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Solid−Liquid Equilibria of the *trans*-1,2-Cyclohexanediol + Ethyl Acetate + Water Ternary System

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Using a laser observation technique, the solubilities of *trans*-1,2-cyclohexanediol in ethyl acetate + water were measured in the temperature range (300.15 to 323.15) K by a synthetic method at atmospheric pressure. The Scatchard−Hildebrand equation and the modified UNIFAC model were used to correlate the experimental data. The modified UNIFAC was more accurate than the Scatchard−Hildebrand method to this system.

Introduction

trans-1,2-Cyclohexanediol is used for making fine chemical products such as the polyesters, pharmaceuticals, and agriculture chemicals.[1] For the purification of *trans*-1,2-cyclohexanediol, accurate solubility data are required. Solubilities of binary system of *trans*-1,2-cyclohexanediol have been reported,[2,3] but its solubility data for the ternary system at different temperatures have not been published at present. We measured solubilities of *trans*-1,2-cyclohexanediol in ethyl acetate + water at the temperature range from 300.15 K to 323.15 K. The experimental data were correlated with the Scatchard−Hildebrand equation and the modified UNIFAC model. The modified UNIFAC model agreed with experimental data and provided a good prediction to this system.

Experimental Section

Materials. *trans*-1,2-Cyclohexanediol was synthesized through oxidizing cyclohexene with H_2O_2 by ourselves, which was recrystallized with ethyl acetate at least three times.[4] The mass fraction of the *trans*-1,2-cyclohexanediol was 99.5 % by gas chromatography, and the melting point was (376.40 ± 0.55) K by digital determined melting point apparatus (type RY-51, Shanghai Precision & Scientific Instrument Co. Ltd), and the value in the literature is (375.65 ± 0.50) K.[5] Ethyl acetate, which was purchased from Tianjing Kemio Chemical Reagent Develop Center, was of AR grade with a purity of 99.5 %. Deionzied water was used.

Procedure. Synthetic method and analytical method are general methods of measurement of solid solubility among liquids.[6,7] The synthetic method was employed in the experiment. Figure 1 is a diagram of a laser-monitoring observation technique. The solubility apparatus consisted of a jacketed glass vessel (120 cm^3) maintained at the desired temperature by circulating water that was provided by a constant-temperature bath (type CS501, Shanghai Pudong Rongfeng Laboratory Instrument Works Co. Ltd). Water temperature was controlled, the uncertainty in the measured temperature was ± 0.1 K. A magnetic stirrer (type 85-2, Shanghai Sile Co.) achieved continuous stirring. A thermometer with an uncertainty of ± 0.01 K was used to determine the temperature of the system. A laser beam was used to observe the system of the dissolving solid in liquid, The signal transmitted through the vessel was collected by a detector (type FGF-III), which decided the rate of temperature rise and estimated the equilibrium point of the given system on the basis of the signal change.

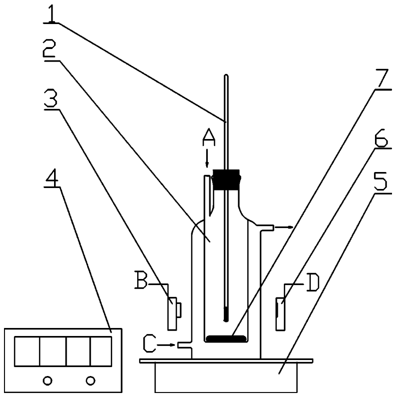

Figure 1. Concise experimental devices diagram: 1, accurate thermometer with a plug; 2, glass vial; 3, transistor laser generator; 4, control and digital display; 5, electromagnetic agitator; 6, photoelectric converter; 7, magnetic stirrer; A, port of dripping water; B and D, lead to control and digital display; C, port of circulating water for temperature controlling.

The solute and the solvent were prepared using an electronic balance (type AB204-N, Mettler-Toledo Group), which had a range measurement of up to 210 g with an uncertainty of ± 0.0001 g. The estimated uncertainty in the mole fraction was ± 0.001. The solubility of *trans*-1,2-cyclohexanediol in ethyl acetate + water was measured as follows. A predetermined quantity of *trans*-1,2-cyclohexanediol and ethyl acetate was placed into the jacketed vessel. Water was added slowly into the vessel from an automated microburet with an uncertainty of ± 0.005 cm^3. When the *trans*-1,2-cyclohexanediol particles disappeared completely, the signal approached a maximum value, and the volume of water added was recorded. Moreover, the reliability of the technique was verified by the measurement of solubility of benzoic acid in water. The experimental data shown in Figure 2 are compared with the literature values.[8] The average relative error was 0.022. It was proven that this experimental technique was reliable.

