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Solid−Liquid Equilibria of Nonanedioic Acid in Binary Ethanol + Water Solvent Mixtures from (292.35 to 345.52) K

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Solubilities of nonanedioic acid in binary ethanol + water solvent mixtures have been determined by the dynamic method using a laser monitoring observation technique over a temperature range from (292.35 to 345.52) K and a solvent composition, mole fraction of ethanol of solute-free x_2^0, range from 0.0 to 1.0. The experimental results showed that in pure water the solubility of nonanedioic acid increased slowly with temperature below 342.77 K but increased significantly above 342.77 K. The nonanedioic acid + ethanol + water system was found to exhibit a synergistic effect on solubility. The fusion enthalpy and melting temperature of nonanedioic acid were measured by differential scanning calorimetry. The modified λh equation, the Wilson equation, and the NRTL equation have been applied to correlate a subset of the experimental data. These models can successfully describe the solubility of nonanedioic acid in the binary mixtures with an ethanol mole fraction higher or equal to 0.2811.

Introduction

Nonanedioic acid (COOH)-$(CH_2)_n$-(COOH) with $n = 7$, also known as azelaic acid (CASRN 123-99-9), as one of the most important organic chemical products, is a raw material used in the production of plasticizers, lubricants, nylon, capacitors, and skin drugs, etc.[1−4] Currently, nonanedioic acid is manufactured from the oxidative cracking of oleic acid. In our study on the recrystallization process of decanedioic acid, (COOH)-$(CH_2)_n$-(COOH) with $n = 8$, i.e., sebacic acid, it was found that nonanedioic acid was a most poorly removable admixture in sebacic acid product. Nonanedioic acid is one of the difficult to remove impurities due to its similar properties with sebacic acid. Therefore, solubilities of nonanedioic acid in various solvents are needed not only for the production process of nonanedioic acid but also for the purification of sebacic acid. Unfortunately, limited information on the solubility of nonanedioic acid exists in the literature now. The solubilities of nonanedioic acid in NaCl(aq) (0.5 to 4.5) mol·L^{-1}, $(CH_3)_4NCl$(aq) (0.25 to 3) mol·L^{-1}, $(C_2H_5)_4NI$ (0.25 to 1) mol·L^{-1}, and pure water at $t = 25$ °C were investigated by Clemente et al.[5] Sparks et al.[6] determined solubilities of nonanedioic acid in supercritical carbon dioxide at (313.15 and 333.15) K and over the pressure range of (10 to 30) MPa using a flow-type dynamic apparatus. Breathnach[7] published the solubility of nonanedioic acid in water, and the results showed that the solubilities were 0.1 % at 274 K, 0.24 % at 293 K, 0.82 % at 323 K, 2.2 % at 338 K, and freely soluble in boiling water and alcohol. Apelblat[8] reported the solubility of nonanedioic acid in water from (278.25 to 361.35) K.

The phenomenon of enhanced solubility in binary solvent systems, that is, the synergistic effect, has been observed by Buchowski et al.[9] and Domanska et al.[10] It is said that the synergistic effect can be interpreted on the basis of the Scatchard−Hildebrand (S−H) theory.[11] Draucker et al.[12] verified the prediction of S−H theory by measuring the solubilities of 5-fluoroisatin in the mixtures of the propanol and nitromethane system. But according to the results of Domanska et al.[13] and Ghanima et al.,[14] no synergistic effect was observed for the systems which were predicted to reveal the enhanced solubility. The synergistic effect has also been noticed by Chen and Ma[15] and Wang et al.[16]

In this work, the solubility data of nonanedioic acid in ethanol + water binary mixtures have been measured by the dynamic method at a temperature range from (292.35 to 345.52) K and a solvent composition range from $x_2^0 = (0.0 \text{ to } 1.0)$. A subset of the experimental data were correlated by the modified λh model,[17] the Wilson model,[18] and the NRTL model.[19] The nonanedioic acid + ethanol + water system was found to exhibit a synergistic effect.

