (2) compensate each other to some extent. However, it is obvious that temperature affects the shape of the solubility curves. At 298.15 K, the highest temperature in this work, the solubility increases with x_{TBA} in the solvent concentration range. This is because the temperature is relatively high and fewer clathrates are formed. Factor (2) is dominant. At 283.15 K, the lowest temperature in this work, minima appears at about $x_{TBA} = 0.045$, where the total composition is the same as the composition of the clathrate. The lower temperature is favourable for clathrate formation. Thus the quantity of clathrate is larger, and so the effect of factor (1) is relatively larger. At 288.15 and 293.15 K, the shapes of the two solubility curves fall into the above two extreme instances.

The solubility increases sharply with x_{TBA} when x_{TBA} is higher than 0.05, due to the destruction of the clathrate and free TBA increasing dramatically with x_{TBA}.

Table 3
Standard thermodynamic functions (ΔG, ΔH, ΔS) of CH_4 in TBA–water mixtures

x_{TBA}	$-\Delta H^{\ominus}$/ (kJ mol^{-1})	$\Delta G^{\ominus}$/(kJ mol^{-1})				$-\Delta S^{\ominus}$/(J mol^{-1})			
		283.15 K	288.15 K	293.15 K	298.15 K	283.15 K	288.15 K	293.15 K	298.15 K
0.000	14.38	24.14	24.92	25.52	26.21	136.0	136.4	136.1	136.1
0.010	15.39	23.98	24.74	25.38	26.09	139.0	139.3	139.1	139.1
0.020	13.72	24.04	24.74	25.36	26.06	133.4	133.5	133.3	133.4
0.030	10.11	24.16	24.82	25.33	26.01	121.1	121.2	120.9	121.2
0.045	8.84	24.13	24.65	25.29	25.86	116.4	116.2	116.4	116.4
0.060	2.37	24.04	24.50	24.97	25.44	93.26	93.22	93.24	93.26
0.080	−2.70	23.35	23.73	24.08	24.45	72.95	72.99	72.93	72.97
0.100	−4.19	22.67	23.05	23.33	23.67	65.23	65.45	65.26	65.30
0.150	0.59	21.04	21.39	21.80	22.18	76.40	76.29	76.38	76.37
0.300	1.64	18.49	18.81	19.17	19.56	71.56	70.96	70.99	71.08
0.600	2.47	15.91	16.21	16.57	16.87	64.91	64.82	64.94	64.87

3.2. *Standard thermodynamic functions*

The standard Gibbs free energy, standard enthalpy, and standard entopy of solution of the gas in the mixed solvent can be calculated using the equations [11]

$$\Delta G^{\ominus} = RT \ln H \tag{2}$$

$$\frac{\mathrm{d} \ln H}{\mathrm{d}T} = -\frac{\Delta H^{\ominus}}{RT^2} \tag{3}$$

$$\Delta H = \Delta G + T\,\Delta S \tag{4}$$

where $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are standard Gibbs' free energy, standard enthalpy, and standard entropy of solution, respectively.

It is found that $\ln H$ is a linear function of $1/T$, and so the standard enthalpy is independent of temperature.

Table 3 gives the standard thermodynamic functions, which are calculated from Eqs. (2)–(4) using the data in Table 2. The data in Table 3 indicate clearly that the thermodynamic functions are closely related to the clathrate sturcture of the mixture solvent.

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