Results and Discussion

The experimental data of the solubilities of *trans*-1,2-cyclohexanediol in ethyl acetate + water over the temperatures

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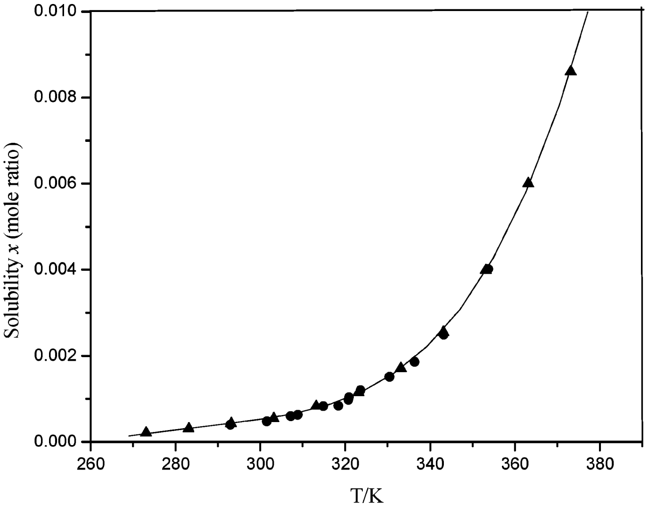

Figure 2. Solubility of benzonic acid in water compared with literature data by synthetic method: ●, experimental solubility values; ▲, solubility values in the literature.[8]

Table 1. Solid−Liquid Equilibrium Data of *trans*-1,2-Cyclohexanediol (1) + Ethyl Acetate (2) + Water (3) at 300.15 K

		modified UNIFAC		Scatchard−Hildebrand	
100 x_1	100 x_2	100 x_1 (cal)	100 AAD	100 x_1 (cal)	100 AAD
3.012	96.99	2.456	18.4	9.767	224
5.427	86.56	4.448	18.1	10.91	101
5.433	87.08	4.439	18.3	10.85	99.7
7.954	78.24	6.958	12.6	11.96	50.3
7.974	0.000	8.273	3.76	7.974	0.00
10.64	1.452	10.94	2.82	11.08	4.21
11.08	67.38	10.09	8.98	13.51	21.8
12.16	2.516	11.16	8.23	12.91	6.25
12.60	2.771	11.60	7.94	13.33	5.82
13.48	56.65	12.48	7.42	15.31	13.5
15.14	4.629	15.44	1.98	15.75	4.06
16.43	7.542	16.73	1.83	18.14	10.4
16.48	6.896	15.48	6.07	17.70	7.38
16.53	47.73	15.53	6.05	16.81	1.70
16.77	43.39	17.07	1.79	17.70	5.54
17.47	39.96	17.77	1.72	18.34	4.99
18.13	11.03	18.43	1.65	19.83	9.35
18.16	9.923	17.16	5.51	19.37	6.67
18.18	11.31	18.48	1.65	19.92	9.61
18.94	13.48	19.24	1.58	20.47	8.06
19.06	34.12	19.36	1.57	19.28	1.17
19.32	30.38	19.62	1.55	19.92	3.10
19.35	33.47	19.65	1.55	19.36	0.0516
20.08	19.67	20.38	1.49	20.90	3.91
20.11	18.89	20.41	1.49	20.89	3.19
20.35	26.22	20.65	1.47	20.36	0.0491

Table 2. Solid−Liquid Equilibrium Data of *trans*-1,2-Cyclohexanediol (1) + Ethyl Acetate (2) + Water (3) at 305.15 K

		modified UNIFAC		Scatchard−Hildebrand	
100 x_1	100 x_2	100 x_1 (cal)	100 AAD	100 x_1 (cal)	100 AAD
4.060	95.94	3.060	24.6	13.50	232
7.464	85.09	6.464	13.4	14.63	96.1
10.82	0.000	9.819	9.24	12.71	17.5
11.98	71.80	10.98	8.35	16.21	35.2
12.66	0.7478	11.66	7.90	14.38	13.6
14.81	61.95	13.81	6.75	17.51	18.2
15.43	2.577	14.43	6.48	17.11	10.9
15.87	55.90	14.87	6.30	18.38	15.8
15.92	56.70	14.92	6.28	18.26	14.7
17.39	4.158	16.39	5.75	18.78	8.00
17.80	51.46	16.80	5.62	18.99	6.71
19.08	6.306	18.08	5.24	20.29	6.40
20.21	40.00	20.51	1.48	20.69	2.39
21.29	11.02	21.59	1.41	22.08	3.68
21.48	24.91	21.78	1.39	22.49	4.70
21.84	12.23	22.14	1.37	21.32	2.19
21.98	28.63	22.28	1.36	22.18	0.909
22.01	19.92	22.31	1.36	22.83	3.71
22.47	15.15	22.76	1.33	22.67	0.890
22.54	24.88	22.84	1.33	22.52	0.0887
22.78	17.84	23.08	1.32	22.79	0.0438
22.79	19.97	23.09	1.31	22.78	0.0439

