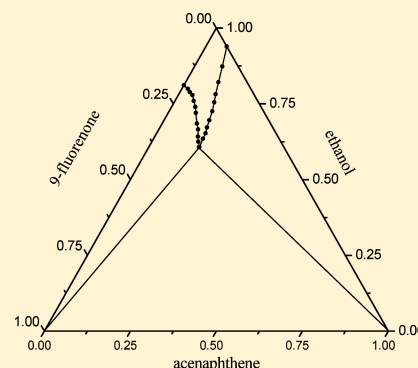


Solid–Liquid Phase Equilibrium and Solubility of Dibenzo[*b,d*]furan and 9*H*-Fluoren-9-one in Organic Solvents

Yufeng Wei, Leping Dang, Xiangyang Zhang, Weimin Cui, and Hongyuan Wei*

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, People's Republic of China

ABSTRACT: The solubilities of 9*H*-fluoren-9-one and dibenzo[*b,d*]furan in ethanol, butan-1-ol, ethyl ethanoate, methylbenzene, 2-isopropoxypropane, and tetrachloromethane were measured using the isothermal method from (283.15 to 333.15) K. The experimental data were then correlated with the Apelblat equation, and the activity coefficients were correlated using the Scatchard–Hildebrand regular solution equation and nonrandom two-liquid (NRTL) equation. Besides, ternary phase diagrams of 9*H*-fluoren-9-one + dibenzo[*b,d*]furan + ethanol, 9*H*-fluoren-9-one + 9*H*-fluorene + ethanol, and 9*H*-fluoren-9-one + 1,2-dihydroacenaphthylene + ethanol were also presented. The results show that all systems were simple eutectic systems, and the significant change of solubility in 9*H*-fluoren-9-one + dibenzo[*b,d*]furan + ethanol system can be attributed to the intermolecular forces between dibenzo[*b,d*]furan and 9*H*-fluoren-9-one.



INTRODUCTION

As the major components of the fractionation cut obtained from coal tar, dibenzo[*b,d*]furan and 9*H*-fluorene have many industrial applications. Among them, dibenzo[*b,d*]furan is mainly used as raw materials for the production of dyestuffs, anticeptics, insecticides, *o*-phenylphenol, and polychlorodibenzofurans.^{1,2} 9*H*-Fluorene is widely used in the applications of thermo and light sensitizers, liquid crystal chemistry, luminescence chemistry, spectrophotometric analysis, molecular chemistry, and biocompatibility industry.³

The commercial process for the production of 9*H*-fluorene was achieved by the distillation, and further oxidation of which in the presence of oxidizing agents can be used to manufacture 9*H*-fluoren-9-one. Crystallization would take place to isolate 9*H*-fluoren-9-one and 9*H*-fluorene; however, as the boiling point of 9*H*-fluorene is close to that of several polynuclear aromatic hydrocarbons (PAHs) such as dibenzo[*b,d*]furan and 1,2-dihydroacenaphthylene, the contamination of these components in the distilled 9*H*-fluorene was unavoidable, and further drawn into the final product of 9*H*-fluoren-9-one, which consequently increased the difficulty of the crystallization process of 9*H*-fluoren-9-one and further impurity content. Given this situation, to obtain dibenzo[*b,d*]furan and 9*H*-fluoren-9-one with high purities, their thermodynamic properties should be investigated.

The study of solid–liquid equilibrium (SLE) is an important tool in analyzing crystallization and extraction processes. There is much research concerning the SLE of 9*H*-fluorene or 1,2-dihydroacenaphthylene.^{2,4–6} The SLE for binary mixtures composed of 1,2-dihydroacenaphthylene, dibenzo[*b,d*]furan, 9*H*-fluorene, phenanthrene, and 1,1-methanediylidibenzene were determined by Lee et al. with a solid-disappearance method.^{5,6} Eckert et al. have investigated the SLE of dibenzo[*b,d*]furan in water and supercritical fluid carbon dioxide.^{7,8} Bouroukba et al. have reported the SLE of

dibenzo[*b,d*]furan and normal long-chain alkanes such as octacosane, eicosane, and so forth.⁹ McLaughlin et al. have studied the solid–liquid phase equilibria of binary and ternary mixtures of benzene, dibenzo[*b,d*]furan, and 9*H*-fluorene.^{10,11} The SLE of 9*H*-fluoren-9-one in undecane, *tert*-butyl, cyclohexane, diethyl ether, and supercritical fluid carbon dioxide has been studied by various researchers.^{8,12} However, there are limited number of papers that address the solubilities of dibenzo[*b,d*]furan and 9*H*-fluoren-9-one in solvents such as ethanol and tetrachloromethane, and so forth, which do not match the significance of the problem. In this work, solubility data of dibenzo[*b,d*]furan and 9*H*-fluoren-9-one in ethanol, butan-1-ol, ethyl ethanoate, methylbenzene, 2-isopropoxypropane, and tetrachloromethane have been measured from (283.15 to 333.15) K. All measured data were reproduced quantitatively by several different empirical equations and thermodynamic models. Moreover, three ternary phase diagrams including 9*H*-fluoren-9-one + 9*H*-fluorene + ethanol, 9*H*-fluoren-9-one + dibenzo[*b,d*]furan + ethanol, and 9*H*-fluoren-9-one + 1,2-dihydroacenaphthylene + ethanol were presented.

EXPERIMENTAL SECTION

Materials. The 1,2-dihydroacenaphthylene, dibenzo[*b,d*]furan, 9*H*-fluorene, and 9*H*-fluoren-9-one were obtained from Tianjin Kewei Chemical Reagents Co. Ltd., China, and recrystallized twice. Its purity, determined by gas chromatography (FID, Agilent, GC6820) equipped with a phenyl methyl silicone capillary column, was better than 0.995 mole fraction. Ethanol, butan-1-ol, ethyl ethanoate, methylbenzene, 2-

Received: January 15, 2012

Accepted: March 19, 2012

Published: March 26, 2012

Table 1. Physical Properties of Solutes and Solvents

compounds	T_i/K		$\Delta_{fus}H$	$V_i^{a,b}$	δ^b
	lit.	this work	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$(\text{J}\cdot\text{cm}^{-3})^{1/2}$
dibenzo[<i>b,d</i>]furan	355.70 ^c	355.54	18.60 ^c	152.5 ^c	20.41 ^c
9 <i>H</i> -fluoren-9-one	356.40 ^c	356.27	18.12 ^d	144.83 ^d	21.55 ^{d,e}
ethanol ^{f,g}				63.95	24.81
butan-1-ol ^{f,g}				98.77	22.36
ethyl ethanoate ^{f,g}				106.99	17.46
methylbenzene ^{f,g}				113.76	17.55
2-isopropoxypropane ^{f,g,h}				84.21	18.61
tetrachloromethane ^{f,g}				104.08	16.82

^aTaken from ref 21. ^bTaken from ref 22. ^cTaken from ref 23. ^dTaken from ref 24. ^eTaken from ref 25. ^fTaken from ref 26. ^gTaken from ref 27. ^hTaken from ref 28.

isopropoxypropane, and tetrachloromethane (purchased from Tianjin Damao Chemical Reagent Co., China) used for experiments were of analytical reagent grade and used without further purification. Their purities were better than 0.995 mole fraction. Distilled deionized water was used.