Experimental Section

Materials. The sample of nonanedioic acid (purity > 0.985) and ethanol (purity > 0.997) were purchased from Guangfu Chemical Reagents Co., Tianjin, China, and were used without further purification. Distilled water was obtained from Nankai Chemical Reagents Co., Tianjin, China, and also used as obtained.

Apparatus and Procedure. Solubilities were measured by the dynamic method. In our previous report,[18,20] the apparatus and procedure have been presented in detail. Briefly, the apparatus includes a jacketed glass solid−liquid equilibrium vessel, a laser detecting system, a temperature controlling and measurement system, and a magnetic stirring system. The experiment was carried out by heating slowly the predetermined sample in the solid−liquid equilibrium vessel with continuous stirring and the laser monitoring system running to detect. Water was forced into continuous circulation from a refrigerated/heating circulator (Julabo FP45-HE, Germany, temperature stability ± 0.01 K) to the jacket of the vessel to maintain the temperature. A Pt-100 thermal resistance thermometer was used for the temperature measurement with precision of ± 0.01 K. To prevent the evaporation of the solvent, a condenser was connected on the top of vessel, whose open end was sealed by a rubber plug.

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Table 1. Solubility of Nonanedioic Acid (1) in the Ethanol (2) + Water (3) Binary Solvent System ($x_2^0 = 0.0000$ and $x_2^0 = 0.0891$)

x_1	T^{exptl}/K	x_1	T^{exptl}/K	x_1	T^{exptl}/K
		$x_2^0 = 0.0000$			
$1.055 \cdot 10^{-5}$	299.19	$6.204 \cdot 10^{-4}$	322.02	$3.810 \cdot 10^{-3}3$	340.96
$3.736 \cdot 10^{-5}$	302.49	$8.923 \cdot 10^{-4}$	325.14	$5.080 \cdot 10^{-3}$	342.77
$7.823 \cdot 10^{-5}$	308.49	$1.220 \cdot 10^{-3}$	328.91	$6.450 \cdot 10^{-3}$	343.79
$1.385 \cdot 10^{-4}$	311.71	$1.520 \cdot 10^{-3}$	331.93	$7.960 \cdot 10^{-3}$	344.48
$2.244 \cdot 10^{-4}$	313.13	$1.860 \cdot 10^{-3}$	334.26	$9.880 \cdot 10^{-3}$	344.92
$3.226 \cdot 10^{-4}$	316.74	$2.280 \cdot 10^{-3}$	336.89	$1.219 \cdot 10^{-2}$	345.22
$4.252 \cdot 10^{-4}$	318.00	$2.910 \cdot 10^{-3}$	338.65	$1.503 \cdot 10^{-2}$	345.52
		$x_2^0 = 0.0891$			
$2.594 \cdot 10^{-5}$	295.65	$2.550 \cdot 10^{-3}$	308.92	$1.529 \cdot 10^{-2}$	324.70
$7.709 \cdot 10^{-5}$	296.85	$3.360 \cdot 10^{-3}$	311.38	$1.918 \cdot 10^{-2}$	325.49
$1.646 \cdot 10^{-4}$	297.94	$4.270 \cdot 10^{-3}$	313.70	$2.416 \cdot 10^{-2}$	327.20
$2.844 \cdot 10^{-4}$	298.73	$5.320 \cdot 10^{-3}$	315.97	$3.057 \cdot 10^{-2}$	328.98
$4.510 \cdot 10^{-4}$	299.54	$6.520 \cdot 10^{-3}$	317.79	$4.005 \cdot 10^{-2}$	330.94
$6.774 \cdot 10^{-4}$	300.80	$8.000 \cdot 10^{-3}$	320.19	$5.514 \cdot 10^{-2}$	334.16
$1.140 \cdot 10^{-3}$	302.97	$9.780 \cdot 10^{-3}$	321.52	$7.592 \cdot 10^{-2}$	337.62
$1.820 \cdot 10^{-3}$	306.03	$1.227 \cdot 10^{-2}$	323.18		

