Thermochimica Acta, 169 (1990) 27–38
Elsevier Science Publishers B.V., Amsterdam

VAPOUR PRESSURE OF AQUEOUS *tert.*-BUTANOL IN THE WATER-RICH REGION: TRANSITION IN THE MIXING SCHEME *

YOSHIKATA KOGA **, TERRANCE Y.H. WONG and WILLIAM W.Y. SIU ***

Department of Chemistry, The University of British Columbia, Vancouver,
B.C. V6T 1Y6 (Canada)

(Received 18 October 1989)

ABSTRACT

The total vapour pressure of aqueous *tert.*-butanol (TBA) was measured in small increments in the range $x_{\mathrm{TBA}} < 0.2$ at 25.15 and 30.00 °C, where x_{TBA} is the mole fraction of TBA in the liquid phase. The partial pressure of TBA, and hence the excess partial molar free energy of TBA, $G_{\mathrm{m}}^{\mathrm{E}}(\mathrm{TBA})$, were calculated by the Boissonnas method. Since the values of the excess partial molar enthalpy, $H_{\mathrm{m}}^{\mathrm{E}}(\mathrm{TBA})$, had been directly measured in small increments, the values of the excess partial molar entropy, $S_{\mathrm{m}}^{\mathrm{E}}(\mathrm{TBA})$, were calculated accurately.

From the concentration derivative of $G_{\mathrm{m}}^{\mathrm{E}}(\mathrm{TBA})$, the Kirkwood–Buff parameters were calculated for the range $x_{\mathrm{TBA}} < 0.05$. The concentration dependence of the partial molar entropy, as well as that of the enthalpy, indicated that, at about $x_{\mathrm{TBA}} = 0.045$, there is a transition from one scheme of mixing in the solution to the other. As the temperature increases this threshold value decreases; there is a boundary which is marked by the maxima in various quantities that are proportional to the *third* derivative of the free energy. Below this boundary, the mixing scheme is consistent with such ideas as the "iceberg formation", the "structure enhancement of the solvent water", and the "hydrophobic interaction (attraction)". The second scheme above this boundary appears to be that of TBA cluster formation.

INTRODUCTION

In previous papers [1–3], we have reported the values of the excess partial molar enthalpies in *tert.*-butanol (TBA)–water mixtures, $H_{\mathrm{m}}^{\mathrm{E}}(\mathrm{i})$ (i = TBA or H_2O). These quantities were measured directly and were therefore much more accurate than those obtained by graphical differentiation of existing values of the integral molar enthalpy [4,5]. As a result, we were able to evaluate, with sufficient accuracy, the derivative of $H_{\mathrm{m}}^{\mathrm{E}}(\mathrm{TBA})$ with respect to

---

* Presented at the International Conference on Chemical Thermodynamics and Calorimetry, Beijing, P.R. China, 25–28 August 1989.

** To whom correspondence should be addressed.

*** Present address: Department of Pharmacology, The University of British Columbia, Vancouver, B.C. V6T 1Y6, Canada.

the concentration [2,6]. As argued previously [6], this derivative is the measure of the solute–solute interaction in terms of enthalpy. The results indicated that the TBA–TBA interaction is repulsive in terms of enthalpy, and its concentration dependence showed that, at about $x_{TBA} = 0.045$, such an interaction among TBA molecules collapses and a new scheme, that of TBA cluster formation, appears to set in. This transition from one scheme of mixing to the other is consistent with the suggestion that there is a "pseudo-phase transition", since the partial molar heat capacity shows an anomaly at about this concentration [7].