Apparatus and Procedure. The solubilities of 9*H*-fluoren-9-one and dibenzo[*b,d*]furan were measured by the isothermal method under the pressure of 101.32 kPa. The solubility was determined using an apparatus similar to that described in the literature and described only briefly here.¹³ A 50 mL sealed jacked vessel was used to determine the solubility. The temperature was controlled to be constant (fluctuates within ± 0.05 K) by a thermostatted bath. A mercury-in-glass thermometer with an uncertainty of ± 0.05 K was inserted into the inner chambers of the vessels to measure the solution temperature. The dissolution of the solute was examined by the laser beam penetrating the vessel. To prevent the evaporation of the solvent, a condenser vessel was introduced. The masses of the solutes and solvents were weighed using an analytical balance (Metler Toledo AB204-N, Switzerland) with an accuracy of ± 0.0001 g.

The method is based on adding excess solute to a stirred solution kept at a fixed temperature for at least 24 h. After the stirring was stopped, the suspension was allowed to settle for 4 h to allow complete sedimentation of the fine crystals. Three samples of about 10 mL each were carefully withdrawn from the clear solution and then filtered by a 0.45 μm PTFE filter. The weighed samples of saturated solutions were analyzed using a gas chromatograph with a flame ionization detector. All of the experiments were repeated three times at each temperature, and estimated uncertainties of the values were tested covering the entire temperature range. The experimental uncertainties of the ethanol and butan-1-ol systems and the ethyl ethanoate, methylbenzene, 2-isopropoxypropane, and tetrachloromethane systems are estimated to be $\pm 6\%$ and $\pm 3\%$ mass fraction, respectively.

Ternary phase diagrams of 9*H*-fluoren-9-one with 9*H*-fluorene, dibenzo[*b,d*]furan, and 1,2-dihydroacnaphthylene in ethanol at 303.15 K were measured using the same procedure mentioned above, respectively.¹⁴

DATA ANALYSIS

The temperature dependence of thermodynamic properties can be correlated by the following semiempirical equation and models deduced from the solid–liquid phase equilibrium.

Apelblat Solubility Model. The solubility data of 9*H*-fluoren-9-one and dibenzo[*b,d*]furan in solution is expressed by Apelblat equation:^{4,13}

$$\ln x_1 = A + \frac{B}{T/K} + C \ln(T/K) \quad (1)$$

where x_1 is the mole fraction of that compound, T is the absolute temperature (K), and A , B , and C are the model parameters. The average absolute relative deviation (AAD) is calculated by eq 2,^{5,6} which is defined as follows:

$$\text{AAD}_1 = \frac{100}{n} \sum \left| \frac{x_1^{\text{exp},i} - x_1^{\text{cal},i}}{x_1^{\text{exp},i}} \right| \quad (2)$$

where $x_1^{\text{exp},i}$ and $x_1^{\text{cal},i}$ denote the experimental and calculated value of solubility, respectively. The superscript i represents the number of experiment, and n is the number of experimental points.

The solubility data can also be used to evaluate the activity coefficient of dibenzo[*b,d*]furan and 9*H*-fluoren-9-one in the solution. In the case of no solid–solid transition occurring in the experimental temperature range, the solid–liquid equilibrium of binary systems can be calculated using a simplified thermodynamic relation reported by Cheon et al.^{15–17}

$$\ln x_i = -\frac{\Delta_{fus}H_i}{RT} \left(1 - \frac{T}{T_{fus,i}} \right) \quad (3)$$

where γ_i , $\Delta_{fus}H_i$, and $T_{fus,i}$ denote the activity coefficient, the molar enthalpy of fusion, and the melting temperature of pure component i , respectively.

Usually, the nonideality of the liquid phase should be taken into account when calculating the activity coefficient; thus some models were used for correlation of the activity coefficients.¹⁶ In our study, two different models were proposed.

Scatchard–Hildebrand Regular Solution Model. The Scatchard–Hildebrand regular solution model was widely used to calculate the activity coefficient of PAHs in single solvent^{18,19}

$$\ln \gamma_i = V_i(1 - \varphi_i) \frac{[(\delta_1 - \delta_2)^2 + 2l_{12}\delta_1\delta_2]}{R(T/K)} \quad (4)$$

where V_i , φ_i , and l_{12} denote the molar liquid volume, volume fraction, and adjustable binary parameter for the pure components, respectively. The solubility parameters δ_i are the

Table 2. Comparison of the Experimental and the Calculated Data of Dibenzo[*b,d*]furan in Different Solvents^a

