Measurement and Correlation of Solubilities of Decanedioic Acid in C_4-C_6 Alcohol Solvents

Su-Ning Chen, Qing Xia,* Li-Fei Lu, Min-Shi Zhang, Yi-Shan Chen, Feng-Bao Zhang, and Guo-Liang Zhang

School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, P.R. China

The solubility data have been measured experimentally for decanedioic acid in *n*-butanol, 2-butanol, *n*-pentanol, *n*-hexanol, and binary solvents 2-propanol + water from (294 to 351) K. The system containing decanedioic acid + 2-propanol + water exhibited a synergistic effect on solubility. The Wilson model, the nonrandom two-liquid (NRTL) model, and the universal quasi-chemical functional group activity coefficient (UNIFAC) model were applied to describe the solid−liquid equilibrium (SLE). It is shown that the Wilson model and the NRTL model can give better results. The primary reason for relatively larger deviations in the case of using the UNIFAC model was discussed.

Introduction

Solubility data of solid compounds in solvents or solvent mixtures play a significant role in all crystallization processes which is a crucial step in the manufacturing of many industrial chemicals. In our previous report,[1] the industrial preparation and application of decanedioic acid $C_{10}H_{18}O_4$ (CAS RN 111-20-6) have been introduced in detail. Thus, as an important organic industrial chemical, the solubility data of decanedioic acid in various solvents for the augment of production rate and yield, as well as the process development are needed. Tudorovskaya et al.,[2] Bonhomme and Lab,[3] and Xia et al.[1,4] respectively published the solubilities of decanedioic acid in water and alcohol + water binary mixtures.

The universal quasi-chemical functional group activity coefficient (UNIFAC) model has been widely applied to the prediction of liquid-phase activity coefficients in nonelectrolyte, nonpolymeric mixtures at low to moderate pressures and temperatures. It was originally reported by Fredenslund et al.[5] and was revised and updated by Gmehling et al.[6] in 1982, Hensen et al.[7] in 1991, and Wittig et al.[8] in 2003. The modified forms of the UNIFAC model were proposed respectively by Weidlich and Gmehling[9] and Larsen et al.[10] Besides having a modified combinatorial part, these modified models introduced temperature-dependent group interaction parameters which allowed a better prediction of the vapor−liquid equilibrium (VLE) than did the original UNIFAC model.

Much attention has been taken into the prediction of solid−liquid equilibrium (SLE) by the UNIFAC model after the work of Gmehling et al.[11] Zhou et al.[12] measured the solubilities of *trans*-1,2-cyclohexanediol in butyl acetate + water, and it was found that the solubility data predicted by UNIFAC agreed with experimental data. Although for some groups of compounds the results were successful, the shortcomings and limitations of the UNIFAC model for prediction of SLE were proposed.[13,14] Kan and Tomson[15] predicted the aqueous and nonaqueous solubilities of a vast number of environmentally significant chemicals using the UNIFAC model. Good agreement was observed between the UNIFAC model predicted and the literature-reported aqueous solubilities for 11 groups of compounds, that is, short-chain alkanes, alkenes, alcohols, and chlorinated alkanes, and so forth. However, the error between predicted and literature-reported aqueous solubilities was larger for three groups of chemicals: long-chain alkanes, phthalates, and chlorinated alkenes. Gracin et al.[16] used the UNIFAC model to correlate solubilities of nine different solid organic fine chemical compounds in water and organic solvents. Unfortunately, it suggested that the UNIFAC model in its original form was not quite satisfactory for the solubility prediction of the interested systems.

In this study, for the purpose of further investigations on the solubility of decanedioic acid as well as the investigation on the synergistic effect, the measurements were carried out in *n*-butanol, 2-butanol, *n*-pentanol, *n*-hexanol, and binary mixed solvents 2-propanol + water which involved 2-propanol solute-free mole fraction range from ($x_2^0 = 0.0$ to 1.0), over a temperature range from (294 to 351) K. The system of decanedioic acid + 2-propanol + water was found to exhibit a synergistic effect. The Wilson model, the nonrandom two-liquid (NRTL) model, and the UNIFAC model were applied to describe the experimental SLE data. The possible reason for the relatively larger discrepancy appearing in the UNIFAC model was discussed.

