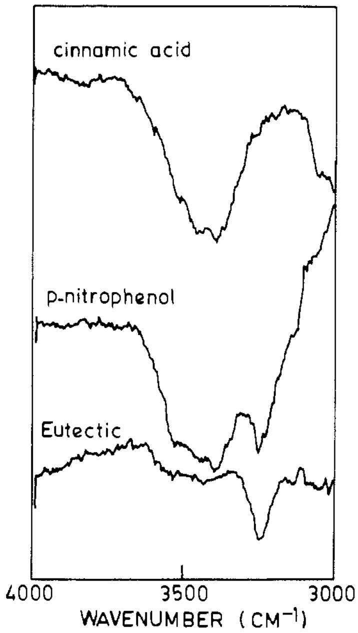

Figure 2. Infrared spectra of *p*-nitrophenol-cinnamic acid eutectic, *p*-nitrophenol, and cinnamic acid.

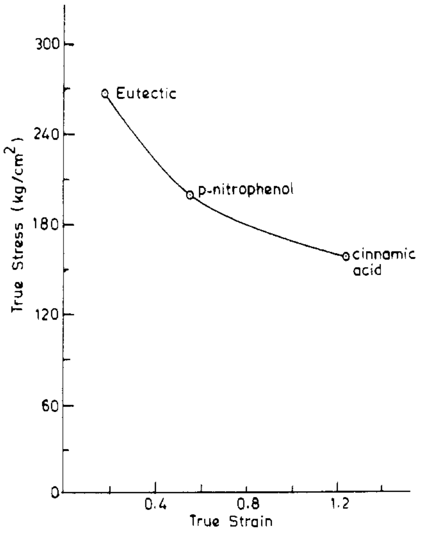

Figure 3. Stress-strain variation.

tructure is changed completely. The flat crystal surfaces of CA disappear and it becomes microcrystalline.

During the solidification process, the molecules lose rotational, positional, and configurational entropy, so that their arrangement at the liquid-solid interface may be just as important as the number of molecules present. This in turn implies that molecular crystals usually have high entropies of melting and according to theories of interface morphology, higher entropies of melting can be associated with an atomically flat crystal face. Jackson (*6*) has presented a statistical model in which the interface roughness is defined in terms of a parameter α, which is given by

$$\alpha = \xi \frac{\Delta_f H}{RT_m} \tag{8}$$

where ξ is a geometrical coefficient which generally lies between $^1/_2$ and 1. When $\xi = 1$, flat crystal surfaces are essential with $\alpha > 2$. In the present case, $\alpha = 23.4$, which shows that surface nucleation theory (*7*) holds good in the present eutectic system.

In order to assess the regularity of structure and its effect on material property, the compressive strengths of the eutectic and the components have been measured. Compressive strength measurements show that the eutectic has the highest strength as compared to the components. This further confirms the regularity of structure and association of molecules in the eutectic. In Figure 3, the stress-strain relationship is given, which shows that the eutectic has the highest stress even at a lower strain.

Acknowledgment

We are thankful to Prof. S. C. Tripathi, Head, Chemistry Department, for providing laboratory facilities.

Registry No. CA, 621-82-9; pNP, 100-02-7.

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Liquid–Liquid Phase Equilibria in the Propylene Carbonate + Methyl Isobutyl Ketone + Water System

Nandani Rajapakse, Harmon L. Finston, and Vojtech Fried*
Chemistry Department, The City University of New York, Brooklyn College, Brooklyn, New York 11210

The mutual solubility of propylene carbonate + methyl isobutyl ketone + water was studied at different temperatures. The temperature effect upon solubility is relatively small.