Table 3. Solid−Liquid Equilibrium Data of *trans*-1,2-Cyclohexanediol (1) + Ethyl Acetate (2) + Water (3) at 313.15 K

		modified UNIFAC		Scatchard−Hildebrand	
100 x_1	100 x_2	100 x_1 (cal)	100 AAD	100 x_1 (cal)	100 AAD
6.0396	93.96	5.039	16.6	15.19	151
9.599	83.49	8.599	10.4	16.78	74.8
10.79	80.68	9.789	9.27	17.23	59.7
15.77	67.95	14.76	6.34	19.45	23.4
17.57	63.27	16.56	5.69	20.33	15.8
18.21	0.000	17.21	5.49	18.21	0.00
18.83	58.78	17.83	5.31	21.25	12.8
19.90	57.51	18.90	5.02	21.45	7.77
20.15	55.71	19.15	4.96	21.84	8.41
20.66	1.549	19.66	4.84	21.12	2.21
21.18	52.44	20.18	4.72	22.52	6.34
22.31	3.424	21.31	4.48	23.48	5.22
23.47	45.09	23.77	1.28	24.07	2.53
23.65	4.608	23.95	1.27	24.68	4.30
24.60	7.627	24.90	1.22	26.66	8.33
25.49	36.17	25.79	1.18	25.97	1.88
26.12	9.057	26.42	1.15	27.28	4.45
27.07	30.04	27.37	1.11	27.08	0.0369
27.93	16.98	28.23	1.07	28.49	2.01
28.07	23.12	28.37	1.07	28.09	0.0713

ranging from 300.15 K to 323.15 K are given in Table 1 to Table 4. The experimental value and the predicted tie lines at each temperature are shown in Figure 3. At given temperature, it is shown that the solubilities of *trans*-1,2-cyclohexanediol in ethyl acetate + water were affected greatly by the proportion of ethyl acetate and water and presented a maximum value. Furthermore, the solubilities of *trans*-1,2-cyclohexanediol increased with the increase of the temperature. The higher the mole fraction of ethyl acetate, the less the effect of temperature.

The non-ideal behavior of the liquid mixtures was calculated from the activity coefficient as follows:[9]

$$\ln a_i = \ln(\gamma_i x_i) = -\frac{\Delta_{\text{fus}}H_i}{RT_{\text{tp},i}}\left(\frac{T_{\text{tp},i}}{T} - 1\right) - \frac{\Delta C_{p,i}}{R}\left(1 - \frac{T_{\text{tp},i}}{T} + \ln\frac{T_{\text{tp},i}}{T}\right) - \frac{\Delta V}{RT}(P - P_{\text{tp},i}) \quad (1)$$

where a_i, $\Delta_{\text{fus}}H_i$, $T_{\text{tp},i}$, $\Delta C_{p,i}$, $P_{\text{tp},i}$, and γ_i are activity, molar enthalpy of fusion, triple-point temperature, difference of heat capacities between subcooled liquid and solid, triple-point pressure, and activity coefficient for compoud i, respectively. x_i is the solid solubility (mole fraction) of the component i at the system temperature (T) and pressure (P); R is the universal gas constant. The above equation is frequently simplified by replacing the triple-point temperature ($T_{\text{t},i}$) with the normal melting temperature ($T_{\text{m},i}$) and canceling the last two terms of the right-hand side on the hypothesis[9] so that the pressure correction may be negligible. The contribution of heat-capacity difference is often minor, and there is not solid-to-solid conversion ranging from T to T_{tp}. In our experiment, the above terms were fitted well according to the studies of Zhou et al.[10,11] Equation 1 thus becomes

$$\ln(x_i\gamma_i) = \frac{\Delta_{\text{fus}}H_i}{R}\left(\frac{1}{T_{\text{m},i}} - \frac{1}{T}\right) \quad (2)$$