T/K	x_1	x_1^{AP}	γ_1^{exp}	regular solution		NRTL	
				γ_1^{S-H}	$\Delta\%$	γ_1^{NRTL}	$\Delta\%$
Ethanol							
283.15	0.0211	0.0192	9.458	10.07	6.467	9.461	0.026
288.15	0.0271	0.0248	8.446	9.079	7.493	8.637	2.256
293.15	0.0322	0.0322	8.115	8.305	2.331	7.988	1.560
298.15	0.0414	0.0422	7.173	7.338	2.285	7.178	0.068
303.15	0.0489	0.0558	6.873	6.634	3.483	6.582	4.240
308.15	0.0707	0.0743	5.359	5.369	0.203	5.488	2.400
313.15	0.1023	0.0994	4.158	4.167	0.212	4.399	5.812
318.15	0.1341	0.1340	3.549	3.359	5.348	3.633	2.357
323.15	0.1971	0.1816	2.692	2.435	9.559	2.694	0.067
328.15	0.2831	0.2474	2.083	1.794	13.89	1.990	4.461
333.15	0.3341	0.3385	1.955	1.568	19.81	1.731	11.44
Butan-1-ol							
283.15	0.0281	0.0276	7.103	7.135	0.452	7.273	2.401
288.15	0.0326	0.0326	7.022	6.697	4.618	6.814	2.951
293.15	0.0421	0.0397	6.207	6.133	1.192	6.187	0.309
298.15	0.0531	0.0500	5.593	5.594	0.0181	5.599	0.122
303.15	0.0671	0.0649	5.010	5.047	0.755	5.011	0.029
308.15	0.0877	0.0865	4.320	4.435	2.665	4.361	0.960
313.15	0.1068	0.1184	3.984	3.962	0.536	3.875	2.734
318.15	0.1664	0.1659	2.861	3.032	5.992	2.920	2.076
323.15	0.2301	0.2379	2.306	2.395	3.847	2.296	0.400
328.15	0.3638	0.3482	1.621	1.676	3.386	1.613	0.472
333.15	0.5141	0.5197	1.271	1.296	1.971	1.265	0.469
Ethyl Ethanoate							
283.15	0.1455	0.1359	1.371	1.383	0.827	1.429	4.294
288.15	0.1679	0.1657	1.363	1.346	1.304	1.388	1.885
293.15	0.1989	0.1998	1.313	1.302	0.901	1.340	2.094
298.15	0.2315	0.2383	1.289	1.262	1.622	1.296	0.578
303.15	0.2685	0.2813	1.251	1.223	2.275	1.253	0.206
308.15	0.3277	0.3289	1.156	1.174	1.519	1.198	3.637
313.15	0.3872	0.3806	1.098	1.134	3.163	1.152	5.006
318.15	0.4411	0.4371	1.069	1.104	2.281	1.119	4.726
323.15	0.5017	0.4977	1.057	1.077	1.793	1.089	3.033
328.15	0.5651	0.5622	1.044	1.055	1.046	1.063	1.889
333.15	0.6249	0.6304	1.045	1.038	0.704	1.044	0.016
Methylbenzene							
283.15	0.1577	0.1553	1.265	1.228	2.992	1.300	2.781
288.15	0.1855	0.1868	1.234	1.203	2.479	1.266	2.656
293.15	0.2231	0.2221	1.171	1.175	0.354	1.228	4.905
298.15	0.2656	0.2613	1.118	1.148	2.691	1.191	6.588
303.15	0.3013	0.3043	1.115	1.128	1.109	1.164	4.458
308.15	0.3437	0.3510	1.102	1.107	0.438	1.137	3.207
313.15	0.3991	0.4012	1.066	1.085	1.744	1.107	3.911
318.15	0.4547	0.4548	1.046	1.066	1.807	1.083	3.564
323.15	0.5145	0.5114	1.031	1.049	1.712	1.061	3.003
328.15	0.5817	0.5707	1.013	1.034	2.021	1.043	2.967
333.15	0.6238	0.6323	1.047	1.027	1.973	1.033	1.297
2-Isopropoxypropane							
283.15	0.0838	0.0834	2.381	2.452	2.961	2.362	0.801
288.15	0.1042	0.1035	2.196	2.264	3.052	2.213	0.810
293.15	0.1302	0.1278	2.007	2.072	3.243	2.058	2.579
298.15	0.1548	0.1571	1.918	1.921	0.106	1.932	0.742
303.15	0.1832	0.1922	1.834	1.778	3.074	1.809	1.325
308.15	0.2366	0.2340	1.602	1.583	1.138	1.633	1.976
313.15	0.2845	0.2837	1.495	1.451	2.951	1.508	0.890
318.15	0.3411	0.3426	1.395	1.335	4.334	1.392	0.210
323.15	0.4119	0.4121	1.288	1.231	4.487	1.281	0.487
328.15	0.5081	0.4938	1.161	1.136	2.119	1.174	1.204

Table 2. continued

T/K	x_1	x_1^{AP}	γ_1^{exp}	regular solution		NRTL	
				γ_1^{S-H}	$\Delta\%$	γ_1^{NRTL}	$\Delta\%$
2-Isopropoxypropane							
333.15	0.5798	0.5896	1.128	1.088	3.414	1.117	0.903
Tetrachloromethane							
283.15	0.1339	0.1335	1.491	1.505	0.984	1.499	0.545
288.15	0.1614	0.1591	1.418	1.444	1.854	1.444	1.876
293.15	0.1913	0.1888	1.366	1.387	1.590	1.392	1.965
298.15	0.2158	0.2228	1.376	1.345	2.240	1.353	1.609
303.15	0.2639	0.2619	1.273	1.280	0.507	1.292	1.526
308.15	0.3066	0.3065	1.235	1.231	0.351	1.245	0.857
313.15	0.3542	0.3573	1.201	1.186	1.222	1.201	0.038
318.15	0.4119	0.4148	1.155	1.142	1.123	1.157	0.198
323.15	0.4914	0.4798	1.080	1.096	1.552	1.109	2.730
328.15	0.5479	0.5530	1.076	1.071	0.471	1.082	0.581
333.15	0.6348	0.6352	1.029	1.042	1.292	1.050	2.065

x_1^{AP} and x_1^{AP} are the experimental solubilities and calculated solubilities of the Apelblat equation, respectively. γ_1^{exp} , γ_1^{S-H} , and γ_1^{NRTL} are the experimental activity coefficients and calculated activity coefficients based on the regular solution equation and the NRTL equation, respectively.

square root of the cohesive-energy densities and can be defined as

$$\delta_i = \left[\frac{E_V}{V_i} \right]^{1/2} \quad (5)$$

where E_V is the internal energy change for component i upon going from the liquid to the ideal gas state.

The solubility parameters of PAHs and solvent can be obtained from literature.^{20–27} While the solubility parameters of PAHs can be used directly, those of solvent need to be calibrated using the “floating datum point method” reported by Choi and McLaughlin concerning the improved accuracy.^{27,28} The calculated results are listed in Table 1.