For a very dilute solution, the free energy [8] and the enthalpy [9] have been treated by the virial expansion with respect to the molarity, m_{TBA}. The coefficient of the second term gives the solute–solute interaction as a pair-only interaction parameter. Perron and Desnoyers analysed these data using the values of heat capacity [10], and calculated the pair-only interaction parameters in terms of free energy, enthalpy and entropy, as a function of temperature. Their results indicated that the solute–solute interaction is repulsive in terms of enthalpy but attractive in terms of entropy. Furthermore, the latter entropy effect is stronger, and hence the net interaction is attractive in terms of free energy, supporting the idea of the "hydrophobic attraction" [11]. It should be noted, however, that the above argument is based on the virial expansion and that only the term with a pair interaction parameter is used. Such an expansion is valid only in a very dilute solution, $m_{TBA} < 0.2$ or $x_{TBA} < 0.004$ [12]. After all, the virial expansion is powerful only when the system is nearly ideal. Indeed, it has been pointed out [2] that the virial expansion for H_m^E(TBA) even with three interaction parameters [9] is applicable only for the range $x_{TBA} < 0.05$.

The purpose of the present study is to measure the vapour pressure of TBA–water mixtures and hence the excess partial molar free energy, G_m^E(TBA), in small increments. We can then calculate the excess partial molar entropy, S_m^E(TBA), and thus gain further information about the solute–solute interaction in terms of entropy directly from the measured quantities. There have been some free energy data for this system in the literature, obtained by measuring the freezing point depression [8] and the vapour pressure [4,13]. The former, while the data were taken in small increments, covered only up to $x_{TBA} < 0.02$. The latter, on the other hand, covered the entire concentration range, but in the water-rich region, $x_{TBA} < 0.1$, in which we are interested, only a few data points are available.

EXPERIMENTAL

Vapour pressures were measured by a static method. A glass cell of about 3 ml was connected to a gas-handling manifold and a high-vacuum line capable of reaching 10^{-6} Torr. A connection was made by a cupronickel tube of 0.8 mm i.d. which was wound with heating wire to keep the temperature of the tube about 20 degrees higher than that of the cell. The gas-handling manifold together with an MKS Baratron pressure gauge (100 Torr full scale with a sensitivity of ± 0.001 Torr) was encased in a box, the temperature of which was kept at $37.5 \pm 0.5\,^\circ$C. The cell was immersed in a water bath which was in turn placed in a larger water bath with an air space between them. The temperature of the outer bath was controlled within 0.1 °C by a mercury regulator, about 5 °C lower than that of the inner bath. The latter was controlled by a Fisher proportional controller. The temperature of the inner bath was measured within 0.02 °C by a mercury thermometer previously calibrated at the ice point and the melting point of $Na_2SO_4 \cdot 10H_2O$. The temperature fluctuation of the inner bath was monitored by a Beckmann thermometer. The short-term fluctuation was about 1 mK, while the long-term fluctuation, reflecting a wide variation of the room temperature, was found to be about 30 mK. The measured vapour pressures were corrected for such a temperature variation by using the temperature dependence of the vapour pressure obtained from two series of measurements at 25.15 and 30.00 °C.

Freshly distilled water which had undergone several freeze–pump–thaw operations was vacuum-distilled into a buret with 0.01 ml markings which had previously been calibrated. About 0.4 ml of water (~ 20 mmol) was then vacuum-transferred into the cell. *tert.*-Butanol (BDH assured) was also degassed by several freeze–pump–thaw operations. A small dose (0.05–0.5 mmol) of TBA vapour was measured volumetrically before being transferred into the cell. The second virial coefficients of TBA and water vapour were estimated by extrapolating the existing data [14] to the temperature of the box. The amounts of TBA and water adsorbed on the inner walls of the manifold and the cell were small (a few percent of the total amounts in the system), but were corrected for by the adsorption data measured previously.

RESULTS AND DISCUSSION

Figure 1 shows the total vapour pressure plotted against the mole fraction of the total amount of TBA introduced in the system, z_{TBA}. When the partial pressures of TBA and water are known, the amounts in the gas phase and those adsorbed on the inner walls are subtracted to calculate the respective amounts in the liquid phase. The mole fraction in the solution, x_{TBA}, is then calculated. The uncertainty in the mole fraction is estimated to be about 0.5%. The values of p together with x_{TBA} are listed in Table 1.

