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Liquid−Liquid Equilibria in Binary Mixtures of Water with Malonitrile, Succinonitrile, and Glutaronitrile

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Liquid−liquid equilibria of binary mixtures of water and dinitrile solvents malononitrile, succinonitrile, and glutraronitrile have been studied in temperature range of 15 to 70 °C. The phase diagrams show that the critical mole fraction and consolate temperature (°C) (x_c, T_c) are (0.25, 58) for malononitrile and (0.19, 56) and (0.12, 68) for succinonitrile and glutraronitrile, respectively. The nonrandom two-liquid (NRTL) equation has been used to correlate of the activity coefficients of the components in binary mixtures. The parameters needed for the calculation are the energy parameters ($g_{12} - g_{22}$) and ($g_{21} - g_{11}$) and the nonrandom parameter α, which are determined by solving the NRTL equation with the aid of a nonlinear least-squares curve-fitting program. From the parameters of this equation, the excess Gibbs energies, G^E, were calculated. Good agreement between the experimental data of phase diagrams and model results was achieved.

Introduction

Liquid−liquid equilibria (LLE) data are essential for the design and development of separation processes and in the chemical industry. Such data are also valuable in theoretical studies. The use of aqueous two-phase systems (ATPS) for the purification and recovery of biocompounds has gained attention since the early studies of Albertsson et al.[1]

Thermodynamic models, such as the nonrandom two-liquid (NRTL), are frequently applied to model phase equilibria in many binary and ternary mixture systems.[2−6]

This paper presents phase equilibrium data for binary mixtures of water with malononitrile, succinonitrile, and glutraronitrile. The NRTL model was employed to model phase equilibrium, allowing the calculation of the phase composition, activity coefficients, and molar excess Gibbs energies. The need for thermodynamic data for liquid systems containing nitriles increases as new applications of these solvents are found.[7−10] A literature search shows that no LLE data measurements involving malononitrile, succinonitrile, and glutraronitrile have been published.

Experimental Section

Materials and Method. Malononitrle, succinonitrile, and glutranitrile were purchased from Merck and used without further treatment. Doubly distilled water was used. The mixtures of the dinitriles and water were prepared by mass with mole fractions ranging from 0.1 to 0.9 with a step of 0.05 with the total volume of the mixture being about 10 mL in a jacketed glass cell. The masses of liquids added were determined with an uncertainty of ±0.0002 g, and that gave an uncertainty in the mole fraction of better than 1 part in 10^4. The temperature was maintained at the desired value within ±0.1 °C by circulating thermostat water through the jacketed glass cell while the mixture solution was continuously stirred using a magnetic stirrer. The attainment of miscibility temperatures is accompanied by a sudden, visible change in the mixture from cloudy to clear. A schematic diagram of the apparatus used in this work is shown in Figure 1. The miscibility temperatures of the dinitriles in water and vice versa were measured with variation of light transmittance of the mixture versus temperature by a probe-type photometer (Metrohm 662) at $\lambda = 650$ nm. Temperature measurements were made with a thermal sensor (Heidolph EKT 3001) connected to a heating control unit. The mixtures were homogenized (one phase) by repeating the process of heating/cooling three to four times. The optical property of the mixture was changed in the homogeneous region of the tested solution. The typical experimental results are illustrated in Figure 2. The miscibility temperatures were determined from the intersection of two extrapolated segments of the miscibility curve. The uncertainty in the critical mole fraction x_c is estimated at ±0.05. The plots of miscibility points and the corresponding compositions gave the phase diagram of each system (Figure 3).

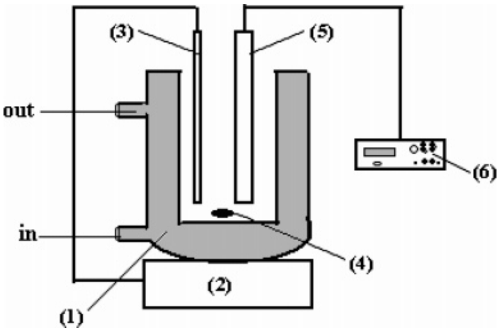

Figure 1. Schematic diagram of the apparatus for measuring the miscibility curve: (1) equilibrium glass cell, (2) heating unit, (3) thermal sensor, (4) magnetic stirrer, (5) probe type (light sensor), and (6) photometer.

