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Solid−Liquid Equilibrium and Excess Enthalpy Measurements in Binary {Dibenzofuran or Xanthene + Normal Long-Chain Alkane} Systems

R. Mahmoud, R. Solimando, and M. Bouroukba

Laboratoire de Thermodynamique des Séparations, INPL-ENSIC, BP 451, 54001 Nancy Cédex, France

M. Rogalski*

Laboratoire de Thermodynamique et d'Analyze Chimique, Université de Metz, Ile du Saulcy, BP 80794, F-57012 Metz Cédex 01, France

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This paper is a continuation of our previous studies on thermodynamic properties of binary systems formed by a long-chain *n*-alkane and a polyaromatic. Solid−liquid equilibrium and enthalpies of mixing data of the following systems were measured: {dibenzofuran (DBF) (CASRN 132-64-9), $C_{12}H_8O$ + eicosane (CASRN 112-95-8), $C_{20}H_{42}$}, {DBF + pentacosane (CASRN 629-99-2), $C_{25}H_{52}$}, {DBF + octacosane (CASRN 630-02-4), $C_{28}H_{58}$}, {DBF + hexatriacontane (CASRN 630-08-6), $C_{36}H_{74}$}, {xanthene (CASRN 92-83-1), $C_{13}H_{10}O$ + eicosane}, {xanthene + octacosane}, {xanthene + hexatriacontane}. All data were correlated using the group contribution model based on the lattice theory of Kehiahian et al. (*J. Chim. Phys.* **1978**, *75*, 1032−1048).

Introduction

The flocculation of asphaltenes and their codeposition with *n*-alkanes constitute a major problem occurring during the exploitation, transport, and storage of the crude oil. Asphaltenes contain polyaromatic structures often substituted with oxygen, sulfur, or nitrogen. Therefore, thermodynamic properties of systems formed with polycyclic aromatics and long-chain *n*-alkanes can be helpful to understand the phase behavior of heavy oils. Recently, Aoulmi et al. (1995) and Mahmoud et al. (1998) reported solid−liquid equilibria (SLE) and enthalpies of mixing (H^E) of mixtures formed by polyaromatics and normal alkanes from octadecane to pentacosane. This paper is a continuation of the previous studies and presents SLE and H^E data of binaries composed of *n*-alkanes and dibenzofuran (DBF), $C_{12}H_8O$, or xanthene (XTH), $C_{13}H_{10}O$. Both polyaromatics contain oxygen atoms in the “ether position” inside the aromatic structure (see Figure 1).

The following systems were studied: {DBF + eicosane, $C_{20}H_{42}$}, {DBF + pentacosane, $C_{25}H_{52}$}, {DBF + octacosane, $C_{28}H_{58}$}, {DBF + hexatriacontane, $C_{36}H_{74}$}, {XTH + eicosane}, {XTH + octacosane}, and {XTH + hexatriacontane}.

Experimental Section

All chemicals were purchased from Aldrich Chemie and were used as delivered. Their purity was better than 99%, except *n*-hexatriacontane. The purity of the latter was better than 98%. Differential scanning calorimetry (DSC) thermograms were analyzed with a view of checking announced purities. Temperatures of fusion measured in this experiment are reported in Table 1 together with the values from the literature.

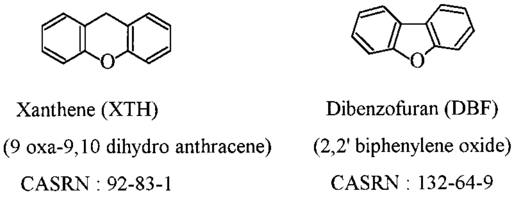

Figure 1. Developed formulas of aromatic compounds.

Enthalpy of Mixing. Enthalpies of mixing were measured using a SETARAM C80 calorimeter. The sensitivity of this calorimeter decreases slightly with temperature and is 31.5 μV/mW at 290 K and 29.5 μV/mW at 390 K. Measurements were performed at 371.9 K with mixtures containing DBF and at 391.8 K with XTH. All samples were liquid at these temperatures.