Experimental Section

Materials. The solid sample of decanedioic acid ($T_{m1} = 405.62 \pm 0.02$ K and $\Delta H_{m1} = 45.3 \pm 0.7$ kJ·mol^{-1})[1,4] was commercially obtained from the Shanghai Jinchun Reagent Co. Ltd., Shanghai, China, with a purity of 0.995 mass fraction. *n*-Butanol (mass fraction > 0.997), 2-butanol (mass fraction > 0.998), *n*-pentanol (mass fraction > 0.998), *n*-hexanol (mass fraction > 0.997), and 2-propanol (mass fraction > 0.998) were purchased from the Guangfu Chemical Reagents Co., Tianjin, China, and used without further purification.

Apparatus and Procedure. All systems were measured by the dynamic method which has been described in detail previously.[1,4] Predetermined solute and solvents mixtures were heated slowly (less than 0.2 K·h^{-1} close to the SLE temperature) inside a vessel with continuous stirring, and a laser monitoring system was run to observe the dissolving processes. It was the

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* To whom correspondence should be addressed. E-mail: xiaqing@tju.edu.cn. Fax: 86-022-27408778.

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Table 1. Experimental Solubility Data for the System Decanedioic Acid (1) + 2-Propanol (2) + Water (3)

x_1	T^{exp}/K	x_1	T^{exp}/K	x_1	T^{exp}/K
		$x_2^0 = 0.1988$			
$2.820\cdot10^{-03}$	294.80	$1.108\cdot10^{-02}$	315.06	$3.071\cdot10^{-02}$	332.37
$3.930\cdot10^{-03}$	298.82	$1.351\cdot10^{-02}$	318.41	$3.778\cdot10^{-02}$	336.14
$5.850\cdot10^{-03}$	304.71	$1.669\cdot10^{-02}$	321.85	$4.653\cdot10^{-02}$	339.85
$7.380\cdot10^{-03}$	308.71	$2.080\cdot10^{-02}$	325.60	$5.715\cdot10^{-02}$	343.65
$9.090\cdot10^{-03}$	311.87	$2.523\cdot10^{-02}$	328.87		
		$x_2^0 = 0.3974$			
$1.095\cdot10^{-02}$	295.44	$3.509\cdot10^{-02}$	318.12	$9.363\cdot10^{-02}$	340.53
$1.416\cdot10^{-02}$	300.02	$4.286\cdot10^{-02}$	322.27	$1.070\cdot10^{-01}$	344.03
$1.782\cdot10^{-02}$	304.57	$5.290\cdot10^{-02}$	327.07	$1.205\cdot10^{-01}$	347.31
$2.239\cdot10^{-02}$	308.81	$6.199\cdot10^{-02}$	330.75	$1.341\cdot10^{-01}$	350.21
$2.839\cdot10^{-02}$	313.52	$7.986\cdot10^{-02}$	336.60		
		$x_2^0 = 0.5712$			
$1.933\cdot10^{-02}$	297.91	$4.837\cdot10^{-02}$	317.78	$1.060\cdot10^{-01}$	338.49
$2.389\cdot10^{-02}$	302.22	$5.730\cdot10^{-02}$	321.91	$1.215\cdot10^{-01}$	342.51
$2.870\cdot10^{-02}$	305.88	$6.735\cdot10^{-02}$	326.02	$1.376\cdot10^{-01}$	346.52
$3.393\cdot10^{-02}$	309.65	$7.728\cdot10^{-02}$	329.52	$1.536\cdot10^{-01}$	349.98
$4.021\cdot10^{-02}$	313.39	$9.105\cdot10^{-02}$	334.32		
		$x_2^0 = 0.8112$			
$1.959\cdot10^{-02}$	295.12	$4.649\cdot10^{-02}$	313.75	$1.036\cdot10^{-01}$	335.38
$2.457\cdot10^{-02}$	299.62	$5.589\cdot10^{-02}$	318.31	$1.172\cdot10^{-01}$	339.13
$2.927\cdot10^{-02}$	303.06	$6.805\cdot10^{-02}$	323.60	$1.313\cdot10^{-01}$	342.81
$3.414\cdot10^{-02}$	306.61	$8.002\cdot10^{-02}$	328.05	$1.469\cdot10^{-01}$	346.43
$3.954\cdot10^{-02}$	310.01	$9.124\cdot10^{-02}$	331.70	$1.632\cdot10^{-01}$	349.84
		$x_2^0 = 1.000$			
$1.280\cdot10^{-02}$	294.33	$5.423\cdot10^{-02}$	319.77	$1.080\cdot10^{-01}$	337.34
$1.699\cdot10^{-02}$	297.47	$6.258\cdot10^{-02}$	323.87	$1.162\cdot10^{-01}$	339.72
$2.311\cdot10^{-02}$	302.02	$7.192\cdot10^{-02}$	326.72	$1.282\cdot10^{-01}$	342.76
$3.102\cdot10^{-02}$	307.72	$8.080\cdot10^{-02}$	329.57	$1.372\cdot10^{-01}$	344.84
$3.856\cdot10^{-02}$	312.15	$8.859\cdot10^{-02}$	331.75	$1.461\cdot10^{-01}$	346.41
$4.617\cdot10^{-02}$	316.22	$9.811\cdot10^{-02}$	334.97	$1.613\cdot10^{-01}$	349.60