Table 2. Solubility of Nonanedioic Acid (1) in the Ethanol (2) + Water (3) Binary Solvent System ($x_2^0 = 0.2811$)

x_1	T^{exptl}/K	$\Delta_{\lambda h}$/K	Δ_W/K	Δ_N/K
$1.466 \cdot 10^{-2}$	296.40	3.26	0.27	0.48
$1.693 \cdot 10^{-2}$	298.46	2.95	0.38	0.64
$2.083 \cdot 10^{-2}$	301.95	2.98	1.00	1.29
$2.536 \cdot 10^{-2}$	303.96	1.62	0.19	0.51
$3.222 \cdot 10^{-2}$	307.25	0.73	−0.06	0.26
$4.020 \cdot 10^{-2}$	310.45	−0.04	−0.26	0.06
$5.009 \cdot 10^{-2}$	314.02	−0.50	−0.19	0.13
$5.555 \cdot 10^{-2}$	315.49	−0.96	−0.41	−0.10
$6.086 \cdot 10^{-2}$	316.89	−1.27	−0.52	−0.21
$6.767 \cdot 10^{-2}$	318.60	−1.52	−0.60	−0.30
$7.510 \cdot 10^{-2}$	320.40	−1.78	−0.58	−0.30
$8.442 \cdot 10^{-2}$	322.38	−2.06	−0.64	−0.39
$9.608 \cdot 10^{-2}$	325.19	−1.79	−0.14	0.07
$1.101 \cdot 10^{-1}$	327.70	−1.99	−0.12	−0.01
$1.261 \cdot 10^{-1}$	330.30	−2.10	−0.05	−0.12
$1.447 \cdot 10^{-1}$	333.49	−1.70	0.51	0.11
$1.708 \cdot 10^{-1}$	337.51	−1.08	1.25	0.13

Table 3. Solubility of Nonanedioic Acid (1) in the Ethanol (2) + Water (3) Binary Solvent System ($x_2^0 = 0.6101$)

x_1	T^{exptl}/K	$\Delta_{\lambda h}$/K	Δ_W/K	Δ_N/K
$4.201 \cdot 10^{-2}$	293.09	0.09	−0.15	−1.41
$5.174 \cdot 10^{-2}$	297.60	−0.10	−0.05	−0.68
$5.852 \cdot 10^{-2}$	299.99	−0.55	−0.37	−0.73
$6.849 \cdot 10^{-2}$	303.80	−0.43	−0.15	−0.25
$8.003 \cdot 10^{-2}$	307.60	−0.36	−0.05	0.02
$9.303 \cdot 10^{-2}$	311.18	−0.46	−0.19	−0.03
$1.056 \cdot 10^{-1}$	314.85	0.06	0.23	0.42
$1.164 \cdot 10^{-1}$	317.36	0.11	0.16	0.37
$1.281 \cdot 10^{-1}$	320.10	0.42	0.31	0.54
$1.424 \cdot 10^{-1}$	323.28	0.88	0.55	0.80
$1.678 \cdot 10^{-1}$	327.84	1.15	0.36	0.65
$1.858 \cdot 10^{-1}$	330.77	1.38	0.25	0.55
$2.053 \cdot 10^{-1}$	333.20	1.14	−0.36	−0.07
$2.279 \cdot 10^{-1}$	336.45	1.58	−0.33	−0.12

Table 4. Solubility of Nonanedioic Acid (1) in the Ethanol (2) + Water (3) Binary Solvent System ($x_2^0 = 0.8016$)