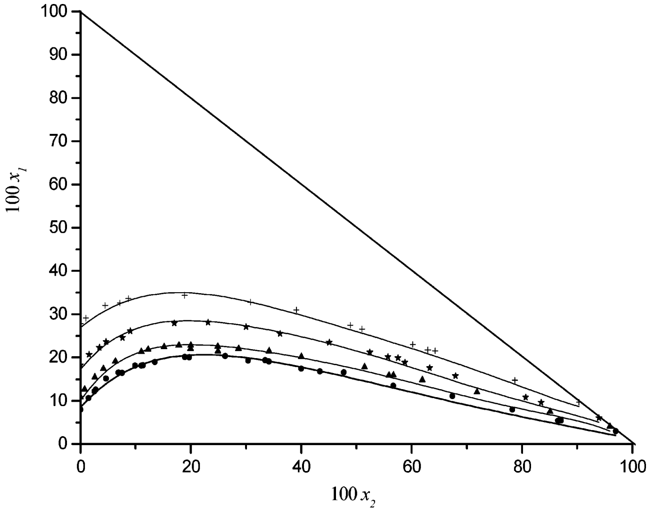

Figure 3. Ternary diagram for SLE of *trans*-1,2-cyclohexanediol (1) + ethyl acetate (2) + water (3) at various temperatures: ◆, experimental value at 300.15 K; ▲, experimental value at 305.15 K; ✸, experimental value at 313.15 K; +, experimental value at 323.15 K; −, calculated value tie-line by the modified UNIFAC at corresponding temperatures.

Table 4. Solid−Liquid Equilibrium Data of *trans*-1,2-Cyclohexanediol (1) + Ethyl Acetate (2) + Water (3) at 323.15 K

		modified UNIFAC		Scatchard−Hildebrand	
$100\,x_1$	$100\,x_2$	$100\,x_1$ (cal)	100 AAD	$100\,x_1$ (cal)	100 AAD
9.646	90.35	8.646	10.4	20.89	117
14.76	78.70	13.76	6.78	22.91	55.3
21.51	64.27	20.51	4.65	25.69	19.4
21.77	62.93	20.77	4.59	25.98	19.3
22.99	60.23	21.99	4.35	26.53	15.4
26.55	50.99	25.55	3.77	28.49	7.30
27.47	48.87	26.47	3.64	28.90	45.3
27.80	0.000	26.79	3.59	27.80	0.00
29.11	0.9484	28.11	3.44	29.13	0.0687
31.03	39.11	30.03	3.22	31.02	0.0322
31.99	4.447	30.99	3.13	32.16	0.531
32.61	7.117	31.61	3.07	33.34	2.26
32.76	30.80	33.06	0.916	32.74	0.0611
33.61	8.648	33.91	0.893	33.85	0.714
34.40	18.84	34.70	0.872	34.46	0.174

The correct description of the dependence on both the temperature and the composition requires reliable thermodynamic models in multicomponent systems, which allows the calculation of these properties from available experimental data. First, the Scatchard−Hildebrand equation was used to correlate the data for the system of *trans*-1,2-cyclohexanediol + ethyl acetate + water. The activity coefficient γ_1 was calculated by the following equations:[8,12]

$$\ln \gamma_1 = \frac{V_1^{\mathrm{L}}}{RT}[A_{12}\phi_2 + A_{13}\phi_3 + (A_{12} + A_{13} - A_{23})\phi_2\phi_3] \quad (3)$$

and

$$\phi_i = \frac{x_i V_i^{\mathrm{L}}}{x_1 V_1^{\mathrm{L}} + x_2 V_2^{\mathrm{L}} + x_3 V_3^{\mathrm{L}}} \quad i = 1, 2, 3$$

The subscripts of 1, 2, and 3 are *trans*-1,2-cyclohexanediol, ethyl acetate and water, respectively. V_i^{L} is molar volume of component i. A_{12}, A_{13}, and A_{23} are model parameters determined by the experimental data. The related physical properties data of every component and values of A_{12}, A_{13}, and A_{23} fitted by the experimental data in the system are listed in Table 5 and Table 6, respectively. The following objective function (F_{obj}) was chosen:

$$F_{\mathrm{obj}} = \sum_{i=1}^{N}\left(\frac{\gamma_{\mathrm{exp}} - \gamma_{\mathrm{cal}}}{\gamma_{\mathrm{exp}}}\right)^2 \quad (4)$$

Average absolute deviation (AAD) is given as follows:

$$\mathrm{AAD} = \frac{\sum_{i=1}^{N}|(x_{i,\mathrm{exp}} - x_{i,\mathrm{cal}})/x_{i,\mathrm{exp}}|}{N} \quad (5)$$

where the subscripts exp and cal are experimental value and calculated value, respectively. N is the number of experimental points. We can see that this model is poor according to AAD listed in Table 6.