The Boissonnas method [15,16] was used to calculate the partial pressure of TBA from an increment in the total vapour pressure, Δp. Starting from $x_{\mathrm{TBA}} = 0$, the change in the partial pressure of TBA, Δp_{TBA}, was calculated

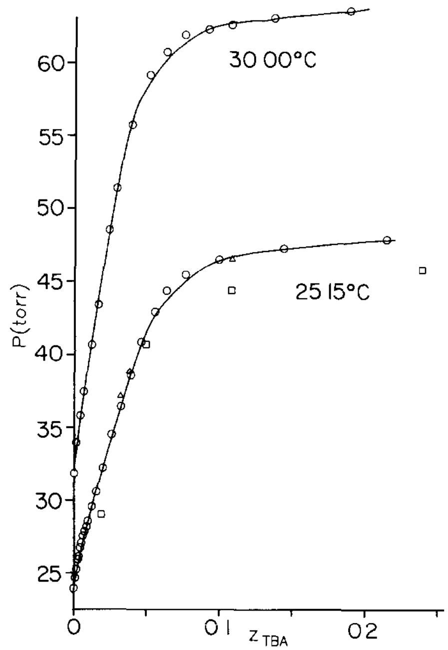

Fig. 1. Total vapour pressure, *p*, vs. mole fraction of the total amount of TBA charged in the cell. △, ref. 4; □, ref. 13.

from

$$\Delta p_{TBA} = \Delta p + p_w \, \Delta x_{TBA} \qquad \text{for } x_{TBA} = 0$$
$$\Delta p_{TBA} = \frac{\Delta p}{1 - (p_w x_{TBA})/(p_{TBA} x_w)} \qquad \text{for } x_{TBA} \neq 0 \tag{1}$$

where the subscript w indicates water. Thus, the uncertainty involved in this method is small in the range where the total vapour pressure changes sharply, i.e. $x_{TBA} < 0.07$. For the range $x_{TBA} > 0.1$, this method of analysis is not adequate.

The excess partial molar free energy, $G_m^E(\mathrm{i})$, was calculated from

$$G_m^E(\mathrm{i}) = RT \ln\left(\frac{p_i}{x_i p_i^0}\right) + (B_{ii} - V_i^0)(p - p_i^0) \tag{2}$$

where B_{ii} is the second virial coefficient for species i and i = TBA or H_2O. Figure 2 shows the plots of $G_m^E(\mathrm{TBA})$ against the mole fraction of TBA (x_{TBA}). The uncertainty in the total pressure is expected to be about ±0.002 Torr after the temperature correction mentioned above. However, judging from the plots in the range $x_{TBA} \approx 0.15$, the uncertainty is more realistically ±0.01 Torr, presumably because of a small inhomogeneity in the temperature of the water bath. Since the increments in the total pressure are from 2 to 5 Torr, Δp_{TBA} is determined within 0.2–0.5%. It follows that the values

TABLE 1

Total vapour pressure

x_{TBA}	p/Torr	x_{TBA}	p/Torr
Temp. = 25.15 °C			
0	23.967	0.09687	46.477
0.002089	25.145	0.1394	47.181
0.006095	27.631	0.2090	47.819
0.007646	27.846		
0.01000	28.513	0.001112	24.612
0.01251	29.518	0.003367	25.858
0.01544	30.504	0.005729	27.043
0.01971	32.169	0.008157	28.166
0.02596	34.496		
0.03174	36.429	0.001058	24.609
0.03809	38.574	0.002120	25.201
0.04528	40.912	0.003455	25.989
0.05344	42.914	0.004961	26.732
0.06183	44.299	0.006712	27.518
0.07422	45.455		
Temp. = 30.00 °C			
0	31.838	0.03803	55.656
0.002421	33.947	0.05003	59.211
0.004783	35.774	0.06153	60.807
0.007086	37.371	0.07407	61.994
0.01190	40.659	0.08984	62.365
0.01637	43.435	0.1062	62.642
0.02358	48.458	0.1352	63.013
0.02879	51.322	0.1883	63.524