With a view of testing the reproducibility of the experiment, two series of measurements in the concentration range from 0.4 to 0.85 mole fraction were performed with the binary {9-fluorenone + octacosane} at 396.7 K. A relative mean deviation of about 1.3% was found between two data sets. This result is satisfactory with measurements performed at such a high temperature.

Experimental data of the enthalpy of mixing are reported in Table 2.

SLE Measurements. Mixtures of known concentrations were prepared by mass. Before each experiment a sample of about 50 mg was melted, and the liquid solution was rapidly cooled with liquid air to obtain a homogeneous solid mixture. SLE were determined using a DSC 111 of SETARAM. The detailed description of the experimental procedure was given elsewhere (Mahmoud, 1999; Mahmoud et al., 1998). The accuracy of the temperature measurements was of about 0.1 K.

The reproducibility of measurements was tested with the system pyrene + DBF. An average deviation of 0.3 K was found with results covering the entire composition range. Experimental SLE data are given in Table 3.

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Table 1. Thermodynamic Properties of Pure Components[j]

	T_{fus}/K		$\Delta_{fus}H$/(J·mol^{-1})		T_{tr}/K		$\Delta_{tr}H$/(J·mol^{-1})	
compound	exp.	lit.	exp.	lit.	exp.	lit.	exp.	lit.
eicosane	310.0	310.0[a]	69 880	69 880[a]				
		309.8[b]		69 870[b]				
pentacosane	326.0	326.1[c]	54 040	56 700[c]	319.3	319.4[c]	24 430	27 340[c]
		326.3[d]		56 610[d]		319.9[d]		25 230[d]
		326.7[e]		57 740[e]		320.2[e]		25 240[e]
octacosane	334.2	334.0[f]	64 600	66 520[f]	331.2	330.4[f]	35 460	33 660[f]
		333.6[a]		62 930[g]		330.1[g]		36 010[g]
		334.4[b]		64 640[b]		331.3[b]		35 440[b]
hexatriacontane	348.8	348.1[g]	91 330	82 730[g]	347.0	336.1[g]	30 560	37 970[g]
		349.1[h]		88 830[h]		347.0[h]		30 540[h]
dibenzofurane	355.2	355.7[i]	17 640	18 600[i]				
xanthen	374.3	373.7[i]	15 870	19 200[i]				

[a] Lide (1995). [b] Company (1973). [c] Provost (1997). [d] Bosselet et al. (1983). [e] Broadhurst (1962). [f] Domanska and Wyrzikowska-Stankiewicz (1991). [g] Fredricks (1986). [h] Schaerer et al. (1955). [i] Coon et al. (1989). [j] Other numerous data concerning n-alkanes can be found in Calange (1996).

Table 2. Excess Enthalpies of DBF (1) + n-Alkane (2) at T = 371.9 K and XTH (1) + n-Alkane (2) at T = 391.8 K

x_1	H^E/(J·mol^{-1})	x_1	H^E/(J·mol^{-1})	x_1	H^E/(J·mol^{-1})
		Dibenzofuran (1) + n-C20 (2)			
0.1004	276.5	0.3507	1061.5	0.7494	928.6
0.1498	440.0	0.4013	1140.1	0.7992	768.7
0.2000	643.8	0.5012	1246.7	0.8495	625.9
0.2506	843.2	0.5501	1246.7	0.8999	462.4
0.3019	982.7	0.6994	1017.3	0.9497	240.6
		Dibenzofuran (1) + n-C28 (2)			
0.0516	94.2	0.3250	905.0	0.7496	1096.9
0.1015	186.6	0.3497	978.5	0.8497	814.3
0.1528	398.0	0.4513	1153.9	0.8995	669.9
0.2038	590.0	0.5500	1305.5	0.9495	392.5
0.2500	735.3	0.6500	1300.4		
		Dibenzofuran (1) + n-C36 (2)			
0.1507	305.9	0.5000	1105.2	0.8997	994.9
0.2518	512.3	0.5993	1147.6	0.9500	371.1
0.4000	1066.7	0.7998	1387.6		
		Xanthene (1) + n-C20 (2)			
0.0516	200.0	0.4500	1206.7	0.7986	870.0
0.1024	445.6	0.5005	1223.5	0.8488	750.0
0.2014	680.0	0.6000	1162.5	0.8995	516.3
0.3015	910.0	0.6498	1100.0	0.9501	380.0
0.3502	1050.0	0.7004	1015.6		
		Xanthene (1) + n-C28 (2)			
0.0529	163.4	0.5002	1325.1	0.7987	1216.1
0.1527	551.5	0.5504	1398.0	0.8501	917.9
0.2013	709.6	0.6492	1398.4	0.9495	500.1
0.2999	914.3	0.7004	1379.3		
0.3992	1137.4	0.7506	1333.5		
		Xanthene (1) + n-C36 (2)			
0.1500	563.7	0.4000	1768.2	0.7500	1894.8
0.2541	1126.1	0.6000	1975.6	0.8993	804.0