Table 2. Experimental Solubility Data for the System Decanedioic Acid (1) + *n*-Butanol (4)

x_1	T^{exp}/K	x_1	T^{exp}/K	x_1	T^{exp}/K
$1.221\cdot10^{-02}$	295.36	$3.032\cdot10^{-02}$	313.13	$6.464\cdot10^{-02}$	329.20
$1.782\cdot10^{-02}$	302.27	$3.382\cdot10^{-02}$	315.15	$7.847\cdot10^{-02}$	333.93
$1.982\cdot10^{-02}$	303.95	$4.510\cdot10^{-02}$	321.01	$9.652\cdot10^{-02}$	339.10
$2.468\cdot10^{-02}$	308.51	$5.347\cdot10^{-02}$	325.66	$1.152\cdot10^{-01}$	343.19

Table 3. Experimental Solubility Data for the System Decanedioic Acid (1) + 2-Butanol (5)

x_1	T^{exp}/K	x_1	T^{exp}/K	x_1	T^{exp}/K
$7.430\cdot10^{-03}$	294.37	$2.121\cdot10^{-02}$	309.58	$6.486\cdot10^{-02}$	331.36
$9.360\cdot10^{-03}$	295.65	$2.751\cdot10^{-02}$	313.78	$7.837\cdot10^{-02}$	335.78
$1.243\cdot10^{-02}$	299.28	$3.264\cdot10^{-02}$	317.00	$9.491\cdot10^{-02}$	340.19
$1.392\cdot10^{-02}$	301.36	$3.825\cdot10^{-02}$	320.24	$1.155\cdot10^{-01}$	345.16
$1.414\cdot10^{-02}$	301.75	$4.502\cdot10^{-02}$	323.84		
$1.793\cdot10^{-02}$	306.05	$5.401\cdot10^{-02}$	327.84		