NRTL Model. The NRTL equation with two parameters was also applied to represent the activity coefficients of the solutes.⁵ According to the NRTL equation, the activity coefficient is given by

$$\ln \gamma_i = x_j^2 \left[\frac{G_{ji}^2 \tau_{ji}}{(x_i + x_j G_{ji})^2} + \frac{G_{ij} \tau_{ij}}{(x_j + x_i G_{ij})^2} \right] \quad (6)$$

with

$$G_{ji} = \exp \left(\frac{-\alpha_{ji}(g_{ji} - g_{ij})}{R(T/K)} \right) \quad (7)$$

where parameter α_{ji} is a measure of the nonrandomness of the mixture, which can be arbitrarily set from 0.20 to 0.47 and is generally taken as 0.3 for organic compounds.¹⁷ The adjustable binary parameter l_{12} in the regular solution model and parameters of $(g_{12} - g_{22})$ and $(g_{21} - g_{11})$ in the NRTL model were obtained by minimizing the objective function F_{obj} over the entire composition range

$$F_{obj} = \sum_{j=1}^m (\gamma_1^{exp,i} - \gamma_1^{cal,i})^2 \quad (8)$$

The percentage deviations ($\Delta\%$) of the values from the experimental results is defined as

$$\Delta\% = 100 \cdot \left| \frac{\gamma_1^{exp,i} - \gamma_1^{cal,i}}{\gamma_1^{exp,i}} \right| \quad (9)$$

where $\gamma_1^{exp,i}$ is the experimental value and $\gamma_1^{cal,i}$ is the calculated value.

The following equation of average absolute relative deviation (AAD) is also used to compare the deviations calculated by the regular solution model and NRTL model.

$$AAD_2 = \frac{100}{n} \sum \left| \frac{\gamma_1^{exp,i} - \gamma_1^{cal,i}}{\gamma_1^{exp,i}} \right| \quad (10)$$

RESULTS AND DISCUSSION

Binary Phase Equilibrium of Dibenzo[*b,d*]furan and 9*H*-fluoren-9-one. The solubilities of 9*H*-fluoren-9-one and dibenzo[*b,d*]furan in solvents were measured using the isothermal method from (283.15 to 333.15) K, and the results are listed in Tables 2 and 3.

As indicated in Tables 2 and 3, solubilities of 9*H*-fluoren-9-one and dibenzo[*b,d*]furan in all solvents increase with increasing temperature. Among which, methylbenzene and ethyl ethanoate have more capacity to dissolve the dibenzo[*b,d*]furan and 9*H*-fluoren-9-one. As to methylbenzene, the higher solubility can be attributed to the similar molecular structure, while ethyl ethanoate is due to the intermolecular hydrogen bond interaction. Referring to the molecular packing mode of dibenzo[*b,d*]furan and 9*H*-fluoren-9-one,^{29,30} the ethyl ethanoate can form intermolecular hydrogen bonds between the oxygen atom of solute molecules and hydrogen atom of solvent in solution,³¹ and thus the solubilities of dibenzo[*b,d*]furan and 9*H*-fluoren-9-one in ethyl ethanoate are quite high.

Table 4 shows the model parameters and AAD_1 regressed from Apelblat model. As shown in Table 4, the AAD_1 values verify that Apelblat model provide an accurate mathematical representation for the solubilities of dibenzo[*b,d*]furan and 9*H*-fluoren-9-one in different solvents.

The experimental and the calculated activity coefficients using the regular solution model and NRTL model are also

Table 3. Comparison of the Experimental and the Calculated Thermodynamic Data of 9H-Fluoren-9-one in Different Solvents^a

T/K	x_1	x_1^{AP}	γ_1^{exp}	regular solution		NRTL	
				γ_1^{S-H}	$\Delta\%$	γ_1^{NRTL}	$\Delta\%$
Ethanol							
283.15	0.0209	0.0163	9.835	9.746	0.902	10.31	4.911
288.15	0.0241	0.0237	9.748	9.074	6.919	9.583	1.691
293.15	0.0301	0.0344	8.880	8.248	7.112	8.659	2.483
298.15	0.0430	0.0495	7.041	7.083	0.601	7.338	4.228
303.15	0.0562	0.0710	6.088	6.146	0.924	6.311	3.671
308.15	0.0976	0.1014	3.932	4.408	12.10	4.407	12.09
313.15	0.1445	0.1444	2.973	3.266	9.845	3.216	8.184
318.15	0.2074	0.2046	2.311	2.406	4.098	2.346	1.534
323.15	0.2923	0.2889	1.823	1.795	1.527	1.745	4.290
328.15	0.4087	0.4064	1.445	1.388	3.942	1.352	6.393
333.15	0.5479	0.5694	1.191	1.163	2.294	1.143	4.027
Butan-1-ol							
283.15	0.0267	0.0253	7.421	7.257	2.206	7.810	5.244
288.15	0.0321	0.0320	7.319	6.836	6.595	7.234	1.155
293.15	0.0402	0.0411	6.649	6.323	4.901	6.593	0.835
298.15	0.0498	0.0532	6.080	5.822	4.239	5.981	1.628
303.15	0.0685	0.0695	4.986	5.140	3.079	5.146	3.200
308.15	0.0848	0.0916	4.635	4.671	0.768	4.556	1.707
313.15	0.1261	0.1217	3.411	3.764	10.35	3.577	4.860
318.15	0.1622	0.1626	2.955	3.194	8.081	2.985	1.029
323.15	0.2362	0.2188	2.256	2.449	8.150	2.238	0.796
328.15	0.3108	0.2961	1.901	1.959	3.087	1.797	5.471
333.15	0.3998	0.4028	1.632	1.596	2.190	1.482	9.220
Ethyl Ethanoate							
283.15	0.1235	0.1239	1.664	1.670	0.343	1.696	1.902
288.15	0.1418	0.1474	1.656	1.611	2.725	1.636	1.219
293.15	0.1731	0.1749	1.544	1.533	0.793	1.554	0.628
298.15	0.2214	0.2070	1.369	1.434	4.713	1.452	6.070
303.15	0.2436	0.2445	1.402	1.390	0.857	1.408	0.443
308.15	0.2843	0.2880	1.350	1.326	1.743	1.343	0.528
313.15	0.3351	0.3385	1.278	1.261	1.412	1.275	0.173
318.15	0.3951	0.3971	1.213	1.200	1.102	1.212	0.090
323.15	0.4652	0.4647	1.145	1.144	0.167	1.153	0.7260
328.15	0.5479	0.5427	1.0781	1.094	1.490	1.101	2.130
333.15	0.6301	0.6325	1.035	1.058	2.168	1.063	2.697
Methylbenzene							
283.15	0.1202	0.1183	1.710	1.787	4.527	1.775	3.828
288.15	0.1422	0.1407	1.652	1.710	3.489	1.721	4.162
293.15	0.1636	0.1666	1.633	1.642	0.478	1.670	2.294
298.15	0.1974	0.1962	1.533	1.555	1.211	1.603	4.592
303.15	0.2281	0.2302	1.497	1.484	0.892	1.546	3.285
308.15	0.2639	0.2689	1.454	1.415	2.745	1.486	2.217
313.15	0.3153	0.3127	1.362	1.333	2.169	1.412	3.657
318.15	0.3707	0.3624	1.293	1.262	2.416	1.341	3.717
323.15	0.4101	0.4183	1.299	1.218	6.265	1.294	0.349
328.15	0.4855	0.4811	1.216	1.153	5.214	1.221	0.371
333.15	0.5498	0.5515	1.187	1.110	6.495	1.167	1.711
2-Isopropoxypropane							
283.15	0.0297	0.0298	6.921	7.444	7.552	6.989	0.985
288.15	0.0356	0.0356	6.599	6.907	4.664	6.538	0.917
293.15	0.0426	0.0431	6.274	6.384	1.754	6.098	2.802
298.15	0.0541	0.0530	5.596	5.760	2.925	5.571	0.452
303.15	0.0642	0.0660	5.321	5.271	0.933	5.153	3.159
308.15	0.0815	0.0831	4.709	4.658	1.108	4.624	1.807
313.15	0.1081	0.1059	3.975	3.964	0.286	4.013	0.962
318.15	0.1374	0.1364	3.489	3.386	2.942	3.491	0.0540
323.15	0.1801	0.1773	2.959	2.792	5.664	2.934	0.841
328.15	0.2277	0.2326	2.594	2.328	10.25	2.482	4.305