Results and Discussion

The experimental LLE data of the three mixtures are given in Figure 3 and Tables 1 to 3. Compositions are always expressed in mole fraction x_{1A} where the first index refers to the component and the second refers to the phase

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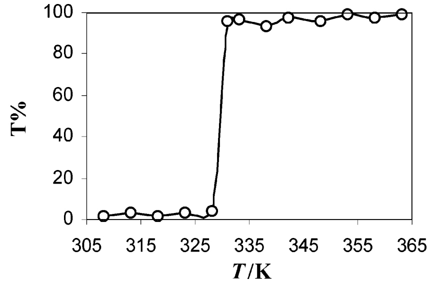

Figure 2. Light transmittance of binary mixtures of malononitrle + water (50 wt %) vs temperature.

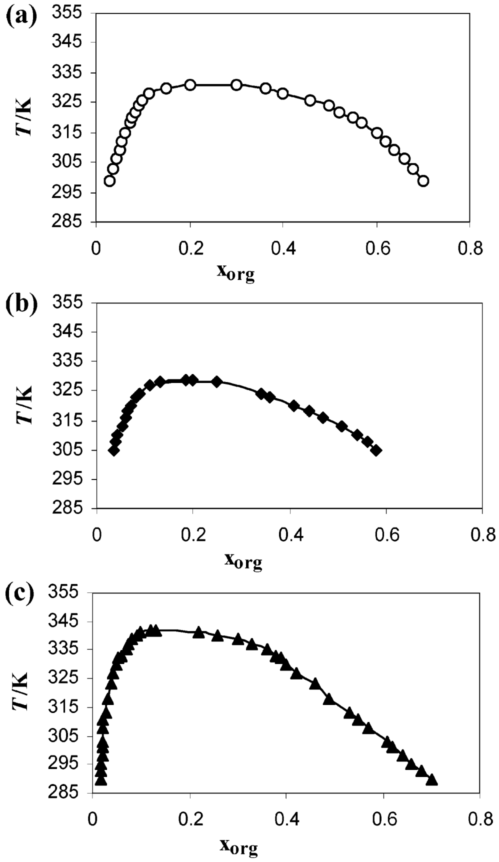

Figure 3. Phase diagram of binary mixtures of dinitrile−water: (a) malononitrile, (b) succinonitrile, and (c) glutranitrile.

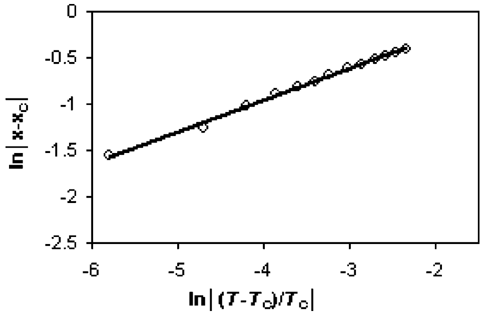

Figure 4. log−log plot of $|x_{1A} - x_C|$ vs $|(T - T_C)/T_C|$ for the malononitrle + water system.

Table 1. Experimental and Calculated Liquid−Liquid Equilibrium Temperatures for the Malononitrle (1) + Water (2) System

$x_1{}^1{}_{(exptl)}$	$x_1{}^1{}_{(calcd)}$	T/K	γ	$x_1{}^1{}_{(exptl)}$	$x_1{}^1{}_{(calcd)}$	T/K	γ
0.030	0.0299	299	33.9264	0.300	0.2973	331	3.4596
0.038	0.0388	303	27.3607	0.362	0.3582	330	2.8617
0.044	0.0450	306	23.7039	0.400	0.3974	328	2.5877
0.050	0.0507	309	20.8010	0.460	0.4592	326	2.2530
0.054	0.0532	312	18.9524	0.500	0.5002	324	2.0744
0.062	0.0611	315	16.5351	0.525	0.5252	322	1.9752
0.072	0.0711	318	14.2910	0.550	0.5507	320	1.8848
0.078	0.0767	320	13.1649	0.572	0.5728	318	1.8112
0.085	0.0833	322	12.0714	0.600	0.6015	315	1.7243
0.090	0.0870	324	11.3364	0.620	0.6214	312	1.6655
0.100	0.0972	326	10.2308	0.642	0.6409	309	1.6050
0.114	0.1122	328	9.02156	0.662	0.6602	306	1.5528
0.150	0.1525	330	6.9485	0.680	0.6783	303	1.5078
0.200	0.2047	331	5.2259	0.700	0.7017	299	1.4594