Table 4. Experimental Solubility Data for the System Decanedioic Acid (1) + *n*-Pentanol (6)

x_1	T^{exp}/K	x_1	T^{exp}/K	x_1	T^{exp}/K
$7.790\cdot10^{-03}$	294.13	$2.897\cdot10^{-02}$	312.17	$7.998\cdot10^{-02}$	335.24
$1.087\cdot10^{-02}$	294.60	$3.340\cdot10^{-02}$	315.23	$9.064\cdot10^{-02}$	338.50
$1.337\cdot10^{-02}$	298.23	$3.981\cdot10^{-02}$	319.24	$1.013\cdot10^{-01}$	340.91
$1.483\cdot10^{-02}$	299.45	$4.623\cdot10^{-02}$	323.10	$1.135\cdot10^{-01}$	344.40
$1.791\cdot10^{-02}$	304.10	$5.227\cdot10^{-02}$	325.68	$1.230\cdot10^{-01}$	346.01
$2.257\cdot10^{-02}$	307.75	$5.846\cdot10^{-02}$	328.11	$1.337\cdot10^{-01}$	347.20
$2.499\cdot10^{-02}$	309.30	$6.905\cdot10^{-02}$	332.17	$1.436\cdot10^{-01}$	348.84

Table 5. Experimental Solubility Data for the System Decanedioic Acid (1) + *n*-Hexanol (7)

x_1	T^{exp}/K	x_1	T^{exp}/K	x_1	T^{exp}/K
$7.400\cdot10^{-03}$	293.95	$2.482\cdot10^{-02}$	312.05	$7.780\cdot10^{-02}$	337.09
$1.122\cdot10^{-02}$	299.05	$2.808\cdot10^{-02}$	314.61	$8.568\cdot10^{-02}$	339.99
$1.323\cdot10^{-02}$	300.41	$3.122\cdot10^{-02}$	316.45	$9.819\cdot10^{-02}$	343.09
$1.402\cdot10^{-02}$	301.78	$3.853\cdot10^{-02}$	320.80	$1.194\cdot10^{-01}$	348.10
$1.685\cdot10^{-02}$	304.81	$4.439\cdot10^{-02}$	323.48	$1.365\cdot10^{-01}$	350.27
$1.814\cdot10^{-02}$	306.78	$5.289\cdot10^{-02}$	327.65		
$2.120\cdot10^{-02}$	309.61	$6.480\cdot10^{-02}$	332.65		

SLE temperature when the solid disappeared and the intensity of the laser beam reached a maximum. The temperature in the vessel was controlled by the continuous circulation from a refrigerated/heating circulator (Julabo FP45-HE, Germany, temperature stability ± 0.01 K). The measurement procedure was repeated two times, and the uncertainty of measured T was ± 0.1 K.

Result and Discussion

With decanedioic acid as the solute and the binary mixture 2-propanol + water as solvent, the experimental solubilities of the ternary system decanedioic acid + 2-propanol + water are summarized in Table 1. With decanedioic acid as the solute and *n*-butanol, 2-butanol, *n*-pentanol, and *n*-hexanol as solvents, respectively, the experimental solubilities of binary systems are listed in Tables 2, 3, 4, and 5, where T^{exp}, x_1, and x_2^0 respectively stand for measured temperature, the mole fraction solubility, and solute-free mole fraction of 2-propanol in the solvent mixtures.

As shown in Figure 1, the solubility of decanedioic acid increases evidently with temperature, and it is found that the 2-propanol + water binary solvent with a 2-propanol mole fraction (solute-free) of 81.12 % presents the highest dissolving power among the 2-propanol + water binary solvents: that is to say, the decanedioic acid + 2-propanol + water system exhibits a synergistic effect on solubility. The results further enhance the prediction of the occurrence of a synergistic effect when the alcohols exist in the solvent mixtures. The solubility data of decanedioic acid in binary solvent mixtures containing alcohol which were researched in this work and previous reports[4] all reveal synergistic effects, so it can be further assumed that the synergistic effect may be related to the hydrogen bonds in the systems.

It can be found from Figure 2 that the solubility of decanedioic acid in *n*-butanol, 2-butanol, *n*-pentanol, and *n*-hexanol increases with the temperature and decreases with the number of carbon atoms contained in the alcohols. It may be the result of the weakening of the polar alcohol molecules with the number of carbon atoms containing in alcohols. The solubilities of decanedioic acid in *n*-butanol are a bit larger than that in 2-butanol.