Table 3. continued

T/K	x_1	x_1^{AP}	γ_1^{exp}	regular solution		NRTL	
				γ_1^{S-H}	$\Delta\%$	γ_1^{NRTL}	$\Delta\%$
2-Isopropoxypropane							
333.15	0.3091	0.3075	2.111	1.829	13.36	1.970	6.663
Tetrachloromethane							
283.15	0.1141	0.1066	1.801	1.791	0.617	1.823	1.191
288.15	0.1418	0.1342	1.656	1.692	2.148	1.720	3.830
293.15	0.1583	0.1664	1.688	1.635	3.185	1.661	1.624
298.15	0.1924	0.2033	1.573	1.543	1.936	1.565	0.498
303.15	0.2411	0.2450	1.416	1.438	1.555	1.457	2.846
308.15	0.2912	0.2915	1.318	1.352	2.539	1.367	3.684
313.15	0.3472	0.3426	1.237	1.274	2.903	1.286	3.897
318.15	0.4030	0.3950	1.189	1.211	1.823	1.221	2.677
323.15	0.4624	0.4573	1.152	1.158	0.496	1.167	1.211
328.15	0.5191	0.5201	1.137	1.118	1.741	1.125	1.150
333.15	0.5821	0.5858	1.121	1.083	3.401	1.088	2.938

x_1^{AP} and x_1^{AP} are the experimental solubilities and calculated solubilities of the Apelblat equation, respectively. γ_1^{exp} , γ_1^{S-H} , and γ_1^{NRTL} are the experimental activity coefficients and calculated activity coefficients based on the regular solution equation and NRTL equation, respectively.

Table 4. Curve-Fitting Parameters of Dibenzo[*b,d*]furan and 9*H*-Fluoren-9-one in Solution from (283.15 to 333.15) K Regressed by the Apelblat Model

solvent	A	B	C	AAD ₁
Dibenzo[<i>b,d</i>]furan				
ethanol	-403.9998	13713.5065	62.2785	5.703
butan-1-ol	-893.2039	35912.8812	135.1018	3.447
ethyl ethanoate	118.9662	-7943.9380	-16.4554	1.927
methylbenzene	122.5675	-7894.9178	-17.1002	1.072
2-isopropoxypropane	-42.0351	-1291.9995	7.8134	1.421
tetrachloromethane	-16.0800	-1827.6751	3.6346	1.091
9 <i>H</i> -Fluoren-9-one				
ethanol	-169.4695	1913.6055	28.0898	8.176
butan-1-ol	-418.4545	14531.6475	64.3746	3.664
ethyl ethanoate	-68.0206	424.7422	11.4120	1.486
methylbenzene	-14.4264	-1876.8445	3.3511	1.282
2-isopropoxypropane	-469.6882	17558.7857	71.5842	1.399
tetrachloromethane	182.5350	-11121.2581	-25.7700	2.633

Table 5. Regressed Parameters of Dibenzo[*b,d*]furan and 9*H*-Fluoren-9-one in Solution from (283.15 to 333.15) K Correlated by the Regular Solution Equation and NRTL Equation

solvent	regular solution		NRTL		AAD ₂
	l_{12}	AAD ₂	$g_{12} - g_{22}$	$g_{21} - g_{11}$	
Dibenzo[<i>b,d</i>]furan					
ethanol	0.0198	6.463	-54.2940	5837.9824	3.154
butan-1-ol	0.0321	2.312	72.0683	5129.6926	1.175
ethyl ethanoate	-0.00128	1.574	-683.8106	2046.0248	2.488
methylbenzene	-0.0045	1.757	-895.8959	2011.3019	3.576
2-isopropoxypropane	0.0205	2.807	-165.7635	2764.8616	1.085
tetrachloromethane	-0.00494	1.199	-333.4505	1722.4367	1.272
9 <i>H</i> -Fluoren-9-one					
ethanol	0.0281	4.257	-856.1664	7098.7418	4.864
butan-1-ol	0.0356	4.877	-108.6088	5505.0410	3.195
ethyl ethanoate	-0.00652	1.592	-334.7575	2116.8005	1.510
methylbenzene	-0.00395	3.264	1944.5286	145.4440	2.744
2-isopropoxypropane	0.0343	4.678	959.1489	4176.1191	2.086
tetrachloromethane	-0.0127	2.032	-423.4125	2432.4941	2.322

listed in Tables 2 and 3. It can be noticed that the activity coefficients of dibenzo[*b,d*]furan and 9*H*-fluoren-9-one in ethanol and butan-1-ol are rather high, which are similar with the results presented in literature.¹⁹ As to the higher deviations

obtained in the systems with ethanol and butan-1-ol shown in Tables 2 and 3, it is because of the different molecular structure, dibenzo[*b,d*]furan and 9*H*-fluoren-9-one are nonpolar materials, while ethanol and butan-1-ol exhibit a polar specialty.

Table 5 shows the adjustable binary parameter l_3 in the regular solution model, parameters of $(g_{12} - g_{22})$ and $(g_{21} - g_{11})$ in the NRTL model and AAD_2 . As shown, both the regular solution theory and the NRTL model can be used to calculate the activity coefficients of dibenzo[*b,d*]furan and 9*H*-fluoren-9-one in different solvents with AAD_2 lower than 7%. Comparing the percentage deviations and AAD_2 obtained by two different models, it can be clearly noticed that the regular solution model is more suitable for the correlation of dibenzo[*b,d*]furan in ethyl ethanoate, methylbenzene, tetrachloromethane, and 9*H*-fluoren-9-one in ethanol and tetrachloromethane and the NRTL model for the other systems.

