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The phase diagram of cyclohexane–methanol: a challenge in chemical education[1]

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Abstract

Cloud point and cooling curve studies of the cyclohexane–methanol system were ideally suited as a laboratory exercise for a physical chemistry curriculum. Within 3–4 h, students can obtain a sufficient number of relatively precise experimental data (temperature vs. mol fraction of methanol) to construct the major part of the solid–liquid phase diagram.

The experimental procedure is based on three different methods: (1) cloud points were detected using an H–Ne laser; (2) temperatures of the methanol-rich part below the monotectic were taken when the first crystals of cyclohexane become visible; and (3) cooling curves were recorded in order to determine the melting point of C_6H_{12} and the monotectic temperature.

The results of the system exhibiting an upper critical solution temperature, UCST, agreed reasonably with the most reliable data presently available. Assuming a tetrameric methanol species, the experimental T–x data of the freezing-point depression and the sub-monotectic curve were fitted to a sub-regular model with three adjustable parameters for the liquid phase. However, only an extended Ising model agreed with the experimental curve near the critical temperature. © 1998 Elsevier Science B.V.

Keywords: Cyclohexane; Partial miscibility; Tetrameric methanol

1. Introduction

Cyclohexane–methanol mixtures separate into two liquids below an upper critical solution temperature (UCST). Reasonably accurate experimental data (T, the temperature vs. mol fraction of methanol, x) of these phase-transitions can be obtained by cloud and clear points measurements using a simple laser technique. In fact, the determination of the respective coexistence curve was proposed as an exercise in physical chemistry [1]. With comparatively few additional data, the major part of the C_6H_{12}–CH_3OH solid–liquid phase diagram can be constructed. A modest equipment suffices to complete the experimental information on this system. Cooling curves were taken to determine the melting point of cyclohexane and the monotectic temperature. The crystallization temperatures in the sub-monotectic region are directly observable.

Recently, the phase behaviour of the cyclohexane–methanol system was comprehensively reviewed in a volume of the IUPAC Solubility Data Series [2]. The evaluators demonstrated that the whole region of demixing is best described by the modern theory of critical solution behaviour. No attempt was made,

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however, to apply a common (classical) model to the freezing point depression and the sub-monotectic crystallization curves of cyclohexane, i.e. to data far from the UCST. In this paper, it is shown that an essentially correct phase diagram of the C_6H_{12}–CH_3OH system can be derived from comparatively crude measurements carried out by students in a teaching laboratory. Moreover, these results lead to a physically meaningful description of the freezing-point depression and the sub-monotectic curves of cyclohexane.

2. Experimental

2.1. Apparatus for cloud-point measurements

The cloud points were detected by an He–Ne laser (632.8 nm, 2 mW; ES-Lasersystem, Hechlingen, Germany). The laser beam passing through the liquid mixture is focused on a screen. When the temperature of mixing/demixing is reached, the laser point on the screen disappears/reappears. The experimental setup is a simplified version of an apparatus used for research [3].

2.2. Apparatus for thermal analysis

In order to determine the melting point of C_6H_{12} and the monotectic temperature, the cooling curves were recorded with a simple apparatus equipped with a thermostatting jacket. The temperature of the ethanol–water cooling bath was controlled by a cryostat (Haake Thermostate F3, Germany). The same apparatus was used to find the sub-monotectic liquidus; the respective temperatures were taken when the first crystals of cyclohexane became visible.

2.3. Reagents

The starting materials used in this study were reagent grade cyclohexane with a maximum impurity of 0.01 wt% (Fa. Fluka Nr. 28940) and methanol (Fa. Fluka Nr. 65543).

3. Results and discussion

Typical results obtained by students in different laboratory sessions are listed in Table 1.