An equation for the calculation of SLE has been obtained.[1,4]

$$-\ln x_{\mathrm{i}}\gamma_{\mathrm{i}} = \frac{\Delta H_{\mathrm{mi}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{mi}}}\right) \qquad (1)$$

To solve this equation, the activity coefficient of solute in solvent, γ_{i}, has to be calculated. There are many thermodynamic models that can be used for the calculation of γ_{i}. In this study, two semiempirical models, the Wilson model and the NRTL model, were introduced to describe the SLE of the present

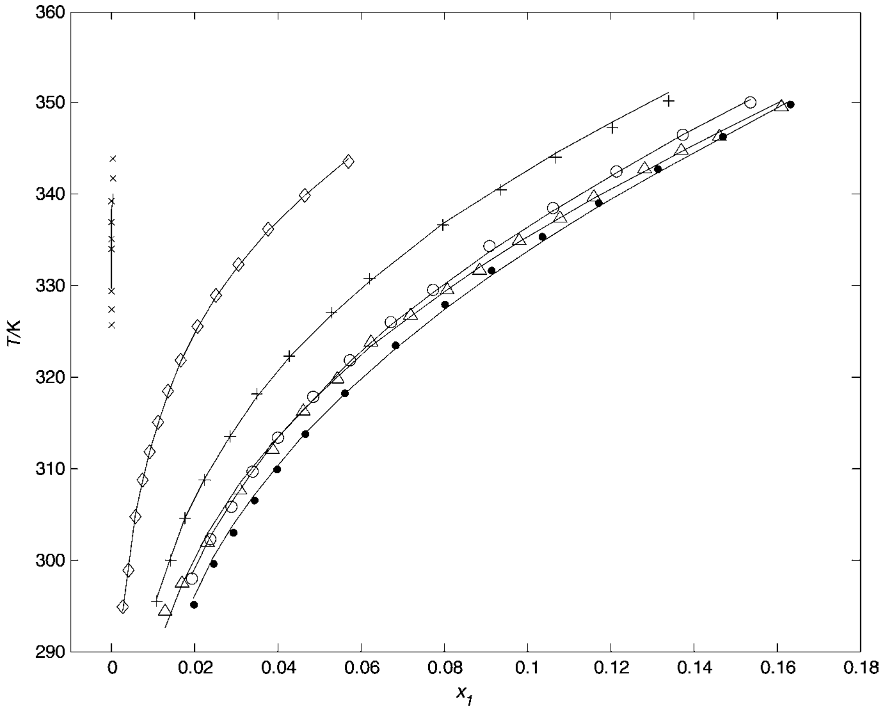

Figure 1. Solubilities of decanedioic acid in binary 2-propanol + water solvent mixtures: ×, $x_2^0 = 0$;[1] ◇, $x_2^0 = 0.1988$; +, $x_2^0 = 0.3974$; ○, $x_2^0 = 0.5712$; ●, $x_2^0 = 0.8112$; △, $x_2^0 = 1.000$; solid line, the Wilson model.

