

**VAPOUR-LIQUID EQUILIBRIUM. THE EFFECT OF TEMPERATURE  
ON THE EQUILIBRIUM VAPOUR PHASE COMPOSITION  
AND ON THE AZEOTROPIC POINT COMPOSITION**

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Received July 13, 1990

Accepted September 15, 1990

On the basis of analysis of calorimetric data, it is shown that the tert-butyl alcohol(1)–water(2) system exhibits the non-monotonous dependence of the equilibrium vapour phase composition on temperature which is reflected in the non-monotonous dependence of azeotropic composition on temperature. This behaviour is conditioned primarily by the fact that the molar heats of vaporization of both the substances have the same value at the temperature of 57°C. From the values of heats of vaporization of C<sub>3</sub> and C<sub>4</sub> alcohols and water it is evident that the analogous behaviour occurs also in aqueous systems of these alcohols at common temperatures.

From the analysis of experimental vapour–liquid equilibrium data in the tert-butyl alcohol(1)–water(2) system (hereinafter we shall use the designation TB–W), it was not evident whether the concentration of more volatile component in the vapour phase  $y_1 = y_1(T, x_1 = \text{const.})$  increases or decreases with temperature, and therefore a more detailed thermodynamic analysis of quantity  $(\partial y_1 / \partial T)_{x_1}$  was carried out.

**THEORETICAL**

In case of the real behaviour of the liquid phase on considering the ideal behaviour of the vapour phase, the relation<sup>1</sup> holds for a binary system

$$p = x_1 \gamma_1 p_1^0 + x_2 \gamma_2 p_2^0, \quad (1)$$

$$y_1 = x_1 \gamma_1 p_1^0 / p = x_1 \gamma_1 p_1^0 / (x_1 \gamma_1 p_1^0 + x_2 \gamma_2 p_2^0), \quad (2)$$

where  $x_i$  and  $y_i$  denote the molar fraction of the  $i$ -th component in the liquid and vapour phase, respectively,  $p$  and  $p_i^0$  the total pressure and the saturated vapour pressure of the  $i$ -th component, and  $\gamma_i$  the activity coefficient of the  $i$ -th component in the liquid phase.

On differentiating Eq. (2) with respect to temperature (at constant  $x_1$ ) we get

$$\left(\frac{\partial y_1}{\partial T}\right)_{x_1} = y_1 y_2 \left[ \frac{\partial \ln p_1^0}{\partial T} - \frac{\partial \ln p_2^0}{\partial T} + \frac{\partial \ln \gamma_1}{\partial T} - \frac{\partial \ln \gamma_2}{\partial T} \right] = \quad (3a)$$

$$= \frac{y_1 y_2}{RT^2} [\Delta H_{v_1} - \Delta H_{v_2} + L_2 - L_1], \quad (3b)$$

where  $\Delta H_{v_i}$  represents the heat of vaporization and  $L_i = \bar{H}_i - H_i^0$  the differential heat of mixing of the  $i$ -th component. It is evident from Eq. (3b) that the sign at  $(\partial y_1/\partial T)_{x_1}$  is determined by the sign of term in square brackets.

### RESULTS AND DISCUSSION

The values of heats of vaporization of some alcohols<sup>2</sup> and water<sup>3</sup> as a function of temperature are presented in Fig. 1. It is evident from this dependence that at the temperature of  $\approx 57^\circ\text{C}$  (not taking account of the differential heats of solution  $L_i$ ), it will hold  $(\partial y_1/\partial T)_{x_1} = 0$  in the TB(1)-W(2) system, and the mole fraction of

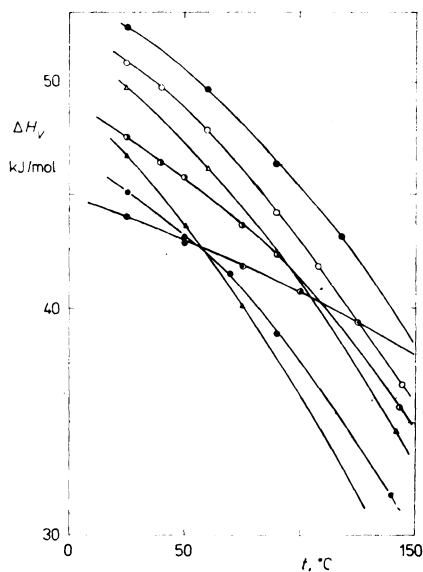


FIG. 1

Dependence of heat of vaporization of water and some alcohols on temperature.  $\odot$   $\text{H}_2\text{O}$ ;  $\bullet$  1-propanol;  $\odot$  2-propanol;  $\bullet$  1-butanol;  $\triangle$  sec-butyl alcohol;  $\circ$  2-methyl-1-propanol;  $\blacktriangle$  tert-butyl alcohol