Ternary Phase Equilibrium of 9*H*-Fluoren-9-one + PHAs + Ethanol. The experimental data of three ternary phase

Table 6. Mass Fraction Solubilities of the Ternary System of 9*H*-Fluoren-9-one (1) + Dibenzo[*b,d*]furan (2) + Ethanol (3) at 303.15 K

9 <i>H</i> -fluoren-9-one	dibenzo[<i>b,d</i>]furan	9 <i>H</i> -fluoren-9-one	dibenzo[<i>b,d</i>]furan
9 <i>H</i> -Fluoren-9-one Saturation Curve			
0.1889	0.0000	0.2231	0.2261
0.1703	0.0373	0.2314	0.2413
0.1610	0.0736	0.2429	0.2593
0.1701	0.0981	0.2567	0.2779
0.1815	0.1347	0.2751	0.2953
0.1955	0.1584	0.2914	0.3140
0.2032	0.1842	0.3028	0.3358
0.2131	0.2095	0.3065	0.3597
Dibenzo[<i>b,d</i>]furan Saturation Curve			
0.000	0.1580	0.1938	0.3001
0.0340	0.1664	0.2080	0.3070
0.0573	0.1829	0.2271	0.3249
0.0878	0.2134	0.2511	0.3365
0.1213	0.2418	0.2691	0.3473
0.1555	0.2706	0.2896	0.3564
0.1792	0.2861	0.3065	0.3597

systems including dibenzo[*b,d*]furan and 9*H*-fluoren-9-one + ethanol, 9*H*-fluoren-9-one + 9*H*-fluorene + ethanol, and 9*H*-fluoren-9-one + 1,2-dihydroacenaphthylene + ethanol are

Table 7. Mass Fraction Solubilities of the Ternary System of 9*H*-Fluoren-9-one (1) + 9*H*-Fluorene (2) + Ethanol (3) at 303.15 K

9 <i>H</i> -fluoren-9-one	9 <i>H</i> -fluorene	9 <i>H</i> -fluoren-9-one	9 <i>H</i> -fluorene
9 <i>H</i> -Fluoren-9-one Saturation Curve			
0.1889	0.0000	0.1966	0.0601
0.1812	0.0145	0.2051	0.0644
0.1817	0.0256	0.2124	0.0651
0.1855	0.0335	0.2213	0.0702
0.1853	0.0472	0.2248	0.0763
0.1879	0.0556	0.2261	0.0886
9 <i>H</i> -Fluorene Saturation Curve			
0.0000	0.1123	0.1473	0.0918
0.0217	0.1054	0.1629	0.0944
0.0399	0.0910	0.1766	0.0917
0.0612	0.0838	0.1868	0.0914
0.0853	0.0834	0.2027	0.0915
0.1121	0.0848	0.2155	0.0897
0.1317	0.0894	0.2261	0.0886

Table 8. Mass Fraction Solubilities of the Ternary System of 9*H*-Fluoren-9-one (1) + 1,2-Dihydroacenaphthylene (2) + Ethanol (3) at 303.15 K

9 <i>H</i> -fluoren-9-one	1,2-dihydroacenaphthylene	9 <i>H</i> -fluoren-9-one	1,2-dihydroacenaphthylene
9 <i>H</i> -Fluoren-9-one Saturation Curve			
0.1889	0.0000	0.2141	0.1007
0.1831	0.0176	0.2201	0.1145
0.1825	0.0286	0.2325	0.1255
0.1798	0.0414	0.2399	0.1350
0.1855	0.0545	0.2466	0.1464
0.1996	0.0803		
1,2-Dihydroacenaphthylene Saturation Curve			
0.0000	0.0609	0.1726	0.1313
0.0455	0.0807	0.1912	0.1366
0.0834	0.0954	0.2052	0.1421
0.1109	0.1073	0.2213	0.1438
0.1284	0.1164	0.2466	0.1464
0.1505	0.1266		

shown in Tables 6, 7, and 8 and plotted in Figures 1, 2, and 3, respectively.

As shown in Figures 1, 2, and 3, these three ternary phase diagrams are all simple eutectic systems and similar to diagrams

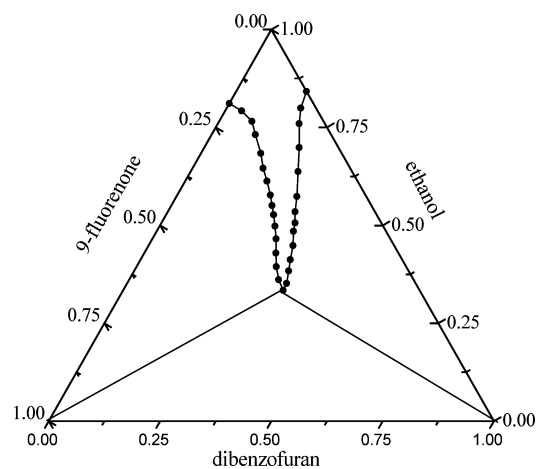


Figure 1. Ternary phase diagram of the 9*H*-fluoren-9-one + dibenzo[*b,d*]furan + ethanol at 303.15 K.

given by McLaughlin et al.³² Furthermore, the phase diagram can be divided into three distinct crystallization fields (9*H*-fluoren-9-one, PHAs, and a mixture of 9*H*-fluoren-9-one + PHAs), and then, these impurities can be easily isolated from 9*H*-fluoren-9-one.^{3,32}

In the 9*H*-fluoren-9-one (1) + dibenzo[*b,d*]furan (2) + ethanol (3) system, the invariant points of dibenzo[*b,d*]furan and 9*H*-fluoren-9-one are much larger than its solubility in ethanol. The mole fraction at the invariant point of dibenzo[*b,d*]furan is 0.1931, and the solubility is 0.0489 at 303.15 K. The mole fraction at the invariant point of 9*H*-fluoren-9-one is 0.1535, and the solubility is 0.0562 at 303.15 K. Further, when using the mole ratios of 9*H*-fluoren-9-one/ethanol to explain this phenomenon, it can be found that the dibenzo[*b,d*]furan in the system can improve the mole ratios of 9*H*-fluoren-9-one/ethanol. Figure 4 showed the tendency of the increasing mole ratios of 9*H*-fluoren-9-one/ethanol with increasing the mole fraction of dibenzo[*b,d*]furan. This phenomenon also can be