of $G_{\mathrm{m}}^{\mathrm{E}}$(TBA) are determined within 0.1 kJ mol^{-1}, as shown by the error bar in Fig. 2. At $x_{\mathrm{TBA}} \approx 0$, the values of $G_{\mathrm{m}}^{\mathrm{E}}$(TBA) take only a small positive value and hence nothing significant can be said about the state of the first TBA molecule dissolved in water. Such discussion may be possible when the enthalpic and the entropic contributions to the free energy are separated. As the concentration increases, however, $G_{\mathrm{m}}^{\mathrm{E}}$(TBA) decreases sharply. This indicates that the solute–solute interaction is attractive in terms of free energy. As indicated by the broken lines in Fig. 2, there appear to be two modes of decrease in $G_{\mathrm{m}}^{\mathrm{E}}$(TBA) (i.e. two types of solute–solute interaction) present and the changeover from one to the other seems to occur at $x_{\mathrm{TBA}} \approx 0.04$ at 30.00 °C and 0.05 at 25.15 °C. These points will be discussed in detail below after the partial molar entropy of TBA is calculated.

Now that we have the values of $G_{\mathrm{m}}^{\mathrm{E}}$(TBA) with reasonable accuracy in the range $x_{\mathrm{TBA}} < 0.05$, we calculate the concentration fluctuation, $N\langle(\Delta x_{\mathrm{TBA}})^2\rangle$, by graphically differentiating the smooth curves in the figure and by using

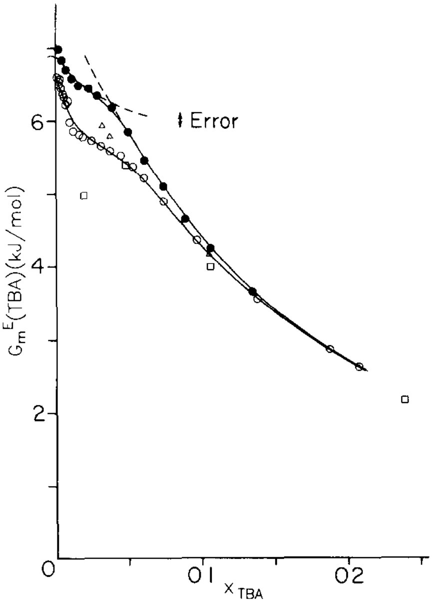

Fig. 2. Excess partial molar free energy, G_m^E(TBA), vs. mole fraction of TBA in the liquid phase, x_{TBA}. ○, 25.15 °C; ●, 30.00 °C.

eqn. (3) below. In this concentration range, the existing data from scattering experiments [17–23] are not accurate.

$$N\langle(\Delta x_{TBA})^2\rangle = \frac{RT(1-x_{TBA})}{\partial\mu_{TBA}/\partial x_{TBA}}$$
$$= \frac{(1-x_{TBA})}{(1/RT)\left(\partial G_m^E(TBA)/\partial x_{TBA}\right)+1/x_{TBA}} \tag{3}$$

The values of the concentration fluctuation are listed in Table 2. The uncertainty was estimated to be about 1% at the lowest concentration, progressively increasing to about 10% at $x_{TBA} \approx 0.5$. We than calculated the Kirkwood–Buff parameters [23–26] by using the data of isothermal compressibility [27] and the partial molar volumes [28] together with the values of the concentration fluctuation. As shown in Fig. 3, the Kirkwood–Buff parameter for the TBA–TBA pair, G_{BB}, is positive and large for $x_{TBA} < 0.02$. This is a direct consequence of the fact that the value of G_m^E(TBA) decreases sharply in this region.