Introduction

Propylene carbonate (4-methyl-1,3-dioxalan-2-one) is a widely used solvent in extraction and in electrochemical studies (*1*–*7*). The problem of applying propylene carbonate in industrial processes is its large solubility in water. The purpose of this work

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Table I. Solubility Data for the Propylene Carbonate + Methyl Isobutyl Ketone + Water System at 30 °C

weight percent			weight percent		
PC	MIBK	water	PC	MIBK	water
0.00	97.00	3.00	0.00	1.60	98.40
9.81	86.90	3.29	0.21	1.69	98.10
23.20	73.20	3.60	0.69	1.71	97.60
48.00	47.50	4.50	1.73	1.77	96.50
72.00	21.20	6.80	5.22	1.77	93.00
82.90	9.68	7.42	12.52	1.38	86.10
91.60	0.00	8.40	21.90	0.00	78.10

Table II. Solubility Data for the Propylene Carbonate + Methyl Isobutyl Ketone + Water System at 50 °C

weight percent			weight percent		
PC	MIBK	water	PC	MIBK	water
0.00	95.60	4.40	0.00	1.70	98.30
11.00	84.20	4.80	0.23	1.77	98.00
26.60	68.50	4.90	0.66	1.84	97.50
46.40	47.70	5.90	1.75	1.85	96.40
68.40	23.00	8.60	5.47	1.83	92.70
80.20	8.80	11.00	13.32	1.48	85.20
86.60	0.00	13.40	26.30	0.00	73.70

was to investigate the possibility of recovering propylene carbonate from aqueous solutions by using methyl isobutyl ketone as an extractive solvent.

Experimental Section

Propylene carbonate, an MCB product of relatively high purity (98% by GC), was further purified by repeated low-pressure distillation. Baker analytic reagent grade methyl isobutyl ketone was further purified by distillation. Twice-distilled deionized water was used in the study. The physical properties of the purified products were in good agreement with the literature values, given in parentheses. Propylene carbonate: d_4^{25} = 1.200 g cm^{-3} ⟨1.190–1.203 g cm^{-3}⟩; nbp 241.9 °C ⟨241.7–242 °C⟩; mp −50.2 °C ⟨−48–50 °C⟩ (*8–11*). Methyl isobutyl ketone: d_4^{20} = 0.8012 g cm^{-3} (0.801 g cm^{-3}); nbp = 117.2 °C ⟨117–118 °C⟩ (*12*, *13*). Water: d^{30} = 0.9957 g cm^{-3} (0.99567 g cm^{-3}) (*14*).

Double-stem pycnometers, of approximately 25 cm^3, were used for the density measurements. Buoyancy corrections were applied in the density evaluation. The error caused by evaporation of the samples during the measurement is estimated to be small and was ignored. The accuracy of the density measurement is estimated to be better than $\pm 1.0 \times 10^{-4}$ g cm^3.

The three-component liquid–liquid phase diagrams, at 30 and 50 °C, were obtained by titrating methyl isobutyl ketone + propylene carbonate solutions of different compositions with water and water with methyl isobutyl ketone + propylene carbonate solutions of different composition. Microburets were used for the titration. The turbidity point was found to be reproducible within one very small drop (0.015 cm^3). The titration flask was equipped with a water jacket. Water flowing from a constant temperature heat bath through the jacket kept the temperature during the titration fixed within ±0.05 °C. The overall accuracy of the measurement is estimated to be better than ±0.3 wt %. The lever rule method was employed to obtain the tie lines. The accuracy is about ±2%.

Results and Discussion

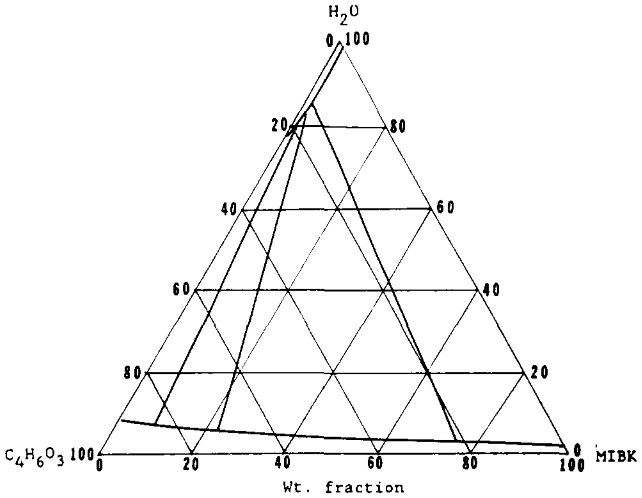

Figure 1. Solubility diagram for the propylene carbonate + methyl isobutyl ketone + water system at 30 °C.