Table 2. Experimental and Calculated Liquid−Liquid Equilibrium Temperatures for the Succinonitrile (1) + Water (2) System

$x_1{}^1{}_{(exptl)}$	$x_1{}^1{}_{(calcd)}$	T/K	γ	$x_1{}^1{}_{(exptl)}$	$x_1{}^1{}_{(calcd)}$	T/K	γ
0.034	0.0313	305	22.9637	0.199	0.1990	329	2.8061
0.040	0.0387	308	19.4564	0.230	0.2303	328	2.4808
0.044	0.0433	310	17.4510	0.253	0.2525	327	2.3017
0.052	0.0527	313	14.4404	0.346	0.3459	324	1.7946
0.060	0.0613	316	12.0183	0.360	0.3592	323	1.7563
0.064	0.0646	318	10.8375	0.410	0.4077	320	1.6282
0.072	0.0732	320	9.3337	0.442	0.4408	318	1.5627
0.082	0.0815	323	7.6938	0.473	0.4729	316	1.5085
0.089	0.0886	324	6.9659	0.514	0.5170	313	1.4509
0.110	0.1092	327	5.2836	0.544	0.5460	310	1.4235
0.130	0.1302	328	4.3884	0.560	0.5604	308	1.4143
0.184	0.1840	329	3.0350	0.579	0.5750	305	1.4104

Table 3. Experimental and Calculated Liquid−Liquid Equilibrium Temperatures for the Glutranitrile (1) + Water (2) System

$x_1{}^1{}_{(exptl)}$	$x_1{}^1{}_{(calcd)}$	T/K	γ	$x_1{}^1{}_{(exptl)}$	$x_1{}^1{}_{(calcd)}$	T/K	γ
0.018	0.0249	290	68.3946	0.130	0.1131	342	8.7945
0.019	0.0240	293	63.9773	0.224	0.2227	341	4.4273
0.019	0.0235	295	60.8872	0.262	0.2588	340	3.7706
0.020	0.0237	298	55.7099	0.300	0.2963	339	3.2906
0.021	0.0237	301	51.1149	0.334	0.3297	337	2.9610
0.023	0.0250	303	47.3330	0.360	0.3549	335	2.7537
0.020	0.0175	308	45.2478	0.382	0.3778	333	2.6015
0.022	0.0215	311	42.5803	0.390	0.3875	332	2.5501
0.026	0.0258	313	35.3077	0.405	0.4058	330	2.2360
0.032	0.0287	318	29.8033	0.425	0.4197	327	2.3469
0.040	0.0368	323	24.1144	0.457	0.4514	323	2.1867
0.044	0.0388	327	21.3757	0.494	0.4898	318	2.0286
0.051	0.0450	330	18.7285	0.535	0.5345	313	1.8742
0.053	0.0458	332	17.8150	0.550	0.5564	311	1.8214
0.060	0.0556	333	16.1089	0.570	0.5745	308	1.7524
0.069	0.0658	335	14.2663	0.607	0.6075	303	1.6327
0.074	0.0708	337	13.1748	0.620	0.6194	301	1.5930
0.083	0.0806	339	11.7921	0.645	0.6442	298	1.5207
0.092	0.0914	340	10.7189	0.668	0.6663	295	1.4560
0.100	0.0989	341	9.8913	0.685	0.6834	293	1.4110
0.120	0.1114	342	8.8675	0.707	0.7087	290	1.3533

(A = water-rich phase, B = dinitrile-rich phase). Near a consolute point of a binary mixture, the difference in the composition of either component in the two coexisting liquid phases at constant pressure asymptotically behaves as[11]

$$|x_{1A} - x_C| = 2B|\frac{T - T_C}{T_C}|^{\beta} \qquad (1)$$

where x_c refers to the critical mole fraction in the phase diagram, T_c is the consolute temperature, and β is a universal critical exponent and a system-dependent coefficient. According to eq 1, the slope of the log−log plot of $|x_{1A} - x_C|$ versus $|(T - T_C)/T_C|$ should equal the universal value of exponent β (Figure 4). The effective exponent $\beta_{eff} = [d\ \ln(x - x_C)/d\ \ln((T - T_C)/T_C)]$ for the malononitrile + water system is 0.54 and for the succinonitrile + water and glutraronitrile + water systems is 0.34 and 0.41, respectively. The linear regression coefficient for these three systems is $r > 0.99$.