Discussion

SLE data can be used to calculate activity coefficients of the mixture components. In the case of the systems studied, the components are not miscible in the solid phase and all diagrams present a simple eutectic. Therefore, the activity coefficient γ_i of the component, i, in the liquid phase can be calculated according to the following expression:

$$-\ln \gamma_i = \frac{\Delta_{fus}H_i}{R}\left(\frac{1}{T} - \frac{1}{T_{fus}}\right) + \ln x_i + \lambda \tag{1}$$

where x_i, T_{fus}, and $\Delta_{fus}H_i$ are respectively the liquid equilibrium composition, melting temperature, and molar enthalpy of fusion of the pure component, i. The last term, λ, corresponds to the enthalpic contribution of the first-order transition observed in the solid octacosane, pentacosane, and hexatriacontane. This term should be used below the transition temperature, T_{tr}, and is given by

$$\lambda = \frac{\Delta_{tr}H_i}{R}\left(\frac{1}{T} - \frac{1}{T_{tr}}\right) \tag{2}$$

where $\Delta_{tr}H_i$ is the enthalpy change corresponding to the transition. All complementary properties necessary to calculate activity coefficients (melting and transition temperatures and enthalpies) were measured using a DSC 111 calorimeter of SETARAM. They are listed and compared with corresponding data taken from the literature in Table 1.

Experimental activity coefficients of DBF or XTH, γ_1, are plotted in Figure 2 and are listed in Table 3 together with activity coefficients of alkanes, γ_2. They are nearly independent of the chain length of n-alkane. In Figure 3 activity coefficients of DBF, XTH, and pyrene (Mahmoud et al., 1998) are plotted in as a function of n-octacosane composition. Very similar behavior of activity coefficients of three polyaromatics can be observed. Therefore, it can be concluded that neither the structure of the polyaromatic compound nor the presence of the oxygen in the ring modifies significantly the activity coefficients.

It was interesting to verify that this behavior could be reproduced with the group contribution formalism. In the case of the systems considered, the method based on the lattice model proposed by Kehiahian et al. (1978) is suitable.

Expressions giving activity coefficients of component i, γ_i, and molar excess enthalpy, H^E, in the case of our binary mixtures are as follows:

$$\ln \gamma_i = \ln \frac{\varphi_i}{x_i} + 1 - \frac{\varphi_i}{x_i} + q_i(1-\xi_i)^2\left\{\frac{g^0}{RT_0} + \frac{h^0}{RT_0}\left[\left(\frac{T_0}{T}\right) - 1\right]\right\} \quad (i = 1, 2) \tag{3}$$

and

$$\frac{H^E}{RT} = -T\left(\frac{\partial(x_1 \ln \gamma_1 + x_2 \ln \gamma_2)}{\partial T}\right)_{P,x} = q_1 q_2 \frac{x_1 x_2}{x_1 q_1 + x_2 q_2}\,\frac{h^0}{RT} \tag{4}$$

In the expressions (3) and (4), T_0 is a reference temperature (T_0 = 298.15 K), φ_i and ξ_i are respectively the volume fraction and the surface fraction defined with the adimensional van der Waals volumes, r_i, and the adimensional van