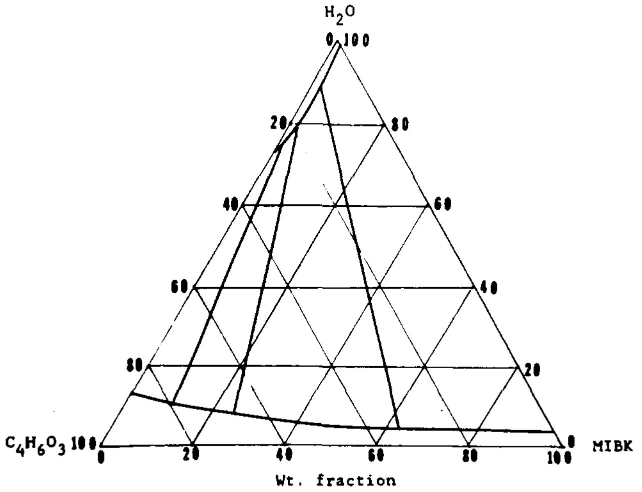

Figure 2. Solubility diagram for the propylene carbonate + methyl isobutyl ketone + water system at 50 °C.

Table III. Composition of the Two Equilibrium Phases for the MIBK + Water + PC System at 30 °C

water phase, wt %			MIBK phase, wt %		
water	PC	MIBK	water	PC	MIBK
85.5	13.0	1.5	3.0	22.5	74.5
84.7	14.0	1.3	6.0	71.0	23.0
83.8	15.0	1.2	7.0	84.0	9.0

Table IV. Composition of the Two Equilibrium Phases for the MIBK + Water + PC System at 50 °C

water phase, wt %			MIBK phase, wt %		
water	PC	MIBK	water	PC	MIBK
89.5	8.5	2.0	5.0	34.0	61.0
80.0	18.5	1.5	8.0	67.0	25.0
75.0	24.5	0.5	10.5	78.5	11.0

The liquid–liquid solubility data and the solubility diagrams for the propylene carbonate (PC) + methyl isobutyl ketone (MIBK) + water system, at 30 and 50 °C, are shown in Tables I and II and in Figures 1 and 2, respectively. The estimated compositions of the equilibrium phases at the two temperatures are given in Tables III and IV. The measured data indicate that as the temperature increases the solubility increases. The solubility increase with temperature is very small and high temperatures are required to achieve a homogeneous phase.

From the data collected in this study, we conclude that methyl isobutyl ketone is not an effective solvent for the extraction of propylene carbonate from aqueous solutions.

Registry No. MIBK, 108-10-1; PC, 108-32-7.

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Excess Enthalpies for the Ternary Systems 1-Propanol–Acetonitrile–Benzene and 2-Propanol–Acetonitrile–Benzene at 25 °C

Kazuhiro Tamura and Isamu Nagata*

Department of Chemical Engineering, Kanazawa University, Kanazawa 920, Japan

Excess enthalpies for the ternary systems 1-propanol–acetonitrile–benzene and 2-propanol–acetonitrile–benzene and for the constituent binaries 1-propanol–acetonitrile and 2-propanol–acetonitrile were measured at 25 °C by an isothermal dilution calorimeter. The experimental data were correlated by means of the association model of Nagata and Tamura, based upon mole fraction statistics.

Introduction

As part of continuing studies of excess enthalpies for binary and ternary mixtures containing an alcohol and acetonitrile, excess enthalpies of mixtures formed by acetonitrile with methanol and ethanol have been previously reported (*1*, *2*). In this paper, excess enthalpies at 25 °C for the binary systems 1-propanol–acetonitrile and 2-propanol–acetonitrile and for the ternary systems 1-propanol–acetonitrile–benzene and 2-propanol–acetonitrile–benzene are presented. A comparison is made between the experimental results for the ternary systems and those predicted by the association model proposed by Nagata and Tamura (*1*–*3*). Excess enthalpies at 25 °C for the five binary systems constituting the ternary systems had been previously reported, namely, 1-propanol–acetonitrile (*4*–*6*); 1-propanol–benzene (*7*); 2-propanol–acetonitrile (*4*, *5*); 2-propanol–benzene (*7*, *8*); and acetonitrile–benzene (*9*).