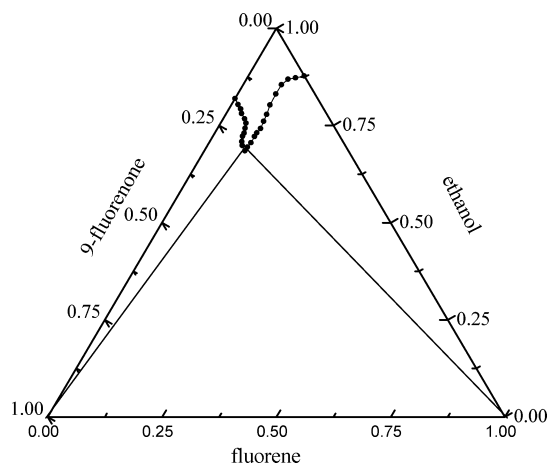


Figure 2. Ternary phase diagram of the 9H-fluoren-9-one + 9H-fluorene + ethanol at 303.15 K.

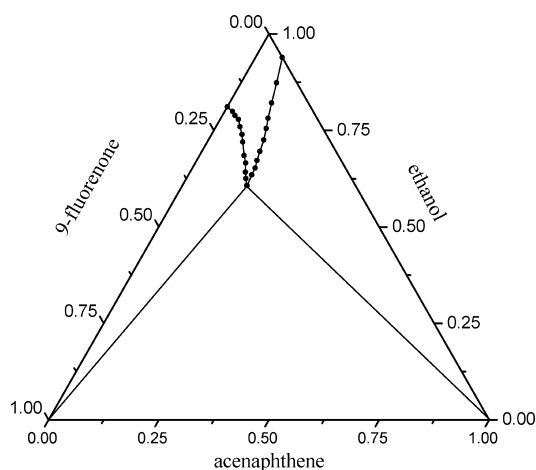


Figure 3. Ternary phase diagram of the 9H-fluoren-9-one + 1,2-dihydroacenaphthylene + ethanol at 303.15 K.

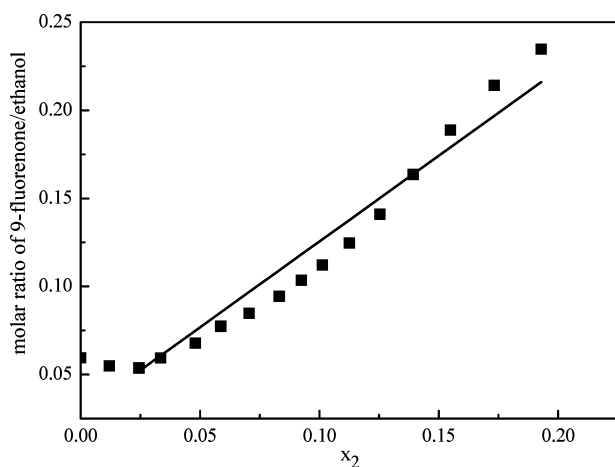


Figure 4. Mole ratio of 9H-fluoren-9-one/ethanol depends on the mole fraction of dibenzo[*b,d*]furan in the 9H-fluoren-9-one (1) + dibenzo[*b,d*]furan (2) + ethanol (3) system; the solid line is the trend line.

found for some PAHs in supercritical fluids.³³ It can be explained by the interaction of dibenzo[*b,d*]furan and 9H-fluoren-9-one.^{31,34} Referring to the space packing of unit cell of dibenzo[*b,d*]furan and 9H-fluoren-9-one,^{29,30} intermolecular

hydrogen bonds can be formed between dibenzo[*b,d*]furan and 9H-fluoren-9-one molecules, which changes the electron density of 9H-fluoren-9-one molecules, and consequently enhances its solubility in ethanol.

CONCLUSIONS

Solubilities of 9H-fluoren-9-one and dibenzo[*b,d*]furan in ethanol, butan-1-ol, ethyl ethanoate, methylbenzene, 2-isopropoxypropane, and tetrachloromethane were measured from (283.15 to 333.15) K. Three models including Apelblat, regular-solution, and NRTL were used to correlate the phase equilibrium of these binary systems. All experimental data are in good agreement with models. In addition, three ternary phase diagrams of 9H-fluoren-9-one + PAHs + ethanol were also measured. The results show that all systems are simple eutectic systems and the invariant points of dibenzo[*b,d*]furan and 9H-fluoren-9-one in the 9H-fluoren-9-one + dibenzo[*b,d*]furan + ethanol system were mainly affected by the intermolecular forces.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +86-22-27405754. Fax: +86-22-27400287. E-mail address: david.wei@tju.edu.cn (H.-Y.W.).

Funding

We thank the National High Technology Research and Development Program of China (Key 863 Program; No. 2009AA063303), Tianjin Municipal Natural Science Foundation (11JCYBJC 04600), and Seed Foundation of Tianjin University for their financial assistance in this project.

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Dean, F. M. *Naturally Occurring Oxygen Ring Compounds*; Butterworth: London, 1963.
- (2) Choudhry, G. G.; Hutzinger, O. Mechanistic aspects of the thermal formation of halogenated organic compounds including polychlorinated dibenzo-p-dioxins 2. Thermochemical generation and destruction of dibenzofurans and dibenzo-p-dioxins. *Environ. Toxicol. Chem.* **1982**, *5*, 67–93.
- (3) Sediawan, W. B.; Gupta, S.; McLaughlin, E. Solid-liquid phase diagrams of binary aromatic hydrocarbon mixtures from calorimetric studies. *J. Chem. Eng. Data* **1989**, *34*, 223–226.
- (4) Zou, Z.; Dang, L. P.; Liu, P. B.; Wei, H. Y. Solubility of fluorene in different solvents from 278.98 to 338.35 K. *J. Chem. Eng. Data* **2007**, *52*, 1501–1502.
- (5) Lee, M. J.; Chen, C. H.; Lin, H. M. Solid-liquid equilibria for binary mixtures composed of acenaphthene, dibenzofuran, fluorene, phenanthrene, and diphenylmethane. *J. Chem. Eng. Data* **1999**, *44*, 1058–1062.
- (6) Lee, M. J.; Chen, C. H.; Lin, H. M. Fundamental study of the phase behavior of wash oil with diphenyl ether. *Ind. Eng. Chem. Res.* **2000**, *39*, 3097–3101.
- (7) Alsten, J. G.; Eckert, C. A. Effect of entrainers and of solute size and polarity in supercritical fluid solutions. *J. Chem. Eng. Data* **1993**, *38*, 605–610.
- (8) Pando, C.; Perez, E.; Cabanas, A.; Renuncio, J. A. R.; Sanchez-Vicente, Y. Cosolvent Effect of Methanol and Acetic Acid on Dibenzofuran Solubility in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2008**, *53*, 2649–2653.
- (9) Aoulmi, A.; Bouroukba, M.; Solimando, R.; Rogalski, M. Thermodynamics of Mixtures Formed by Polycyclic Aromatic-Hydrocarbons with Long-Chain Alkanes. *Fluid Phase Equilib.* **1995**, *110*, 283–297.