Since $(\partial G_m^E(TBA)/\partial x_{TBA})$ is negative, it follows from eqn. (3) that

$$\frac{N\langle(\Delta x_{TBA})^2\rangle}{x_{TBA}x_w} > 1 \tag{4}$$

This brings about a large positive value for G_{BB}. For a small value of x_{TBA},

TABLE 2

Concentration fluctuation

x_{TBA}	$N\langle(\Delta x_{\text{TBA}})^2\rangle$	
	25.15 °C	30.00 °C
0.004	0.00444	0.00431
0.008	0.00954	0.00876
0.012	0.0143	0.0132
0.016	0.0177	0.0177
0.020	0.0215	0.0218
0.024	0.0259	0.0263
0.028	0.0304	0.0313
0.032	0.035	0.038
0.036	0.041	0.047
0.040	0.047	0.060
0.044	0.055	0.08
0.048	0.07	0.11

an approximate expression for G_{BB} can be written as

$$G_{\text{BB}} \approx \frac{V}{N}\left[\frac{x_{\text{w}}}{x_{\text{TBA}}}\left\{\frac{N\langle(\Delta x_{\text{TBA}})^2\rangle}{x_{\text{TBA}}x_{\text{w}}} - 1\right\} - 1\right] \tag{5}$$

Thus, if eqn. (4) is true, then $G_{\text{BB}} \gg 1$ since $x_{\text{w}}/x_{\text{TBA}} \gg 1$. Namely, the information contained in $(\partial G_{\text{m}}^{\text{E}}(\text{TBA})/\partial x_{\text{TBA}})$ and that in G_{BB} are qualita-

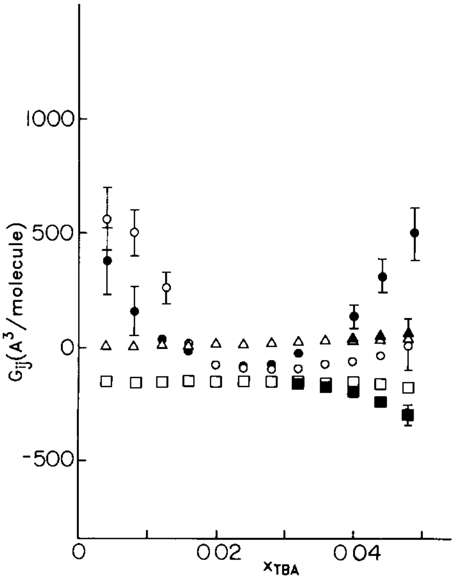

Fig. 3. Kirkwood–Buff parameters. G_{BB}: ○, 25.15 °C; ●, 30.00 °C. G_{WW}: △, 25.15 °C; ▲, 30.00 °C. G_{BW}: □, 25.15 °C; ■, 30.00 °C.

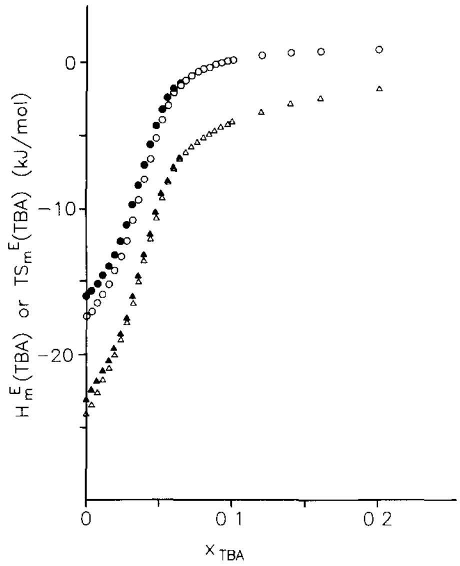

Fig. 4. Excess partial molar enthalpy and entropy. H_m^E(TBA): ○, 25.15 °C; ●, 30.00 °C. TS_m^E(TBA): △, 25.15 °C; ▲, 30.00 °C.