3.1. Partial miscibility

The data obtained in the region of demixing were fitted smoothly to a curve ‘by eye’, as suggested by Bale and Pekton [4]. For this task, the CurveExpert 1.3 system was employed. It has a built-in facility that, provided with the respective data files, sifts through possible curve fits and selects the best [5]. A polynomial of 6th degree seemed to accommodate the experimental data reasonably well and was used to generate a list of tie lines connecting the liquid phases (Table 2) as well as to calculate the upper critical-solution temperature, UCST, resulting in T^c= 318.71 K. The adjustable parameters of the extended Ising model [2], according to Eqs. (2) and (3), were then calculated from the $T{-}x^l{-}x^h$ data of the smoothed coexistence curve. For the simple Ising

Table 1
Experimental temperature vs. mol fraction data of the cyclohexane–methanol system

x_{CH_3OH}	T/K	Remark	x_{CH_3OH}	T/K	Remark
0.0000	278.60	melting point	0.0945	290.75	cloud point
0.1494	302.55	cloud point	0.2258	311.65	cloud point
0.2472	312.85	cloud point	0.2500	276.15	monotectic
0.3964	318.15	cloud point	0.5000	276.15	monotectic
0.5228	318.65	cloud point	0.5680	318.55	cloud point
0.6440	317.55	cloud point	0.7242	313.85	cloud point
0.8402	293.95	cloud point	0.8598	287.75	cloud point
0.9000	272.15	sub-monotectic	0.9000	272.80	sub-monotectic
0.9198	265.35	sub-monotectic	0.9250	263.60	sub-monotectic
0.9330	259.90	sub-monotectic			

Table 2
Isothermal tie lines generated by CurveExpert from 6th degree polynomial

x^l (low)	x^h (high)	T/K	x^l (low)	x^h (high)	T/K
0.0498	0.8873	276.15 [a]	0.2820	0.7064	315.00
0.0600	0.8789	280.00	0.3068	0.6882	316.00
0.0748	0.8668	285.00	0.3405	0.6635	317.00
0.0916	0.8531	290.00	0.3955	0.6233	318.00
0.1114	0.8372	295.00	0.4127	0.6107	318.20
0.1353	0.8182	300.00	0.4350	0.5934	318.40
0.1658	0.7943	305.00	0.4686	0.5666	318.60
0.2084	0.7615	310.00			

[a] Monotectic temperature.

model, the bracketed terms in Eqs. (2) and (3) become unity and vanish, respectively.

$$\theta = 1 - T/T^c \tag{1}$$

$$x^h - x^l = B_1\theta^{0.329}(1 + B_2\theta^{0.5} + B_3\theta) \tag{2}$$

$$x^h + x^l = 2x^c + \theta(A_1 + A_2\theta^{0.39}) \tag{3}$$

The parameters of Eqs. (2) and (3) were found to be as follows: B_1=1.6857, B_2=0.7187, B_3=−2.3157, A_1=−2.9899, A_2=5.2475.The critical value of x is x^c=0.5117.

The experimental data of this work, as well as that of Hradetzky and Bittrich [2] fall nicely on the miscibility curve calculated with these constants (see Fig. 1). Deviations from the recommended curve [2] can only be seen on the enlarged scales of Fig. 2.

3.2. Freezing-point depression and sub-monotectic range

Whereas the melting point of cyclohexane, the monotectic temperature and the monotectic composition are comparatively well known, only the data of Hradetzky and Bittrich are available for the freezing-point depression curve [6]. An ideal model should suffice to describe this curve, because even at the monotectic composition only a few mole percent of methanol are dissolved in cyclohexane. However, with cyclohexane and monomeric methanol as components a much steeper line was calculated (see Fig. 2(A)). A better agreement with the experimental data is achieved when tetrameric $(CH_3OH)_4$ is assumed to be the dominating methanol species [7]. In fact, the presence of this tetramer is also supported by NMR measurements [8]. Thus, the mol fraction x_{tet} was defined by the following equations:

$$x_{tet} = \frac{n_{CH_3OH}/4}{n_{C_6H_{12}} + n_{CH_3OH}/4}; \quad x = \frac{n_{CH_3OH}}{n_{C_6H_{12}} + n_{CH_3OH}} \tag{4}$$