x_1	T^{exptl}/K	$\Delta_{\lambda h}$/K	Δ_W/K	Δ_N/K
$5.312 \cdot 10^{-2}$	293.85	−2.70	−0.50	−1.73
$5.965 \cdot 10^{-2}$	296.85	−2.45	−0.27	−1.32
$6.672 \cdot 10^{-2}$	300.26	−1.73	0.39	−0.53
$7.489 \cdot 10^{-2}$	302.86	−1.95	0.07	−0.76
$7.740 \cdot 10^{-2}$	303.86	−1.76	0.22	−0.59
$8.948 \cdot 10^{-2}$	307.76	−1.47	0.31	−0.43
$1.030 \cdot 10^{-1}$	311.61	−1.20	0.32	−0.36
$1.179 \cdot 10^{-1}$	315.41	−0.88	0.33	−0.28
$1.350 \cdot 10^{-1}$	319.20	−0.65	0.19	−0.31
$1.567 \cdot 10^{-1}$	323.43	−0.38	−0.02	−0.35
$1.806 \cdot 10^{-1}$	327.85	0.21	0.06	−0.09
$1.921 \cdot 10^{-1}$	329.47	0.15	−0.23	−0.30
$2.071 \cdot 10^{-1}$	331.83	0.44	−0.22	−0.18
$2.160 \cdot 10^{-1}$	333.11	0.56	−0.26	−0.16
$2.300 \cdot 10^{-1}$	334.53	0.24	−0.81	−0.64
$2.345 \cdot 10^{-1}$	335.38	0.55	−0.57	−0.39

Table 5. Solubility of Nonanedioic Acid (1) in the Ethanol (2) + Water (3) Binary Solvent System ($x_2^0 = 1.000$)

x_1	T^{exptl}/K	$\Delta_{\lambda h}$/K	Δ_W/K	Δ_N/K
$4.591 \cdot 10^{-2}$	292.35	0.37	−0.24	1.44
$5.416 \cdot 10^{-2}$	296.26	0.37	−0.22	1.05
$6.417 \cdot 10^{-2}$	300.24	0.24	−0.34	0.55
$7.538 \cdot 10^{-2}$	304.20	0.21	−0.39	0.20
$8.646 \cdot 10^{-2}$	308.00	0.54	−0.08	0.29
$9.788 \cdot 10^{-2}$	311.41	0.77	0.10	0.31
$1.083 \cdot 10^{-1}$	314.31	1.03	0.33	0.43
$1.186 \cdot 10^{-1}$	316.76	1.10	0.36	0.39
$1.326 \cdot 10^{-1}$	319.67	1.03	0.24	0.21
$1.459 \cdot 10^{-1}$	322.36	1.15	0.30	0.24
$1.603 \cdot 10^{-1}$	324.94	1.16	0.27	0.20
$1.758 \cdot 10^{-1}$	327.64	1.32	0.39	0.32
$1.920 \cdot 10^{-1}$	330.05	1.29	0.32	0.28
$2.097 \cdot 10^{-1}$	332.15	0.93	−0.08	−0.08
$2.281 \cdot 10^{-1}$	334.35	0.76	−0.28	−0.22
$2.473 \cdot 10^{-1}$	336.76	0.89	−0.16	−0.05

Near the solid−liquid equilibrium temperature, the speed of heating would not exceed 0.2 $\text{K} \cdot \text{h}^{-1}$. When the solute disappeared and the intensity of laser beam reached a maximum, this temperature was taken as the solid−liquid equilibrium temperature. The uncertainty of the measured temperature was ± 0.1 K calculated from two measurement results. All the chemical reagents were prepared by weighing the pure components using an analytical balance with an uncertainty of ± 0.0001 g.

The melting temperature, molar fusion enthalpy at the melting temperature, and the enthalpy of solid−solid phase transition of nonanedioic acid have been measured in triplicate by the differential scanning calorimetry Perkin-Elmer Pyris Diamond at 5 $\text{K} \cdot \text{min}^{-1}$.

Result and Discussion

Solubility of Nonanedioic Acid. The experimental solubility data of nonanedioic acid (1) in ethanol (2) + water (3) solvent mixtures are summarized in Tables 1 to 5, where T^{exptl} is the measured absolute temperature; x_1 is mole fraction solubility of nonanedioic acid; and x_2^0 is mole fraction of ethanol in the solute-free solution. By comparison of all the solubility data, a notable result comes up as shown in Figure 1. For $x_2^0 = 0$ (solubilities of nonanedioic acid in water), below 342.77 K, the solubility increases slowly with the temperature. However, at the temperature higher than 342.77 K, the solubility increases sharply with the temperature. An obvious "sudden increase" appears in the solubility−temperature curve. For $x_2^0 = 0.0891$, a sudden increase appears at 321.52 K. Then, after a further increase of x_2^0, no sudden increase appears in the solubility−temperature curve, and the solubility−temperature curve becomes smooth.