tively equivalent. We note that the derivative, $(\partial G_m^E(\text{TBA})/\partial x_{\text{TBA}})$ is the second derivative of the free energy. We also note that the Kirkwood–Buff parameters are calculated using the isothermal compressibility, the partial molar volumes and the concentration fluctuation, all of which are proportional to the second derivative of the free energy. As pointed out earlier [29,30], it is unfortunate that the structural information contained in the pair correlation function, g_{ij}, is smeared in the integration process to obtain the Kirkwood–Buff parameter, G_{ij}, as

$$G_{ij} = \int_0^{\infty} 4\pi r^2 (g_{ij} - 1)\, \mathrm{d}r \tag{6}$$

Since the values of H_m^E(TBA) are available within ±0.05 kJ mol^{-1} in this concentration range [2], the values of TS_m^E(TBA) are calculated within ±0.15 kJ mol^{-1} and are plotted in Fig. 4 together with those of H_m^E(TBA). What can be deduced from Fig. 4 is as follows. The first TBA molecule dissolves in water with a large enthalpy gain and a larger entropy loss. This is consistent with a conventional interpretation as the "iceberg formation" or, in more recent terminology, the "structure enhancement of the solvent" [31–34]. As the concentration increases, both the enthalpy gain and the entropy loss become smaller. Namely, the solute–solute interaction is repulsive in terms of enthalpy and attractive in terms of entropy, as pointed out earlier [10]. Thus, in terms of enthalpy, it would be advantageous to place the second TBA molecule at an infinite distance from the first, where the effect of the structure enhancement due to the first is negligible and hence

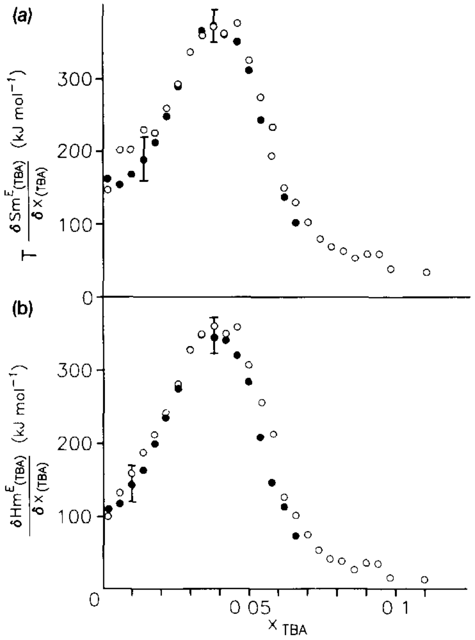

Fig. 5. Solute–solute interaction in terms of (a) entropy and (b) enthalpy. ○, 25.15 °C; ●, 30.00 °C.

the second one causes an almost equal enthalpy gain. In terms of entropy, on the other hand, the second one would tend to settle very close to the first with only a small loss in entropy, where the structure of the solvent water is already enhanced. In reality, since the latter entropy effect is stronger, the net result is that TBA molecules come closer to each other than in the random distribution. This is consistent with "hydrophobic interaction (attraction)" [11,34].

As the concentration of TBA increases, the solute–solute interaction acts progressively more strongly to about $x_{\mathrm{TBA}} \approx 0.04$, and thereupon diminishes rapidly. To display this behaviour more quantitatively, the derivatives $\delta H_{\mathrm{m}}^{\mathrm{E}}(\mathrm{TBA})/\delta x_{\mathrm{TBA}}$ and $\delta S_{\mathrm{m}}^{\mathrm{E}}(\mathrm{TBA})/\delta x_{\mathrm{TBA}}$ were evaluated for $\delta x_{\mathrm{TBA}} = 0.004$ and plotted in Fig. 5. Following the same argument given earlier [6], the latter derivative is a measure of the solute–solute interaction in terms of entropy. As shown in the figure, the behaviour of both derivatives resembles a heat capacity anomaly associated with a bulk phase transition of a pure solid. There has been a vast number of such heat capacity anomalies reported in literature, varying widely in size and shape. Aside from shape, the size of the C_{p} anomaly varies from 6 R for the antiferromagnetic ordering of $\mathrm{FeF_2}$ [35] and 1.5 R for the 102 K transition of $\mathrm{P_2Cl_{10}}$ [36] to 0.1 R for the 40 K transition and 0.01 R for the 17 K transition in biphenyl [37], to name but a few. It is important to note that, however subtle the transition may be, it involves a change in structure with a *long-range* order, and that