Experimental Section

All chemical reagents were supplied by Wako Pure Chemical Industries, Ltd. Analytical grade acetonitrile was used without further purification. C.P. benzene was recrystallized three times. C.P. 1-propanol and 2-propanol were fractionally distilled after drying by means of anhydrous copper sulfate. Pure component densities, determined by means of an Anton Paar densimeter (DMA40) at 25 °C, were in good agreement with literature values (*10*). Excess enthalpies were measured at 25 ± 0.01 °C by an isothermal dilution calorimeter. Detailed descriptions of the apparatus and procedure were given by Nagata and Kazuma (*11*). The experimental uncertainties of the excess enthalpies were ±0.5% over most of the mole fraction range.

Results

The excess enthalpies for the binary systems 1-propanol–acetonitrile and 2-propanol–acetonitrile at 25 °C are measured, and compared with published values. The experimental results obtained in this work are directly available from the authors. The values for the system 1-propanol–acetonitrile obtained in this investigation agree with those from Dohnal et al. (*6*) within experimental error and are about 4% lower than those from Coca Prados (*4*) and Mato and Coca (*5*), near the middle mole fraction range. The data for the system 2-propanol–acetonitrile are slightly higher than those reported in previous papers (*4*, *5*) over the region of high concentration of 2-propanol. The experimental data for the binary systems 1-propanol (1)–acetonitrile (2), 2-propanol (1)–acetonitrile (2), and acetonitrile (2)–benzene (3) were fitted by an unweighted least-squares method with a polynomial equation of the form

$$H_{ij}^{\mathrm{E}} = x_i x_j \sum_{k=1}^{m} a_{ij,k}(x_i - x_j)^{k-1} \qquad (1)$$

Mrazek and Van Ness (*7*) correlated their experimental data for the 1-propanol (1)–benzene (3) and 2-propanol (1)–benzene (3) systems with the following equation.

$$H_{13}^{\mathrm{E}} = (x_1 x_3)10^4 / \sum_{k=1}^{m} a_{13,k}(x_1 - x_3)^{k-1} \qquad (2)$$

Table I lists the coefficients $a_{ij,k}$ for the five binary systems studied in this investigation, as well as the standard deviations.

The excess enthalpy data for the ternary systems 1-propanol (1)–acetonitrile (2)–benzene (3) and 2-propanol (1)–acetonitrile (2)–benzene (3) at 25 °C are presented in Table II and fitted to an equation of the form

$$H_{123}^{\mathrm{E}} = H_{12}^{\mathrm{E}} + H_{13}^{\mathrm{E}} + H_{23}^{\mathrm{E}} + x_1 x_2 x_3 \Delta_{123} \qquad (3)$$

where H_{12}^{E} and H_{23}^{E} were calculated from eq 1, and H_{13}^{E} from eq 2, utilizing the coefficients reported in Table I. The term Δ_{123} is expressed by

$$\Delta_{123}/RT = b_0 - b_1 x_1 - b_2 x_2 - b_3 x_1^2 - b_4 x_2^2 - b_5 x_1 x_2 - b_6 x_1^3 - b_7 x_2^3 - b_8 x_1^2 x_2 \qquad (4)$$

The values of coefficients and standard deviations to fit eq 3 and 4 to the ternary mixtures are $b_0 = 7.7164$, $b_1 = 40.8507$, $b_2 = -5.4003$, $b_3 = -67.5767$, $b_4 = 34.2032$, $b_5 = -38.3734$, $b_6 = -33.5449$, $b_7 = -27.1734$, and $b_8 = 47.4144$, and $\sigma = 5.0$ J mol^{-1} for the 1-propanol–acetonitrile–benzene system, and $b_0 = 9.6191$, $b_1 = 47.2671$, $b_2 = 3.8793$, $b_3 = -76.7335$, $b_4 = 16.2596$, $b_5 = -45.5172$, $b_6 = 39.0163$, $b_7 = -14.9527$, and $b_8 = 52.7360$, and $\sigma = 5.7$ J mol^{-1} for the

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