The UNIFAC method developed by Fredenslund et al.[13] used for estimation of activity coefficients is based on the concept that a mixture may be considered a solution of structural units from which the molecules are formed rather than a solution of the molecules themselves. The activity coefficient equation of component i in the fluid mixture is shown as follows:

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{C}} + \ln \gamma_i^{\mathrm{R}} \quad (6)$$

where γ_i^{C} and γ_i^{R} are combinational contribution and residual contribution, respectively, to the activity coefficient for component i. In this experiment, *trans*-1,2-cyclohexanediol, ethyl acetate, and water can be divided into existing groups in a prototype UNIFAC, but errors are great comparing the calculating results with the binary experimental data.[2] According to the research of Li[14] and Zhou et al.,[3] *trans*-1,2-cyclohexanediol was considered as a new group; the other two types of solvents were still divided into existing groups. The details of subgroup are shown in Table 7. Equation 2 was used to calculate experimental activity coefficient of *trans*-1,2-cyclohexanediol. a_{nm}, a_{mn}, Q_k, and R_k are interaction parameters of the groups between m and n, relative van der Waals surface parameter, and volume parameter of subgroup k, respectively. The values of a_{nm}, a_{mn}, Q_k, and R_k of the existing groups was used according to Bondi.[15] The values of these parameters of new group were obtained by regression equation according to the corresponding binary experimental data listed in ref 2. Values of a_{nm}, a_{mn}, Q_k, and R_k are listed in Table 8 and Table 9, repectively. We used these parameters in the ternary system in this experiment. According to AAD values given in Table 1 and Table 4, it was found that

Table 5. Related Physical Properties Data of *trans*-1,2-Cyclohexanediol, Ethyl Acetate, and Water in the System

compound	*trans*-1,2-cyclohexanediol			ethyl acetate	water
property	$\Delta_{\mathrm{fus}}H$/J·mol^{-1}	T_{m}/K	V_1^{L}/cm^3·mol^{-1}	V_2^{L}/cm^3·mol^{-1}	V_3^{L}/cm^3·mol^{-1}
value	16368[a]	378.15[a]	98.14[a]	99.23[b]	18.06[b]

[a] Ref 10. [b] Ref 8.

Table 6. Correlation Results of the *trans*-1,2-Cyclohexanediol + Ethyl Acetate + Water System by the Scatchard−Hildebrand Equation

N	T/K	A_{12}	A_{13}	A_{23}	100 AAD
26	300.15	25.488	43.997	236.25	22.5
22	305.15	20.379	35.084	170.66	21.5
20	313.15	22.674	36.565	219.15	19.6
15	323.15	20.576	33.412	195.88	16.2

Table 7. Subgroups of Every Compound

compound	group
trans-1,2-cyclohexanediol	1 *trans*-1,2-cyclohexanediol
water	1 H_2O
ethyl acetate	1 CH_3COO, 1 CH_2, 1 CH_3

Table 8. Interaction Parameters in Modified UNIFAC

group			
n	m	a_{nm}/K	a_{mn}/K
trans-1,2-cyclohexanediol	H_2O	357.0[a]	130.5[a]
trans-1,2-cyclohexanediol	CH_3COO	101.2[a]	193.3[a]
trans-1,2-cyclohexanediol	CH_3	−199.5[a]	639.5[a]
trans-1,2-cyclohexanediol	CH_2	−199.5[a]	639.5[a]
H_2O	CH_3COO	−455.4[b]	1135[b]
H_2O	CH_3	580.6[b]	1318[b]
H_2O	CH_2	580.6[b]	1318[b]
CH_3COO	CH_3	114.8[b]	232.1[b]
CH_3COO	CH_2	114.8[b]	232.1[b]
CH_3	CH_2	0.000[b]	0.000[b]

[a] Regressive value by binary solubility data, ref 2. [b] Ref 9.

Table 9. R_k and Q_k Values of the System of Modified UNIFAC

main group no.	group	R_k	Q_k
1	*trans*-1,2-cyclohexanediol	5.591[a]	5.016[a]
2	H_2O	0.9200[b]	1.400[b]
3	CH_3COO	1.903[b]	1.728[b]
4	CH_3	0.9011[b]	0.8480[b]
5	CH_2	0.6744[b]	0.5400[b]

[a] Are regressive values by binary solubility data, refs 2 and 13. [b] Ref 15.

the modified UNIFAC method was more accurate than the Scatchard−Hildebrand method to this system.

The peak value of solubility in every designated temperature is caused by the solution properties of the mixture solvent, which can be described with thermodynamic property functions such as partial molar properties (partial molar enthalpy, partial molar volume), excess molar enthalpies, and excess molar volumes. Further study is necessary.

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