Table 4. Values of the NRTL Parameter

system	α	*a*	*b*	*c*	*d*
malononitrle + water	0.400	18 080.58	−2 852 661	−6771.37	4 500 020
succinonitrile + water	0.425	−35 395.35	1.192264×10^{7}	1609.32	1 845 961
glutranitrile + water	0.405	38 218.73	−9 173 012	−2842.55	3 619 252

Table 5. Molar Excess Thermodynamic Properties and Energies Parameters at 318 K

system	x_C	T_C/K	x_1	G^E/J·mol^{-1}	H^E/J·mol^{-1}	S^E/J·mol^{-1}·K^{-1}	$g_{12}-g_{22}$	$g_{21}-g_{11}$
malononitrle + water	0.25	331	0.072	593.3	−30 634.3	−98.2	9109.95	7379.63
succinonitril + water	0.19	329	0.064	481.8	−19 520.4	−62.9	2097.26	7414.23
glutranitrile + water	0.12	342	0.032	303.1	−31 910.3	−101.3	9372.78	8568.74

The nonrandom two-liquid (NRTL) solution model has been widely used to connect the thermodynamic data of binary systems containing molecular mixtures and an alloy system.[12] In this paper, activity coefficients and other thermodynamic properties were obtained from a miscibility gap in the binary water + dinitrile phase diagram by solving the NRTL equation. The molar excess Gibbs free energy (G^E) of which for a binary system, 1−2, was expressed is[13]

$$G^{E} = RTX_1X_2\left[\frac{\tau_{21}G_{21}}{X_1 + X_2G_{21}} + \frac{\tau_{12}G_{12}}{X_2 + X_1G_{12}}\right] \qquad (2)$$

The relations between τ_{12}, τ_{21} and G_{12}, G_{21} are given by

$$\tau_{12} = \frac{(g_{12} - g_{22})}{RT} \qquad (3)$$

$$\tau_{21} = \frac{(g_{21} - g_{11})}{RT} \qquad (g_{12} = g_{21}) \qquad (4)$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \qquad (5)$$

$$G_{21} = \exp(-\alpha_{21}\tau_{21}) \qquad (\alpha_{12} = \alpha_{21}) \qquad (6)$$

where x_1 and x_2 refer to the mole fractions of the first and second components, respectively, g_{ij} represents the energies of interaction between an $i = j$ pair of molecules, and α_{ij} is the nonrandomness constant for binary ij interactions (i, j =1, 2). When α_{12} is zero, the molecular distribution is completely random, and eq 2 reduces to the regular solution model.

The temperature dependence of ($g_{12} - g_{22}$) and ($g_{21} - g_{11}$) was additionally taken into consideration by

$$g_{12} - g_{22} = a + \frac{b}{T} \qquad (7)$$

$$g_{21} - g_{11} = c + \frac{d}{T} \qquad (8)$$

where a, b, c, and d are undetermined parameters. The number of NRTL parameters can be reduced by two by applying the incipient at consolute temperature condition

$$\frac{d^2\Delta G}{dx_1^{\,2}} = \frac{d^3\Delta G}{dx_1^{\,3}} = 0 \qquad (9)$$

where

$$\Delta_{\rm mix}G = G^{E} + RT(x_1 \ln x_1 + x_2 \ln x_2) \qquad (10)$$

Calculation of the isothermal parameters (in constant α) is step by step from the single mutual solubility from the condition (the activity of each component is the same in both liquid phase)