The solubility of nonanedioic acid in water, which is listed in Table 1, is depicted in Figure 2 together with data of Breathnach[7] and Apelblat.[8] Our results are similar to the data of Breathnach in the measured temperature range and also close with the results of Apelblat at lower temperature. The deviation is mostly attributed to the difference in measurement techniques and experimental error. However, our results show an obvious difference from the values reported by Apelblat at enhanced temperature. This difference is too large to be explained by measurement techniques and experimental error.

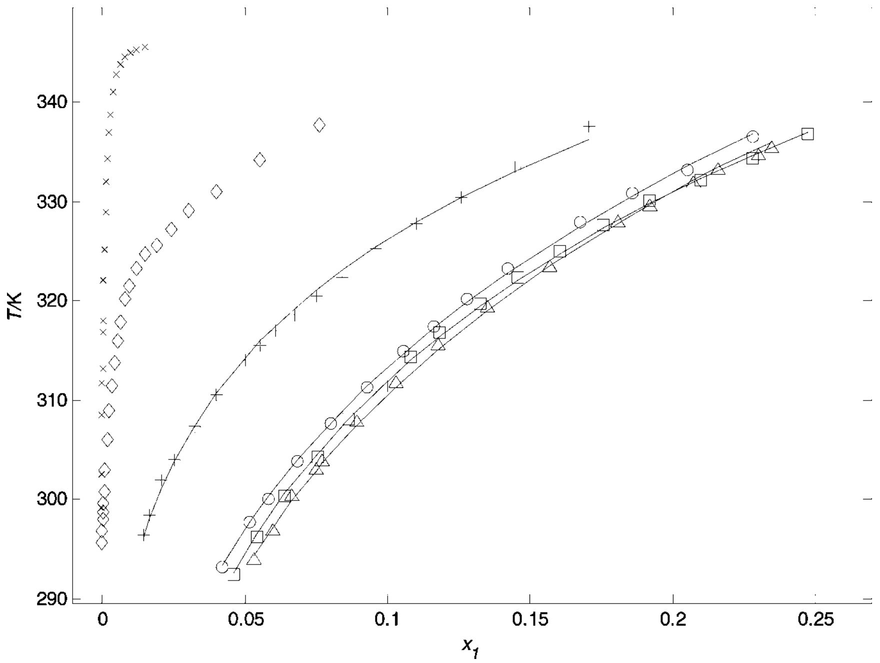

Figure 1. Solubility of nonanedioic acid in binary ethanol + water solvent mixtures: ×, $x_2^0 = 0$; ◇, $x_2^0 = 0.0891$; +, $x_2^0 = 0.2811$; ○, $x_2^0 = 0.6101$; △, $x_2^0 = 0.8016$; □, $x_2^0 = 1.000$; —, calculated by the Wilson model.