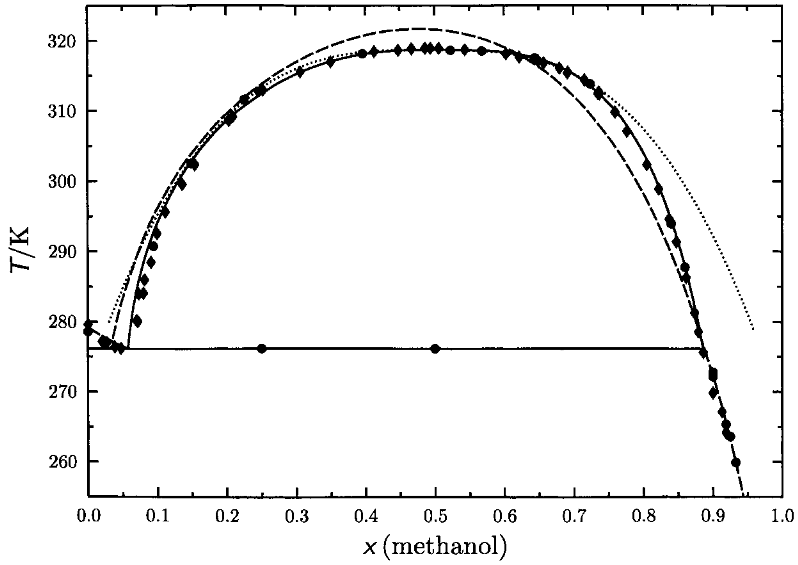

Fig. 1. Phase diagram: Cyclohexane–methanol. (●) This work, (◆) Hradetzky and Bittrich [6]; (· · ·) simple Ising model; (———) extended Ising model; and (- - -) classical three-parameter sub-regular model with tetrameric methanol.

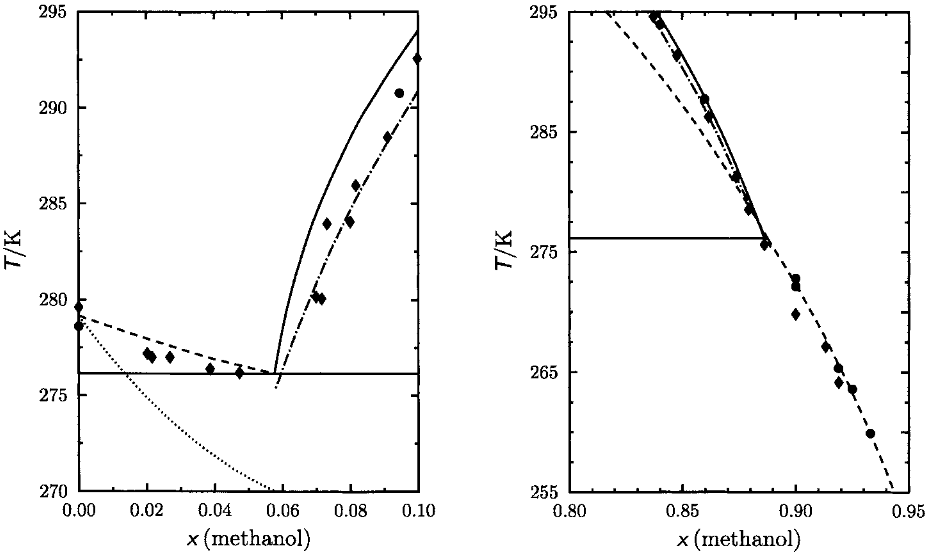

Fig. 2. C_6H_{12}–CH_3OH: (A) freezing-point depression; and (B) sub-monotectic crystallization. (●) This work; (◆) Hradetzky and Bittrich [6]; (———) extended Ising model; (- - -) three-parameter sub-regular model with tetrameric methanol (Eq. (6));(– · –) recommended by [2]; (· · ·) three-parameter sub-regular model with monomeric methanol.

$$x_{\text{tet}} = \frac{x}{4-3x}; \quad x = \frac{4x_{\text{tet}}}{3x_{\text{tet}}+1} \tag{5}$$

The five experimental data pairs of he sub-monotectic range (Table 1) and the calculated mol fraction at the intersection of the coexistence curve with the observed monotectic temperature (Table 2) were used to establish the three adjustable parameters of a sub-regular mixing model. For the equilibrium condition in the sub-monotectic region, we have

$$\mu^{*,s}_{C_6H_{12}} = \mu^{*,\ell}_{C_6H_{12}} + RT\ln(1-x_{\text{tet}}) + x^2_{\text{tet}}[H_1 - TS_1 + H_2(3-4x_{\text{tet}})] \tag{6}$$

The difference of the chemical potentials in Eq. (6) can be approximated by Eq. (7)

$$\mu^{*,\ell}_{C_6H_{12}} - \mu^{*,s}_{C_6H_{12}} = \Delta_{\text{fus}}H_{C_6H_{12}} - T\Delta_{\text{fus}}S_{C_6H_{12}} \tag{7}$$