$$\ln \gamma_{1,A} + \ln x_{1A} = \ln \gamma_{1,B} + \ln x_{1,B} \qquad (11)$$

$$\ln \gamma_{2,A} + \ln x_{2A} = \ln \gamma_{2,B} + \ln x_{2,B} \qquad (12)$$

where $\gamma_{1,A}$, $\gamma_{1,B}$, $\gamma_{2,A}$, and $\gamma_{2,B}$ refer to the activity coefficient components of 1, 2 in phases A and B, respectively. The parameters $x_{1,A}$, $x_{1,B}$, $x_{2,A}$, and $x_{2,B}$ refer to mole fraction components of 1, 2 in phases A and B, respectively. Taking account of the relation between G^E and the activity coefficients of two components $\gamma_{i,m}$ and $\gamma_{j,m}$ (m = A, B), the NRTL equation expression can be written as

$$\ln \gamma_{i,m} = x_{j,m}^{\;2}\left[\frac{\tau_{ji}G_{ji}^{\;2}}{(x_{i,m} + x_{j,m}G_{ji})^2} + \frac{\tau_{ij}G_{ij}^{\;2}}{(x_{j,m} + x_{i,m}G_{ij})^2}\right] \quad (i, j = 1, 2) \qquad (13)$$

Substituting eq 13 into eqs 11 and 12, we obtain

$$\ln x_{i,A} + x_{j,A}^2\left[\frac{\tau_{ji}G_{ji}^2}{(x_{i,A} + x_{j,A}G_{ji})^2} + \frac{\tau_{ij}G_{ij}^2}{(x_{j,A} + x_{i,A}G_{ij})^2}\right] = \ln x_{i,B} + x_{j,B}^2\left[\frac{\tau_{ji}G_{ji}^2}{(x_{i,B} + x_{j,B}G_{ji})^2} + \frac{\tau_{ij}G_{ij}^2}{(x_{j,B} + x_{i,B}G_{ij})^2}\right] \qquad (14)$$

We have chosen to evaluate all parameters by fitting eq 14 to the experimental phase diagram data by a nonlinear least-squares curve-fitting program.[14]

The fitness function is represented by

$$\text{fitness} = -[(\ln a_{1,A} - \ln a_{1,B})^2 + (\ln a_{2,A} - \ln a_{2,B})^2] \qquad (15)$$

where $a_{1,A}$, $a_{1,B}$ and $a_{2,A}$, $a_{2,B}$ refer to the activity of components 1, 2 in phases A and B, respectively. The calculated results have been shown in Tables 1 to 3 for comparison. The good agreement was found to be sufficient. The molar excess enthalpy, H^E, and molar excess entropy, S^E, can be calculated by the following equations:

$$H^E = G^E - T\left(\frac{\partial G^E}{\partial T}\right)_{P,X} \tag{16}$$

$$H^E = x_1x_2\left[c\frac{G_{21}(1 - \alpha\tau_{21})(x_1 + x_2G_{21}) + \alpha x_2\tau_{21}\tau_{12}}{(x_1 + x_2G_{21})^2} + a\frac{G_{12}(1 - \alpha\tau_{12})(x_2 + x_1G_{12}) + \alpha x_1\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right] \tag{17}$$

$$S^E = \frac{(H^E - G^E)}{T} \tag{18}$$

In Tables 1 to 3, we have shown the calculated activity coefficient of binary mixtures of water with malononitrile, succinonitrile, and glutraronitrile. The optimized NRTL parameters are given in Table 4. The values of G^E, H^E, and S^E are given in Table 5.

Conclusions

The phase diagrams of the malononitrile + water, succinonitrile + water, and glutraronitrile + water systems were determined. Experimental results show that generally an increase in the molecular weight of dinitrile molecules can cause an increase in the upper consolute temperature (UCST) and a decrease in the critical mole fraction (x_c). The UCST is higher for the glutraronitrile + water system including the longer chain ($-CH_2-CH_2-$). This may be attributed to the decreasing polarity of the molecule with a larger number of carbon atoms and the same end tails. The NRTL model describes the phase behavior of dinitrile + water systems. Agreement between the calculated and experimental values of the mole fraction is satisfactory for the three systems. The calculations for the excess thermodynamic functions show that the excess enthalpy and excess entropy of dinitrile systems is negative. The negative values suggest that the associative interactions involve hydrogen bonding between water and nitrile groups. For the three systems studied in this work, strong nonideal behavior is evident from the magnitude of the activity coefficients given in Tables 1 to 3. Values of $\gamma_1 > 4$ were obtained at $x_1 < 0.2$ for the three systems.

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