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Vapour pressures of binary mixtures of *t*-butyl alcohol and water

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Abstract

The total vapour pressures of *t*-butyl alcohol (TBA) and water mixtures have been measured at 283.15, 288.15, 293.15, 298.15 and 303.15 K, respectively. Maxima and minima were observed in the vapour pressure versus concentration curves at the three lowest temperatures. The anomalous behaviour of the solution can be explained by the existence of a clathrate-like structure, which has been suggested by other authors.

Keywords: Binary system; Butyl alcohol; Clathrate; TBA; Vapour pressure; Water

1. Introduction

In recent years there has been much interest in the study of non-electrolyte aqueous solutions because these systems can provide very important information, for instance, concerning hydrophobic interaction. TBA is considered a unique solute for water and has attracted much attention. The properties of the TBA–water binary system have been widely studied by various methods [1–11].

Vapour pressure is one of the most important properties of solutions, and is closely related to intermolecular interaction. Brown and Ives [12] determined the

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vapour pressures of TBA–H_2O mixtures at 298.15 K over the entire concentration range. Koga et al. [13] reported the vapour pressures of the system at 298.30 and 303.15 K in the concentration range $X_{TBA} < 0.2$, where X_{TBA} is the mole fraction of TBA. In this work, the vapour pressures of TBA–H_2O mixtures were measured and studied systematically in the temperature range 283.15–303.15 K at various compositions.

2. Experimental

The experimental technique was described earlier [14]. Very briefly, the water and TBA were degassed separately, and then mixed under vacuum. The vapour pressure of the solution was determined using a U-mercury manometer in which the pressure is measured according to the difference in the two mercury levels. An altimeter with a resolution of 0.01 mm was used to determine the height difference of the two mercury levels. The temperature fluctuation of the water bath was ± 0.01 K and the temperature was measured to within 0.02 K by a mercury thermometer. In each experiment the volume ratio of the liquid phase to vapour phase was greater than 5, so that the difference between the total composition and that of the liquid phase is negligible under the experimental conditions. The total composition, which is considered as the liquid phase composition in this paper, was calculated according to the weights of the two components.

The TBA, originally A.R. grade, was first dewatered using CaO for 24 h, and then purified by distillation using a large reflux ratio. The refractive index of the treated TBA at 25°C was the same as that in the handbook [15]. The water used was distilled twice and its conductivity was less than $10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$.

3. Results and discussion

The vapour pressures of TBA–water mixtures determined at 283.15, 288.15, 293.15, 298.15 and 303.15 K are listed in Table 1 and depicted in Fig. 1. For pure TBA, the experiment was not performed at 298.15 K or lower because it becomes solid at these temperatures. The vapour pressures obtained for pure water and TBA agree well with the literature values [16].

The data in Table 1 and Fig. 1 indicate that TBA and water binary systems exhibit marked non-ideal behaviour, especially at lower temperatures. The anomalous phenomenon of the vapour pressure is consistent with the clathrate structure model, which has been suggested by other authors and is discussed below.

Baumgartner and Atkinson [2] measured ultrasonic velocity in aqueous TBA solutions at 283.15 and 298.15 K. The system shows a maximum in sound velocity in the water-rich region. Sakurai [3] measured the partial molar volumes of TBA in water at various temperatures and found minima in the water-rich region, with deeper dips at lower temperatures. Li et al. [4] determined the partial molar volumes of dimethyl sulphoxide and acetone in TBA–water mixtures at 278.15,

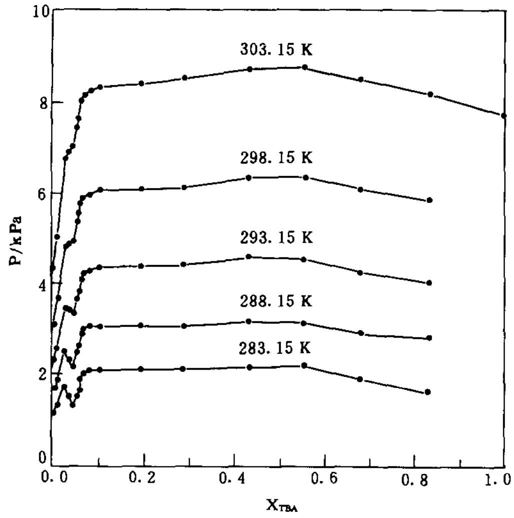

Fig. 1. Vapour pressure of TBA-water mixtures at different temperatures.

Table 1
Vapour pressures in kPa of the TBA-water mixtures at different temperatures

X_{TBA}	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K
0.00000	1.219	1.731	2.381	3.074	4.268
0.00835	1.343	1.863	2.586	3.674	5.000
0.02471	1.751	2.529	3.469	4.880	6.757
0.03242	1.508	2.304	3.397	4.877	6.877
0.04220	1.307	2.120	3.296	4.853	6.989
0.05186	1.528	2.485	3.693	5.317	7.418
0.05568	1.616	2.613	3.802	5.549	7.626
0.05908	1.935	2.869	4.144	5.802	8.026
0.06367	2.034	3.026	4.200	5.910	8.149
0.07974	2.078	3.040	4.285	5.949	8.253
0.10254	2.082	3.056	4.354	6.057	8.330
0.19165	2.106	3.064	4.370	6.059	8.381
0.28736	2.117	3.064	4.408	6.111	8.493
0.43084	2.160	3.178	4.576	6.330	8.723
0.55439	2.176	3.157	4.544	6.351	8.759
0.67746	1.903	2.890	4.245	6.071	8.495
0.83020	1.611	2.824	4.037	5.824	8.167
1.00000					7.703