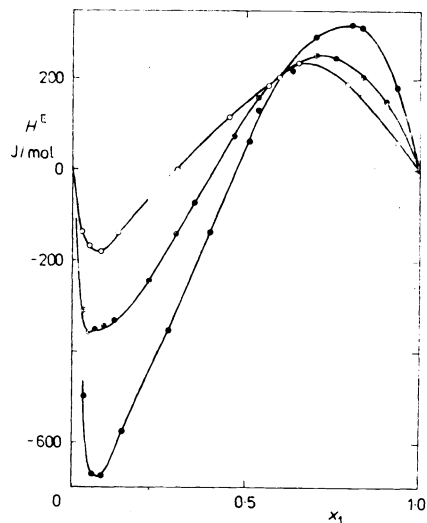


FIG. 2

Dependence of heat of mixing on composition for the tert-butyl alcohol(1)-water(2) mixture.  $\bullet$   $25^\circ\text{C}$ ;  $\odot$   $50^\circ\text{C}$ ;  $\circ$   $70^\circ\text{C}$

components (in the vapour phase) will acquire extreme values at this temperature (for TB(1) it will be maximum and for W(2) minimum).

To judge the value of  $(\partial y_1/\partial T)_{x_1}$  more accurately, it is necessary to take account of the value of  $(L_2 - L_1)$  for which holds the relation

$$L_2 - L_1 = -(\partial H^E/\partial x_1)_{T,p}. \quad (4)$$

To determine the effect of term  $L_2 - L_1$ , the values of  $\Delta H^E/\Delta x_1$  were determined on the basis of experimental data on heat of mixing<sup>4</sup> in the TB(1)-W(2) system (and assigned to the mean values of mole fraction) by which quantity  $(\partial H^E/\partial x_1)_{T,p}$  or  $L_1 - L_2$  is approximated. Considering that  $H^E(x_1)$  at a constant temperature is of an S-shape – see Fig. 2 – quantity  $\Delta H^E/\Delta x_1$  has approximately parabolic course – see Fig. 3.

More detailed conclusions on the sign of  $(\partial y_1/\partial T)_{x_1}$  in the TB-W system can be drawn from Fig. 3 and from the values read in Fig. 1. At the temperature of 25°C, the difference in heats of vaporization ( $\Delta H_{v_1} - \Delta H_{v_2} = 2.7$  kJ/mol) predominates in the whole concentration range over the difference in differential heats of mixing (the lowest value of  $L_2 - L_1 \approx -1.9$  kJ/mol). Therefore,  $(\partial y_1/\partial T)_{x_1} > 0$  holds at this temperature in the whole concentration range. On the contrary at the temperature of 50°C, the difference in heats of vaporization is substantially lower ( $\Delta H_{v_1} - \Delta H_{v_2} \approx 0.65$  kJ/mol), and the condition  $(\partial y_1/\partial T)_{x_1} > 0$  holds only outside the concentration range  $x_1 = 0.10$  to  $x_1 = 0.65$  (approximately). At the temperature of 70°C ( $\Delta H_{v_1} - \Delta H_{v_2} \approx -1.2$  kJ/mol),  $(\partial y_1/\partial T)_{x_1} > 0$  will hold only outside the concentration interval  $x_1 = 0.03$  to 0.93.

This analysis supports the suspicion that the dependence  $y_1 = y_1(T, x_1 = \text{const.})$  is non-monotonous, which cannot be practically revealed on the basis of measuring

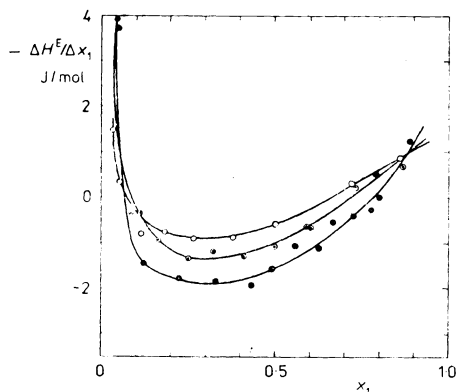


FIG. 3

Difference of partial molar heats of mixing  $L_2 - L_1$  in the tert-butyl alcohol(1)-water(2) system as a function of composition. ● 25°C; ○ 50°C; □ 70°C

the equilibrium data. For the composition of  $x_1 = 0.5$  and for the temperature  $t = 25^\circ\text{C}$ , the value of  $(\partial y_1/\partial T)_{x_1=0.5} \approx 3.3 \cdot 10^{-4}$  whereas at  $t = 70^\circ\text{C}$ , on the contrary,  $(\partial y_1/\partial T)_{x_1=0.5} \approx -3.8 \cdot 10^{-4}$ . However, neither this fact accounts for the great differences in the experimental data. In the Gmehling collection<sup>5</sup>, the values of  $y_1$  (at  $x_1 = 0.5$ ) reported by different authors lie, for the temperature range of 25 to 35°C, within the range of  $y_1 = 0.52$  to  $y_1 = 0.57$ .