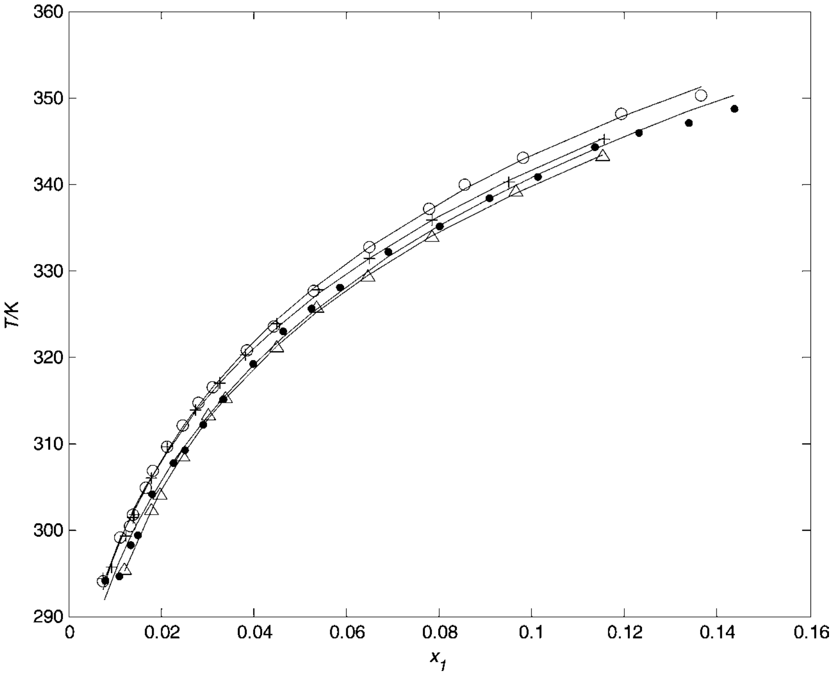

Figure 2. Solubilities of decanedioic acid in C_4-C_6 alcohols: △, *n*-butanol; +, 2-butanol; ●, *n*-pentanol; ○, *n*-hexanol; solid line, the Wilson model.

Table 6. Model Parameters of the Wilson Model for Decanedioic Acid (1) in Binary 2-Propanol (2) + Water (3) Solvent Mixtures

	Λ_{12}	Λ_{21}	Λ_{23}	Λ_{32}
a_{ij}	2.25772	−6.1411	−8.37788	36.2987
b_{ij}/K	−633.658	2979.31	3332.84	−3215.17

Table 7. Model Parameters of the NRTL Model for Decanedioic Acid (1) in Binary 2-Propanol (2) + Water (3) Solvent Mixtures

	τ_{12}	τ_{21}	τ_{23}	τ_{32}
c_{ij}	−0.552470	2.13966	−6.91826	28.3842
d_{ij}/K	174.269	−909.246	2516.58	−7792.81

investigated systems and estimate the model parameters from experimental data. These two models have been used in our previous report[4] and gave satisfactory results. The reports of using the UNIFAC model in SLE have being increased, but the results of the prediction were different. The UNIFAC model was chosen in present study to investigate its applicability.

Table 8. Model Parameters of the Wilson Model for Decanedioic Acid (1) in *n*-Butanol (4), 2-Butanol (5), *n*-Pentanol (6), and *n*-Hexanol (7)

	Λ_{14}	Λ_{41}	Λ_{15}	Λ_{51}	Λ_{16}	Λ_{61}	Λ_{17}	Λ_{71}
a_{ij}	2.58849	−1.66453	4.81575	−4.62450	0.367558	−5.23597	0.328412	−6.23063
b_{ij}/K	−346.312	871.548	−1299.79	2007.36	−100.925	2932.64	−91.2789	3232.834

Table 9. Model Parameters of the NRTL Model for Decanedioic Acid (1) in *n*-Butanol (4), 2-Butanol (5), *n*-Pentanol (6), and *n*-Hexanol (7)

	τ_{14}	τ_{41}	τ_{15}	τ_{51}	τ_{16}	τ_{61}	τ_{17}	τ_{71}
c_{ij}	6.34900	−16.3205	6.41298	−16.2398	7.54750	−11.0228	6.42111	−16.5642
d_{ij}/K	−2747.82	8098.30	−2808.44	7871.31	−3126.06	6453.32	−2813.06	7979.95

1. Wilson Model. The activity coefficient expressed by the Wilson model[17] is:

$$\ln \gamma_i = 1 - \ln\left(\sum_{j}^{n} (\Lambda_{ij} x_j)\right) - \sum_{k}^{n} \left(\frac{\Lambda_{ki} x_k}{\sum_{j}^{n} (\Lambda_{kj} x_j)} \right) \tag{2}$$

where Λ_{ij} is the model parameter which is expressed by the following empirical equation.[18,19]

$$\Lambda_{ij} = a_{ij} + b_{ij}/T \tag{3}$$

where a_{ij} and b_{ij} are constants.