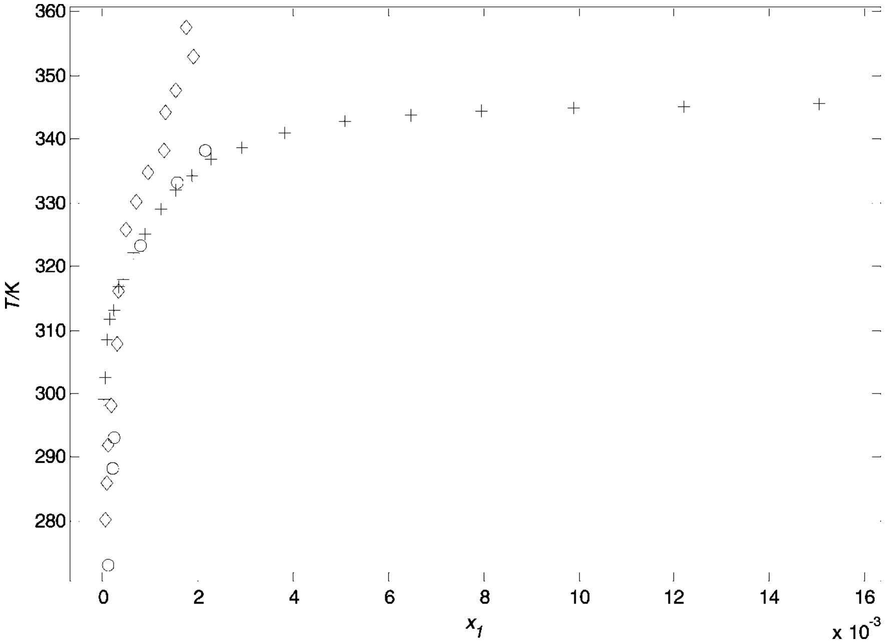

Figure 2. Solubility of nonanedioic acid in water: +, this work; ○, Breathnach;[7] ◇, Apelblat.[8]

Generally, nonanedioic acid is insoluble in water and reasonably soluble in ethanol. However, the solubility of nonanedioic acid does not increase with x_2^0 linearly. Figure 1 shows that nonanedioic acid + ethanol + water system exhibits a synergistic effect on solubility. The solubilities of nonanedioic acid increased with x_2^0, reached the maximum values at $x_2^0 = 0.8016$, and then decreased with a further increase of x_2^0.

The Scatchard−Hildebrand theory[11] suggests that when the solubility parameter of the solute has a value intermediate between the values of the solubility parameters of the solvents constituting the mixture ($\delta_2 < \delta_1 < \delta_3$) the dissolvable power of solvent mixtures becomes much higher than that of their individual components. The value of the solubility parameter of nonanedioic acid at 298.15 K, $\delta_1 = 20.4\ \mathrm{MPa}^{1/2}$, is calculated by the functional group method.[21] The values of the solubility parameters for the two solvents as reported by Barton[22] are $\delta_2 = 26.0\ \mathrm{MPa}^{1/2}$ and $\delta_3 = 47.9\ \mathrm{MPa}^{1/2}$ for ethanol and water, respectively. According to the Scatchard−Hildebrand theory, the nonanedioic acid + ethanol + water system should not reveal the synergistic effect. However, the results are not consistent with this prediction. The present results further confirm that the Scatchard−Hildebrand theory derived from nonpolar systems is not always applicable to predict synergistic effect for some polar systems, and the existence of alcohols in binary solvent systerms tends to reveal the synergistic effect.[18]

Correlation of Experimental Data. The solid−liquid equilibrium can be calculated by[18]

$$-\ln x_1\gamma_1 = \frac{\Delta H_{\text{m1}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{m1}}}\right) + \frac{\Delta H_{\text{tr1}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{tr1}}}\right) - \frac{\Delta Cp_{\text{m1}}}{R}\left(\ln\frac{T}{T_{\text{m1}}} + \frac{T_{\text{m1}}}{T} - 1\right) \quad (1)$$

where T, x_1, γ_1, T_{m1}, ΔH_{m1}, ΔH_{tr1}, T_{tr1}, and ΔCp_{m1} stand for equilibrium temperature, mole fraction of solute, activity coefficient, melting temperature, enthalpy of fusion at melting temperature, enthalpy of solid−solid phase transition, temperature of phase transition, and difference in solute heat capacity between the solid and liquid at the melting temperature, respectively.