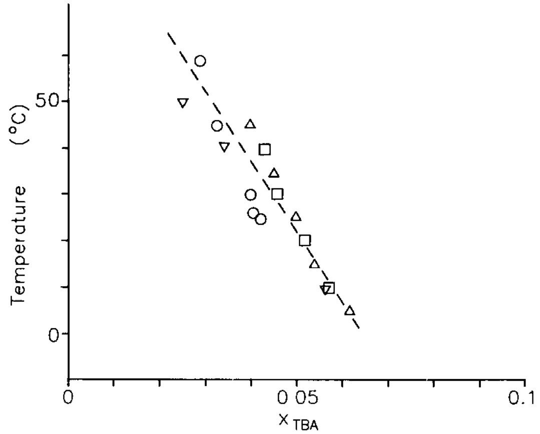

Fig. 6. Locus of maxima in various quantities proportional to the third derivative of the free energy. △, $\partial v_{TBA}/\partial x_{TBA}$, estimated using the data for v_{TBA} of ref. 28; □, partial molar expansibility [28]; ▽, partial molar heat capacity [38]; ○, solute–solute interaction in terms of enthalpy and entropy from this work and ref. 2.

its signature is an anomaly in the heat capacity that is proportional to the *second* derivative of the free energy.

Roux et al. have advanced the idea of "pseudo-phase transition" in aqueous solutions of *tert.*-butanol and 2-butoxyethanol, since there are anomalies in the partial molar heat capacity [7]. We point out that the partial molar heat capacity is the *third* derivative of the free energy. Turning back to Fig. 5, both the quantities of the ordinate are proportional to the *third* derivative of the free energy. As discussed above, the maxima in Fig. 5 mark a transition in the mixing scheme in this solution, or the "structure" of the solution. After all, the liquid state lacks a long-range order but retains a short- to medium-range order. It is thus interesting to note that the transition in the "structure" of this solution without a long-range order appears to be associated with an anomaly in the quantities that are proportional to the *third* derivative of the free energy. We therefore collected various quantities available in the literature that are proportional to the third derivative. The loci of the maxima in such quantities are plotted in Fig. 6. All these points appear to form a boundary, which happens to correspond to the expression of the type $TBA(H_2O)_n$ with $n = 20–25$. In view of the foregoing discussions, it seems unrealistic to claim [17,18] that the species of $TBA(H_2O)_n$ with a fixed value of n are present in the entire range below the boundary.

Above this boundary, the fact that $H_m^E(TBA)$ [2] and $V_m^E(TBA)$ [28] are almost zero indicates that, in terms of enthalpy and volume, TBA molecules in this mixture are in almost the same environment as they are in the pure liquid. Moreover, the concentration fluctuation, $N\langle(\Delta x_{TBA})^2\rangle$, shows a large maximum in this region [17–23]. All of these facts indicate clustering of TBA molecules and that the solution is close to a phase separation. This poses an interesting question as to the size of such clusters; not so large as to attain a spatial consistency as a bulk phase but large enough to have almost the same values in the partial molar enthalpy and the partial molar volume as those in the pure liquid.

ACKNOWLEDGEMENTS

We would like to thank Dr. M. Sakurai for providing us with the partial molar volume data. This research was supported by the Natural Sciences and Engineering Research Council of Canada in the form of an operating grant to Y.K. and a University Undergraduate Student Research Award to W.W.Y.S. One of us (T.Y.H.W.) thanks the governments of Canada and British Columbia for the Award of Challenge 89.