With $\Delta_{\text{fus}}H_{C_6H_{12}} = 2680\ \text{J mol}^{-1}$ and $\Delta_{\text{fus}}S_{C_6H_{12}} = 9.6\ \text{J mol}^{-1}\ \text{K}^{-1}$, the three remaining quantities were evaluated from Eqs. (6) and (7)

$$H_1/R = 4969\,\text{K},\ S_1/R = 16.47 \quad \text{and } H_2/R = 736\,\text{K}$$

As demonstrated by Fig. 2, the freezing-point depression curve is quite sensitive to the degree of CH_3OH association. However, sub-monotectic curves coincide, whether the presence of monomeric or that of tetrameric methanol is implied. In Fig. 1, the calculated curves are compared with the experimental results of this work and the most probable reliable data from the literature [2,6].

3.3. Critical point

Whereas the freezing-point depression and the sub-monotectic curve are nicely reproduced by the sub-regular model selected, the latter fails in the neighbourhood of the UCST. This is to be expected, because any model resulting in an equation that can be expanded as a Taylor series about the critical point will lead to Eq. (8) with β=1/2 (see [9] Eq. 16.16.6).

$$(x^h - x^l) \propto |T^c - T|^\beta \tag{8}$$

The generally accepted experimental value of partially miscible liquids is β=0.329. As shown by Fig. 3, the data obtained in the neighbourhood of the UCST fall indeed closer on the simple Ising model than on the Taylor expansion. On the other hand, Fig. 1 indicates that outside the critical region

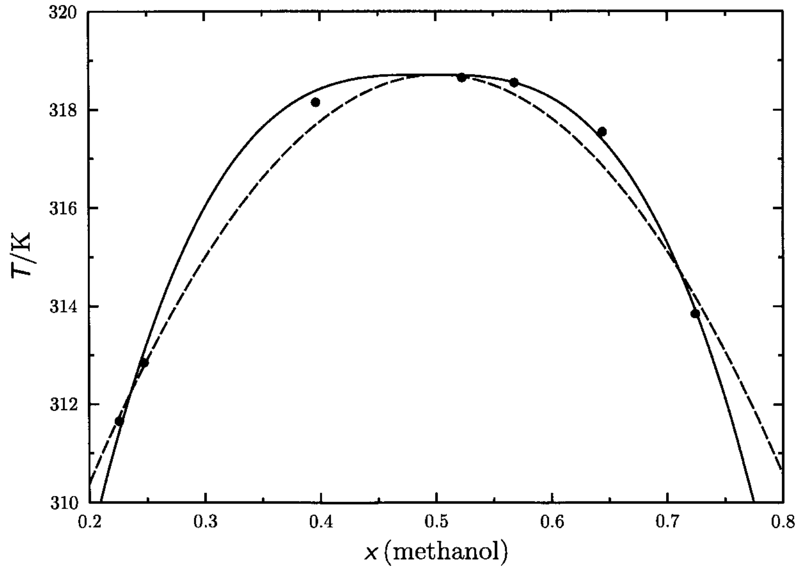

Fig. 3. Partial-miscibility diagram C_6H_{12}–CH_3OH: Comparison of Taylor expansion and Ising model. (●) This work; (———) $\beta=0.329$; (- - -) $\beta=1/2$.

($\theta>0.05$) the experimental data start to deviate dramatically from the former.

4. Conclusions

The results of cloud points and cooling curves, obtained in a teaching laboratory, were used to construct the solid–liquid phase diagram of the C_6H_{12}–CH_3OH system. The preliminary thermodynamic analysis of the admittedly crude data revealed the following phase theoretical subtleties.

1. Under the conditions of this work methanol is presumably forming a tetramer (Fig. 2(A)).
2. As shown in Figs. 1 and 3, any model based on analytic equations of state fails in the region of the critical point.
3. The simple Ising model ($\beta=0.329$ in Eq. (8)) is valid in a very limited range only (Fig. 1).

For a definitive thermodynamic analysis of the complete vapour-liquid–solid phase diagram a powerful Gibbs energy minimizer such as ChemSage [10] is needed, because all data available should be simultaneously evaluated. This work is in progress [7].

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