2. NRTL model. The following NRTL model[20] is used to calculate activity coefficients.

$$\ln \gamma_i = \frac{\sum_{j}^{n} \tau_{ji} G_{ji} x_j}{\sum_{l}^{n} G_{li} x_l} + \sum_{j}^{n} \frac{x_j G_{ij}}{\sum_{l}^{n} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{r}^{n} x_r \tau_{rj} G_{rj}}{\sum_{l}^{n} G_{lj} x_l} \right) \tag{4}$$

where G_{ij} and τ_{ij} are NRTL model parameters that need to be experimentally determined by

$$G_{ij} = \exp(-\eta_{ij}\tau_{ij}) \qquad \tau_{ij} = c_{ij} + d_{ij}/T \tag{5}$$

where c_{ij}, d_{ij} are constants, $\eta_{ij} = \eta_{ji}$, $\tau_{ij} \neq \tau_{ji}$, and $\tau_{ii} = 0$. In the optimization process, as Renon and Prausnitz proposed, η_{ij} was chosen as 0.3.[20]

The optimization algorithm with an application in the parameters estimation and the objective function are taken as previously.[4]

$$\sigma = \left[\sum_{i=1}^{N} (T^{\exp} - T)^2/(N-1)\right]^{0.5} \tag{6}$$

where N is number of experimental data points, $T^{\exp}$ is the experimental equilibrium temperature which is listed in Tables 1 to 5, and T is the calculated equilibrium temperature.

The interaction parameters of decanedioic acid and water in the Wilson model and the NRTL model have been obtained in our previous report.[4] In the present optimization process, these interaction parameters were still adopted as previously obtained, and other parameters were fitted using the experimental data of the present systems, which were summarized in Tables 6, 7, 8, and 9.

3. UNIFAC Model. The UNIFAC model[15] describes the activity coefficient in terms of a combinatorial part and a residual part.

$$\ln \gamma_i = \ln \gamma_i^{C} + \ln \gamma_i^{R} \tag{7}$$

where γ_i^{C} and γ_i^{R} are the combinatorial part and residual contribution, respectively, to the activity coefficient for component i.

Table 10. Interaction Parameters of $COOH_L$ Group with Other Functional Groups

group		interaction parameters a_{nm}		interaction parameters a_{mn}	
n	*m*	A_{nm}/K	B_{nm}	A_{mn}/K	B_{mn}
CH_2	$COOH_L$	11.4743	3.35364	−1.76599	−0.00694819
OH	$COOH_L$	2.28295	1.19536	1.66543	−0.828399
H_2O	$COOH_L$	−7.24817	0.809289	−2.13902	−0.831861

The temperature dependent parameter ψ_m is introduced as follows:

$$\psi_{nm} = \exp\left(-\frac{a_{nm}}{T}\right) \tag{8}$$

where a_{nm} is the group interaction parameters, and $a_{nm} \neq a_{mn}$.

In the UNIFAC model, molecules are composed of functional groups. The properties of a molecule are calculated by adding the contribution of each functional group contained in the molecule. The properties of each group are assumed to be independent of the rest of the groups existing in the mixture. On the basis of this assumption, *n*-butanol and 2-butanol have the same functional groups.

In this work, decanedioic acid, alcohols, and water can be divided into existing functional groups in an original UNIFAC model.[5] The predictive calculation has been first performed to all of the data with the established parameters of functional groups, and the standard deviation calculated by eq 6 was $\sigma^T = 5.23$ K. It was proved that the application of the UNIFAC model with original interaction parameters could not generate a successful prediction for the investigated systems. That may be attributed to the limitation of these predictive model parameters, which were originally established from molecules with low size and nonelectrolyte, nonpolymeric mixtures.[10,21] Therefore, it is not reliable to predict long-chain and polar molecules systems especially containing intense intermolecular hydrogen bonding between components existing in the mixtures.