- (10) Domanska, U.; Groves, F. R.; McLaughlin, E. Solid-liquid phase equilibria of binary and ternary mixtures of benzene and polynuclear aromatic compounds. *J. Chem. Eng. Data* **1993**, *38*, 88–94.
- (11) Dawn, M. S.; Acree, W. E.; Abrahamb, M. H. Solubility of 9-fluorenone, thianthrene and xanthene in organic solvents. *Fluid Phase Equilib.* **2005**, *232*, 113–121.
- (12) Monarrez, C. I.; Stovall, D. M.; Woo, J. H.; Taylor, P.; Acree, W. E. Solubility of 9-fluorenone in organic nonelectrolyte solvents: Comparison of observed versus predicted values based upon mobile order theory. *Phys. Chem. Liq.* **2003**, *41*, 73–80.
- (13) Zhang, J. Y.; Dang, L. P.; Wei, H. Y. Solubility of 5-(Dithiolan-3-yl) pentanoic Acid in the Mixed Solvents of Cyclohexane plus Ethyl Acetate, Heptane plus Ethyl Acetate, and Hexane plus Ethyl Acetate. *J. Chem. Eng. Data* **2010**, *55*, 4025–4028.
- (14) Xu, S. M.; Dang, L. P.; Wei, H. Y. Solid-Liquid Phase Equilibrium and Phase Diagram for the Ternary Carbamazepine-Succinic Acid-Ethanol or Acetone System at (298.15 and 308.15) K. *J. Chem. Eng. Data* **2011**, *56*, 2746–2750.
- (15) Cheon, Y. H.; Kim, K. J.; Kim, J. W.; Kim, S. H. Solid-Liquid Phase Equilibria of Binary and Ternary Mixtures for 2,6-Dimethylnaphthalene and 2,7-Dimethylnaphthalene with Ethanol or Methanol. *J. Chem. Eng. Data* **2005**, *50*, 683–687.
- (16) Jakob, A.; John, R.; Rose, C.; Gmehling, J. Solid-Liquid Equilibria in Binary Mixtures of Organic Compounds. *Fluid Phase Equilib.* **1995**, *113*, 117–126.
- (17) Chen, S. N.; Xia, Q.; Lu, L. F.; Zhang, M. S.; Chen, Y. S.; Zhang, F. B.; Zhang, G. L. Measurement and Correlation of Solubilities of Decanedioic Acid in C₄-C₆ Alcohol Solvents. *J. Chem. Eng. Data* **2010**, *55*, 1411–1415.
- (18) Prausnitz, J. M.; Lichtenthaler, R. N. *Molecular Thermodynamics of Fluid Phase Equilibria*, Third ed.; Prentice Hall, NJ, 1999.
- (19) Choi, P. B.; Williams, Ch. P.; Buehring, K. G.; McLaughlin, E. Solubility of Aromatic Hydrocarbon Solids in Mixtures of Benzene and Cyclohexane. *J. Chem. Eng. Data* **1985**, *30*, 403–409.
- (20) Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van Nostrand Reinhold Company: New York, 1973.
- (21) Barton, A. F. M. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, 2nd ed.; CRC Press LLC: New York, 1991.
- (22) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 83rd ed.; CRC Press LLC: New York, 2002.
- (23) Gupta, A.; Groves, F. R.; McLaughlin, E. Isothermal Vapor-Liquid Equilibrium of Binary and Ternary Systems Composed of Heavy Aromatic Compounds. *J. Chem. Eng. Data* **1992**, *37*, 32–36.
- (24) Sabbah, R.; El, W. L.; Minadakis, C. Thermodynamic study of 9-fluorenone. *C. R. Acad. Sci. Paris* **1988**, *307*, 239–244.
- (25) Acree, W. E. Thermodynamic properties of organic compounds: enthalpy of fusion and melting point temperature compilation. *Thermochim. Acta* **1991**, *189*, 56.
- (26) Coon, J. E.; Sediawan, W. B.; Auwaerter, J. E.; McLaughlin, E. Solubilities of Families of Heterocyclic Polynuclear Aromatics in Organic Solvents and Their Mixtures. *J. Solution Chem.* **1988**, *17*, 519–534.
- (27) Domańska, U. Solubility of acetyl-substituted naphthols in binary solvent mixtures. *Fluid Phase Equilib.* **1990**, *55*, 125–145.
- (28) Wu, J. T.; Meng, X. Y.; Liu, Z. G. Viscosity and Density Measurements of Diisopropyl Ether and Dibutyl Ether at Different Temperatures and Pressures. *J. Chem. Eng. Data* **2009**, *54*, 2353–2358.
- (29) William, J. R.; Judith, C. G.; Alan, P. L.; Roger, E. G. Order and Disorder in the Structure of Dibenzofuran, C₁₂H₈₀. *Acta Crystallogr.* **1984**, *C40*, 1572–1576.
- (30) Henry, R. L.; Douglas, L. S. The Crystal and Molecular Structure of 9-Fluorenone. *Acta Crystallogr.* **1972**, *B28*, 884–887.
- (31) Anderko, A. Prediction of solid-liquid equilibria on the basis of pure compound properties. *Fluid Phase Equilib.* **1987**, *35*, 127–151.
- (32) Gupta, A.; Domanska, U.; Groves, F. R.; McLaughlin, E. Solid-liquid phase equilibria of ternary mixtures containing polynuclear aromatic compounds. *J. Chem. Eng. Data* **1994**, *39*, 175–178.
- (33) Ronald, T. K.; Robert, C. R. Solubility of solid mixtures in supercritical fluids. *Fluid Phase Equilib.* **1982**, *8* (1), 93–105.
- (34) Ruelle, P.; Buchmann, M.; Nam-Tran, H.; Kesselring, U. W. Enhancement of the solubilities of polycyclic aromatic hydrocarbons by weak hydrogen bonds with water. *J. Comput. Aided Mol. Des.* **1992**, *6*, 431–448.