288.15, and 298.15 K. Minima were observed on the partial molar volume curves (partial molar volume against X_{TBA}) at all three temperatures at about $X_{TBA} = 0.03$. Iwasaki and Fujiyama [7] studied the light-scattering spectra of the binary mixture at various concentrations. Anomalous phenomena were also found in the water-rich region. Based on their experimental results, all the above authors suggested the existence of a clathrate structure which is formed in such a way that one TBA molecule is surrounded by a number of water molecules.

The formation and dissociation of the clathrate structure, according to thermodynamic principle, should be in equilibrium under certain conditions, and the quantity of clathrate mainly depends on the composition and temperature. Based on this, it can be deduced that the anomalous variation of the vapour pressure with temperature and X_{TBA} is a result of the combination of the following factors.

1. The formation of the clathrate structure decreases the vapour pressure.

2. The vapour pressure increases with free TBA concentration because its volatility is higher than that of water.

3. From the vapour pressure curves, it can be seen that the binary mixture exhibits positive deviation from Raoult's Law in the entire concentration range. This means that addition of TBA to water will break the structured clusters of water to a certain extent.

4. The vapour pressure increase with temperature and the clathrate structure is enhanced when the temperature is lowered.

Figure 1 shows that in the concentration range $X_{TBA} < 0.025$, the vapour pressure increases with the concentration of TBA at all five temperatures. This is probably because the solutions are very dilute and the number of clathrates is small. So items 2 and 3 above are dominant.

In the range of approx. $0.025 > X_{TBA} > 0.045$, the vapour pressure decreases with the concentration of TBA at the three lower temperatures, but increases with X_{TBA} at 303.15 K. The vapour pressure at 298.15 K is, however, nearly independent of X_{TBA} in the same concentration range. The reason for this seems to be that at the three lower temperatures the concentration of clathrate is high enough and still increases markedly with X_{TBA}. Thus the first factor becomes more important. At the two higher temperatures, there is less clathrate in the solutions than at lower temperatures. So at 298.15 K the effects of the first three factors compensate each other, and at 303.15 K factors 2 and 3 are dominant.

It can also be seen from Fig. 1 that the vapour pressure increases sharply with the concentration of TBA when X_{TBA} is in the range from about 0.045 to 0.08. This may be because the concentration of clathrate decreases with X_{TBA} in this concentration range and free TBA molecules increase significantly.

For the solutions with $X_{TBA} > 0.1$, the vapour pressure of the system is not sensitive to its composition. We believe that in this concentration range the solution is mainly composed of free water and TBA.

Concerning the composition of clathrate in the solution, Baumgartner and Atkinson [2] estimated that the ratio of water to TBA is 17:1. Iwasaki and Fujiyama [7], however, reported that the ratio is about 22:1. It is acceptable to assume that the composition should correspond to the minima of the vapour pressure curves at the three lower temperatures. Based on this assumption, it can be estimated that the composition at about $X_{TBA} = 0.045$, i.e. the ratio of water to TBA, is about 22:1.

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References

[1] M.J. Blandamer, D.E. Clarke, N.J. Hidden and M.C.R. Symons, Trans. Faraday Soc., 64 (1968) 2691.
[2] E.K. Baumgartner and G. Atkinson, J. Phys. Chem., 75 (1971) 2336.
[3] M. Sakurai, Bull. Chem. Soc. Jpn., 60 (1987) 1.
[4] Z.F. Li, Y. Jiang and R.L. Liu, Thermochim. Acta, 183 (1991) 39.
[5] L. Avedikian, G. Perron and J.E. Desnoyers, J. Solution Chem., 4 (1975) 331.
[6] G. Perron and J.E. Desnoyers, J. Chem. Thermodyn., 13 (1981) 1105.
[7] K. Iwasaki and T. Fujiyama, J. Phys. Chem., 81 (1977) 1908; 83 (1979) 463.
[8] T.M. Bender and R. Pecora, J. Phys. Chem., 90 (1986) 1700.
[9] K. Nishikawa, Y. Kodera and T. Iijima, J. Phys. Chem., 91 (1987) 3694.
[10] R.G. Anderson and M.C.R. Symons, Trans. Faraday Soc., 65 (1969) 2550.
[11] J.L. Green, A.R. Lacey and M.G. Sceats, Chem. Phys. Lett., 137 (1987) 537.
[12] A.C. Brown and D.J.G. Ives, J. Chem. Soc., (1962) 1608.
[13] Y. Koga, T.Y.H. Wong and W.W.Y. Siu, Thermochim. Acta, 169 (1990) 27.
[14] B.X. Han, H.K. Yan and R.H. Hu, Acta Physico-Chimica Sinica, 9 (1993) 421.
[15] CRC Handbook of Chemistry and Physics, 69th edn., CRC Press, Boca Raton, Florida, 1988–1989.
[16] J.A. Dean, Lange's Handbook of Chemistry, 11th edn. MacGraw-Hill, New York, 1973.