The fusion enthalpy and melting temperature of nonanedioic acid were determined to be $\Delta H_{\text{m1}} = (35.3 \pm 0.7)$ kJ·mol^{-1} and $T_{\text{m1}} = (375.61 \pm 0.03)$ K calculated from three replicate measurements. Solid−solid phase transition was not observed in the present DSC detection. The ΔH_{m1} value has also been determined by Maria et al.[23] to be (29.7 ± 0.9) kJ·mol^{-1} with a melting temperature of (372.4 ± 1.2) K. However, no solid−solid phase transition has been observed in the present study, which is different from the literature report.[23]

Because solid−solid phase transition does not occur, the second term on the right side of eq 1 can be omitted. If the contributions of the heat capacity can be neglected, eq 1 becomes

$$-\ln x_1\gamma_1 = \frac{\Delta H_{\text{m1}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{m1}}}\right) \quad (2)$$

In this study, the Wilson model and the NRTL model are used to calculate the activity coefficient in eq 2. The λh model which was developed by Buchowski at al.[24] has been applied to most solid−liquid equilibrium systems and gave excellent correlation results without considering the activity coefficients of the components. The three models are described as follows.

1. Modified λh Model.

$$\ln\left[1 + \frac{\lambda(1 - x_i)}{x_i}\right] = \lambda h\left(\frac{1}{T} - \frac{1}{T_{\text{m}}}\right) \quad (3)$$

where λ and h are the model parameters.

The above λh model[24] was effective only for pure solvent or fixed solvent composition. To use the λh model to describe the solubility of nonanedioic acid in solvent mixtures, the parameters λ and h were presumed to be a function of x_2^0, respectively: [17]

$$\lambda = a_1 + b_1\exp(c_1x_2^0) \quad (4)$$

$$h = a_2 + b_2\exp(c_2x_2^0) \quad (5)$$

where a_i, b_i, and c_i are constants

2. Wilson Model. Wilson[18] expressed the activity coefficient for component i in a mixture as follows

$$\ln\gamma_i = 1 - \ln\left(\sum_j^n(\Lambda_{ij}x_j)\right) - \sum_k^n\left(\frac{\Lambda_{ki}x_k}{\sum_j^n(\Lambda_{kj}x_j)}\right) \quad (6)$$

where n is the number of components in the mixture. Λ_{ij} is the model parameter which is expressed by

$$\Lambda_{ij} = d_{ij} + e_{ij}/T \quad (7)$$

where d_{ij} and e_{ij} are constants.

3. NRTL Model. The activity coefficient for any component i can be calculated by the NRTL model as follows.[24]

$$\ln\gamma_i = \frac{\sum_j^n\tau_{ji}G_{ji}x_j}{\sum_l^n G_{li}x_l} + \sum_j^n\frac{x_jG_{ij}}{\sum_l^n G_{lj}x_l}\left[\tau_{ij} - \frac{\sum_r^n x_r\tau_{rj}G_{rj}}{\sum_l^n G_{lj}x_l}\right] \quad (8)$$

where τ_{ij} and G_{ij} are NRTL model parameters which are given by

$$G_{ij} = \exp(-\eta_{ij}\tau_{ij}), \qquad \tau_{ij} = f_{ij} + g_{ij}/T \quad (9)$$

where f_{ij} and g_{ij} are constants; $\tau_{ij} \neq \tau_{ji}$; $\tau_{ii} = 0$; $\eta_{ij} = \eta_{ji}$; and in the optimization process, η_{ij} was chosen as 0.3 as Renon and Prausnitz[19] proposed.

The optimum algorithm applied in the model parameters estimation was the Nelder−Mead method, which is a more efficient but also more complex version of the Simplex method that allows the geometric figures to contract and expand continuously during the search process. This iterative method is based on minimizing the objective function. In this work, the root-mean-square deviation σ as defined by eq 10 is taken as the objective function.

$$\sigma = \left[\sum_{i=1}^{N}(T^{\text{exptl}} - T)^2/(N - 1)\right]^{0.5} \quad (10)$$

where N is the number of experimental data points; T^{exptl} is the experimental equilibrium temperature which is listed in Table 1 to Table 5; and T is the calculated equilibrium temperature obtained from rq 2 to rq 9.