REFERENCES

1 Y. Koga, Can. J. Chem., 64 (1986) 206.
2 Y. Koga, Can. J. Chem., 66 (1988) 1187.
3 Y. Koga, Can. J. Chem., 66 (1988) 3171.
4 J. Kenttamaa, E. Tommila and M. Marti, Ann. Acad. Sci. Fenn. Ser. A2, 93 (1959) 2.
5 S. Westmeier, Chem. Technol., 29 (1977) 218.
6 W. Siu and Y. Koga, Can. J. Chem., 67 (1989) 671.
7 G. Roux, G. Perron and J.E. Desnoyers, J. Phys. Chem., 89 (1978) 966.
8 B.Y. Okamoto and R.H. Wood, J. Chem. Soc. Faraday Trans. 1, 74 (1978) 1990.
9 J.E. Desnoyers, G. Perron, L. Avedikian and J.-P. Morel, J. Solution Chem., 9 (1976) 631.
10 G. Perron and J.E. Desnoyers, J. Chem. Thermodyn., 13 (1981) 1105.
11 F. Franks, Faraday Symp. Chem. Soc., 17 (1982) 7.
12 J.E. Desnoyers, C. Ostiguy and G. Perron, J. Chem. Educ., 55 (1978) 137.
13 A.C. Brown and D.J.G. Ives, J. Chem. Soc., (1962) 1608.
14 J.H. Dymond and E.B. Smith, The Virial Coefficients of Pure Gases and Mixtures, Clarendon Press, Oxford, 1980, pp. 121, 208.
15 C.G. Boissonnas, Helv. Chim. Acta, 22 (1939) 541.
16 I. Prigogine and R. Defay, translated by D.H. Everett, Chemical Thermodynamics, Longman, London, 1965, p. 347.
17 K. Iwasaki and T. Fujiyama, J. Phys. Chem., 81 (1977) 1908.
18 K. Iwasaki and T. Fujiyama, J. Phys. Chem., 83 (1979) 463.
19 G.W. Euliss and C.M. Sorensen, J. Chem. Phys., 80 (1984) 4767.
20 M.F. Vuks and L.V. Shurapova, Opt. Commun., 11 (1972) 150.
21 N. Ito, T. Kato and T. Fujiyama, Bull. Chem. Soc. Jpn., 54 (1981) 2573.
22 Y. Koga, Chem. Phys. Lett., 111 (1984) 176.
23 K. Nishikawa, Y. Kodera and T. Iijima, J. Phys. Chem., 91 (1987) 3694.
24 J.G. Kirkwood and P. Buff, J. Chem. Phys., 19 (1951) 774.
25 A. Ben-Naim, J. Chem. Phys., 67 (1977) 4884.
26 K. Nishikawa, Chem. Phys. Lett., 132 (1986) 50.
27 M. Nakagawa, H. Inubushi and T. Moriyoshi, J. Chem. Thermodyn., 13 (1981) 171.
28 M. Sakurai, Bull. Chem. Soc. Jpn., 60 (1987) 1.

29 M.C.A. Donkersloot, J. Solution Chem., 8 (1979) 293.
30 A.L. Zaitsev, V.E. Petrenko and Yu. M. Kessler, J. Solution Chem., 18 (1989) 115.
31 H. Uedaira and J. Kida, Nippon Kagaku Kaishi, (1982) 539.
32 T.M. Bender and R. Pecora, J. Phys. Chem., 90 (1986) 1700.
33 K. Nakanishi, K. Ikari, S. Okazaki and H. Touhara, J. Chem. Phys., 80 (1984) 1656.
34 H. Tanaka, K. Nakanishi and H. Touhara, J. Chem. Phys., 81 (1984) 4065.
35 J.W. Stout and E. Catalano, J. Chem. Phys., 23 (1955) 2013.
36 H. Chihara, M. Nakamura and K. Masukane, Bull. Chem. Soc. Jpn., 46 (1973) 97.
37 K. Saito, T. Atake and H. Chihara, Bull. Chem. Soc. Jpn., 61 (1988) 679.
38 C. De Visser, G. Perron and J.E. Desnoyers, Can. J. Chem., 55 (1977) 856.