To improve the results of the UNIFAC method, it is essential to adjust the interaction parameters by the data of present systems. The parametric fitting was carried out on the basis of introducing a new main group, COOH, connected to long-chain alkyl, which was defined as $COOH_L$. The interaction parameters of $COOH_L$ with other functional groups were expressed as temperature dependence functions, and other group interaction parameters were taken as constants from the original UNIFAC model. Several kinds of temperature dependence functions were attempted to express the interaction parameters of $COOH_L$ with other functional groups, and the results showed that the expression $a_{nm} = A_{nm} + B_{nm}T$ gave the smallest standard deviations with $\sigma^T = 2.48$ K. The group interaction parameters obtained from the experimental data are presented in Table 10.

Table 11 lists the standard deviations of each system calculated by the Wilson model, the NRTL model, and the UNIFAC model (using the interaction parameters listed in Table 10). It can be seen that the Wilson model and the NRTL model are applicable to describe SLE of decanedioic acid + alcohol

Table 11. Standard Deviations for the UNIFAC Model, the Wilson Model, and the NRTL Model

solvents	σ/K UNIFAC model	Wilson model	NRTL model
19.88 mol % 2-propanol + water	4.24	0.22	0.60
39.74 mol % 2-propanol + water	3.29	0.42	1.21
57.12 mol % 2-propanol + water	2.42	0.32	0.39
81.12 mol % 2-propanol + water	0.72	0.69	0.75
2-propanol	2.92	0.45	1.06
butanol	0.90	0.27	0.28
2-butanol	3.12	0.54	0.48
pentanol	1.41	0.89	0.81
hexanol	1.03	0.43	0.65

+ water systems, and the results are better than that of the UNIFAC model. After defining the new functional group $COOH_L$ and expressing the group interaction parameters concerning $COOH_L$ as a temperature dependence function, the accuracy of the calculation by the UNIFAC model has been improved, but the standard deviations are still dissatisfactory. Because most of values of the interaction parameters used in the present work have been determined from VLE experimental data, extrapolation to describe SLE may cause poor results. Moreover, another significant reason for obtaining poor results is that the basic assumption of the UNIFAC model may not be valid in present systems. The key assumption of the UNIFAC model is that the molecules can be broken down into functional groups. The interaction parameters of functional groups are not affected by other functional groups or molecules contained in the mixture. The present systems contain dicarboxylic acid, alcohol, and water. Hydrogen bonding can exist as intermolecules; strong hydrogen bondings are complex and may overlap in the systems. The interaction of two functional groups may be affected by the other groups or molecules existing in the mixture. So, it is difficult to be well-evaluated, despite that the interaction parameters are expressed as temperature dependence functions.

Conclusions

With decanedioic acid as solute and *n*-butanol, 2-butanol, *n*-pentanol, *n*-hexanol, and binary solvents 2-propanol + water as solvents, respectively, the solubilities of binary and ternary systems were measured by a dynamic method. The system of decanedioic acid + 2-propanol + water exhibits a synergistic effect on solubility, further enhancing the prediction of the occurrence of a synergistic effect when the alcohols exist as solvents. The solubility of decanedioic acid in n-$C_4$$\sim$$n$-$C_6$ alcohols decreases with the number of carbon atoms in the solvent molecules.

For the calculation of the activity coefficient using different activity coefficient models, the Wilson model showed the best result. The deviations of the NRTL model were larger than that of the Wilson model and smaller than that of the UNIFAC model. To improve the results of the UNIFAC model, a new group, $COOH_L$, was introduced, and its interaction parameters were modified as a function of first-order temperature. The inadaptability of the UNIFAC model is mainly due to strong and complex hydrogen bonding existing in the present research systems.

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