If all the experimental solubility data were utilized to determine the model parameters, the description of the nonanedioic acid + ethanol + water systems was unfavorable for the modified λh model, the Wilson model, and the NRTL model. Actually, it mainly results from forming a "sudden increase" on the solubility−temperature curve of $x_2^0 = 0$ and $x_2^0 = 0.0891$. All the models cannot describe the sudden increase on the solubility curves successfully. Therefore, only a subset of the experimental data, containing ethanol mole fraction of solute-free 28.11 %, 61.01 %, 80.16 %, and 100 %, are chosen to be use in the regression. Temperature deviations between the experimental and the calculated temperature ($\Delta = T^{\text{exptl}} - T$) are listed in Table 2 to Table 5, and subscripts λh, W, and N express the temperature deviations for the modified λh model, the Wilson model, and the NRTL model, respectively. The model parameters and the total root-mean-square deviations calculated by the modified λh model, the Wilson model, and the NRTL model are listed in Table 6 to Table 8, and the root-mean-square deviations for each system are listed in Table 9. It can be concluded that the Wilson model gives the best description of the solubility of nonanedioic acid ($\sigma_{\text{W}}^{t}/\text{K} = 0.38$).

Table 6. Model Parameters of the Modified λh Model for the System Nonanedioic Acid + Ethanol + Water

	a_i	b_i	c_i
$i = 1$	−608.98	609.75	−0.00013982
$i = 2$	5231.2 K	25694 K	−9.3864
$\sigma^t_{\lambda h}$/K	1.33		

Table 7. Model Parameters of the Wilson Model for the System Nonanedioic Acid + Ethanol + Water

i	j	d_{ij}	d_{ji}	e_{ij}/K	e_{ji}/K
nonanedioic acid	ethanol	−1.4968	0.72097	904.67	−16.509
ethanol	water	1.8111	12.600	−510.29	−1466.2
nonanedioic acid	water	−23.942	51.290	8682.1	−17645
σ^t_{W}/K		0.38			

Table 8. Model Parameters of the NRTL Model for the System Nonanedioic Acid + Ethanol + Water

i	j	f_{ij}	f_{ji}	g_{ij}/K	g_{ji}/K	$\eta_{ij} = \eta_{ji}$
nonanedioic acid	ethanol	3.0729	−0.51456	−981.15	179.24	0.3
ethanol	water	−9.3183	44.830	3037.4	−12594	
nonanedioic acid	water	−103.26	19.718	36634	39520	
σ^t_{N}/K		0.57				

Table 9. Root-Mean-Square Deviations from the Description by the Modified λh Model, the Wilson Model, and the NRTL Model

solvent system	$\sigma_{\lambda h}$/K	σ_{W}/K	σ_{N}/K
water + 28.11 mol % ethanol	2.14	0.60	0.49
water + 61.01 mol % ethanol	0.77	0.27	0.58
water + 81.16 mol % ethanol	1.39	0.37	0.70
ethanol	0.93	0.28	0.54

The NRTL model and the modified λh model also give satisfactory results ($\sigma^t_{\mathrm{N}}/\mathrm{K} = 0.57$, $\sigma^t_{\lambda h}/\mathrm{K} = 1.33$). However, it must be pointed out that all the parameters which are given in Table 6 to Table 8 are obtained from the correlation of a subset of the experimental data, and they can only be applied to predict the solubilities of nonanedioic acid in solvent mixtures with x_2^0 higher or equal to 0.2811. For x_2^0 lower or equal to 0.0891, the solubility prediction results will be poor.

Conclusions

On the basis of the results of this investigation, the following conclusions are made:

New experimental data have been provided for the solubility of nonanedioic acid in water, ethanol, and binary solvent mixtures composed of ethanol + water, and the investigated system was found to exhibit a synergistic effect on solubility.

The solid−liquid equilibrium data were described by the Wilson model, the NRTL model, and the modified λh model, and the total root-mean-square deviations were 0.38 K, 0.57 K, and 1.33 K, respectively. The Wilson model gave the best result, and the NRTL model and the modified λh model also showed satisfactory results.

All the model parameters obtained in the present study can successfully describe the synergistic effect on the nonanedioic acid−ethanol−water system. However, these parameters can only predict the solubilities of nonanedioic acid in ethanol−water binary mixtures with x_2^0 higher or equal to 0.2811.

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