The extreme in the dependence  $y_1 = y_1(T, x_1 = \text{const.})$  is reflected also in the dependence of azeotropic composition on temperature. For this case, the very similar relation (see Appendix) holds

$$\left(\frac{\partial x_1}{\partial T}\right)_{\text{az}} = \frac{(x_1 x_2)_{\text{az}}}{RT^2[1 - (\partial y_1/\partial x_1)_{\text{az}}]} [\Delta H_{V_1} - \Delta H_{V_2} + L_2 - L_1]_{\text{az}}. \quad (5)$$

In the TB(1)-W(2) system holds  $x_{1,\text{az}} \approx 0.6$  and  $(\partial y_1/\partial x_1)_{\text{az}} < 1$ , and consequently the value of  $(\partial x_1/\partial T)_{\text{az}}$  will be positive at the temperature of 25°C and negative at the temperature of 70°C. At the temperature around 50°C,  $x_1$  will reach its maximum at the azeotropic point. With this and similar systems it is therefore not possible to apply the linear dependence of the azeotropic point composition on temperature which is usually recommended in literature and which is the consequence of the assumption that the sign of  $(\Delta H_{V_1} - \Delta H_{V_2})$  is dominating and independent of temperature<sup>6</sup>.

#### APPENDIX

In a binary system at constant temperature,  $y_1 = x_1$  and  $(\partial P/\partial x_1)_T = 0$  hold at the azeotropic point.

From the relation

$$P y_i = \gamma_i x_i P_i^0, \quad (i = 1, 2) \quad (A1)$$

follows

$$(\gamma_1) P_1^0 = (\gamma_2) P_2^0 \quad (\text{azeotropic point}). \quad (A2)$$

Taking logarithm of Eq. (A2) and subsequent differentiating the relation  $(\gamma_i = \gamma_i(T, x_1))$  with respect to  $T$ , we obtain

$$\begin{aligned} \left(\frac{\partial \ln \gamma_1}{\partial T}\right)_{x_1} + \left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,\text{az}} \left(\frac{\partial x_1}{\partial T}\right)_{\text{az}} + \frac{\partial \ln P_1^0}{\partial T} = \\ = \left(\frac{\partial \ln \gamma_2}{\partial T}\right)_{x_1} + \left(\frac{\partial \ln \gamma_2}{\partial x_1}\right)_{T,\text{az}} \left(\frac{\partial x_1}{\partial T}\right)_{\text{az}} + \frac{\partial \ln P_2^0}{\partial T}. \end{aligned} \quad (A3)$$

Before rearranging this relation, we express the derivatives  $(\partial \ln \gamma_i / \partial x_1)_T$  from Eq. (A1)

$$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_T = \frac{1}{P} \left(\frac{\partial P}{\partial x_1}\right)_T + \frac{1}{y_1} \left(\frac{\partial y_1}{\partial x_1}\right)_T - \frac{1}{x_1}, \quad (A4a)$$

$$\left(\frac{\partial \ln \gamma_2}{\partial x_1}\right)_T = \frac{1}{P} \left(\frac{\partial P}{\partial x_1}\right)_T - \frac{1}{y_2} \left(\frac{\partial y_1}{\partial x_1}\right)_T + \frac{1}{x_2}. \quad (A4b)$$

Considering that  $y_i = x_i$  and  $(\partial P / \partial x_1)_T = 0$  hold at the azeotropic point, we get from Eq. (A4)

$$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,az} = \frac{1}{x_1} \left[ \left(\frac{\partial y_1}{\partial x_1}\right)_T - 1 \right], \quad (A5a)$$

$$\left(\frac{\partial \ln \gamma_2}{\partial x_1}\right)_{T,az} = -\frac{1}{x_2} \left[ \left(\frac{\partial y_1}{\partial x_1}\right)_T - 1 \right]. \quad (A5b)$$

By combining Eqs (A3) and (A5), we obtain after rearranging

$$\left(\frac{\partial x_1}{\partial T}\right)_{az} = \frac{x_{1,az} x_{2,az}}{RT^2} \frac{[\Delta H_{V_1} - \Delta H_{V_2} + L_2 - L_1]_{az}}{[1 - (\partial y_1 / \partial x_1)_{T,az}]}. \quad (A6)$$

## REFERENCES

1. Hála E., Pick J., Fried V., Vilím O.: *Vapour-Liquid Equilibrium*. Pergamon Press, Oxford 1967
2. Majer V., Svoboda V.: *Enthalpies of Vaporization of Organic Compounds*; IUPAC Chem. Data Ser. No. 32. Blackwell, Oxford 1988.
3. Vargaftik N. B.: *Tables on the Thermophysical Properties of Liquids and Gases*. Wiley, New York 1975.
4. Christensen J., Hanks R. W., Izath R. M.: *Handbook of Heats of Mixing*. Wiley, New York 1982.
5. Gmehling J., Onken U., Arlt W.: *Vapour-Liquid Equilibrium Data Collection*, Dechema Chemistry Data Series. Dechema, Frankfurt 1977-1984.
6. Malesinski W.: *Azeotropy and Other Theoretical Problems of Vapour-Liquid Equilibrium*. Wiley, London 1965.

Translated by J. Linek.