Table 3. Solid−Liquid Equilibria of DBF or XTH (1) + *n*-Alkane (2)

x_1	T/K	γ_1	γ_2	x_1	T/K	γ_1	γ_2
Xanthene (1) + *n*-C20 (2)							
0.0000	310.0		1.000	0.4999	353.5	1.481	
0.1007	309.8		1.094	0.5501	356.5	1.409	
0.1514	309.1		1.090	0.5999	358.8	1.337	
0.2034	319.5	2.049		0.6495	361.0	1.275	
0.2507	325.5	1.856		0.6998	362.8	1.215	
0.3011	333.7	1.785		0.7998	365.8	1.110	
0.3499	340.6	1.725		0.8993	369.4	1.039	
0.4007	345.1	1.620		1.0000	374.3	1.000	
0.4503	348.3	1.517					
Xanthene (1) + *n*-C28 (2)							
0.0000	334.2		1.000	0.6005	357.1	1.302	
0.1015	334.2		1.110	0.6500	360.1	1.258	
0.1504	333.8		1.142	0.7000	362.9	1.217	
0.2024	333.4		1.182	0.7497	363.9	1.153	
0.2513	333.0		1.225	0.7992	365.8	1.111	
0.3016	332.8		1.295	0.8496	367.8	1.075	
0.4005	342.3	1.549		0.8992	369.7	1.043	
0.4518	347.9	1.503		0.9498	371.2	1.009	
0.5000	351.9	1.445		1.0000	374.3	1.000	
0.5504	355.0	1.376					
Xanthene (1) + *n*-C36 (2)							
0.0000	348.8		1.000	0.5991	356.4	1.291	
0.1050	348.0		1.036	0.6503	359.3	1.242	
0.2034	346.5		1.015	0.6997	360.9	1.182	
0.3008	345.7		1.034	0.7996	366.2	1.117	
0.3996	344.3		1.013	0.9000	370.2	1.050	
0.5003	350.0	1.402		1.0000	374.3	1.000	
0.5487	354.2	1.364					
Dibenzofuran (1) + *n*-C20 (2)							
0.0000	310.0		1.000	0.5502	335.5	1.280	
0.1008	309.6		1.075	0.6003	337.8	1.225	
0.1527	309.1		1.092	0.6497	341.1	1.203	
0.1999	308.9		1.136	0.6999	343.5	1.166	
0.2499	308.5		1.170	0.7996	347.2	1.090	
0.3512	318.2	1.422		0.8988	351.2	1.040	
0.4000	325.2	1.442		1.0000	355.2	1.000	
0.5012	332.4	1.325					
Dibenzofuran (1) + *n*-C25 (2)							
0.0000	326.0		1.000	0.5010	333.0	1.341	
0.1001	325.3		1.063	0.5997	338.2	1.236	
0.1519	324.4		1.067	0.7004	342.3	1.140	
0.2016	323.0		1.039	0.7996	346.6	1.079	
0.2531	321.8		1.031	0.8994	351.2	1.039	
0.3015	321.1		1.055	1.0000	355.2	1.000	
0.4511	330.2	1.411					
Dibenzofuran (1) + *n*-C28 (2)							
0.0000	334.2		1.000	0.6500	340.1	1.181	
0.1007	334.1		1.101	0.7001	342.4	1.143	
0.2007	332.6		1.116	0.7499	345.3	1.124	
0.3005	331.4		1.171	0.8000	347.8	1.101	
0.4501	330.1		1.034	0.8498	349.8	1.073	
0.5008	332.3	1.324		0.8998	352.1	1.055	
0.5501	334.7	1.261		1.0000	355.2	1.000	
0.6004	337.0	1.207					
Dibenzofuran (1) + *n*-C36 (2)							
0.0000	348.8		1.000	0.7245	342.2	1.101	
0.1021	348.0		1.035	0.7503	343.6	1.091	
0.2021	347.2		1.084	0.8003	346.3	1.071	
0.3011	345.9		1.058	0.8249	347.7	1.066	
0.4513	344.8		1.183	0.8500	349.0	1.058	
0.5765	343.5		1.306	0.8999	351.5	1.044	
0.6503	342.3		1.362	0.9496	353.8	1.029	
0.7006	341.5		1.441	1.0000	355.	1.000	

der Waals area, q_i, of the molecule i (Kehiahian et al., 1978):

$$\varphi_i = \frac{x_i r_i}{\sum_j x_j r_j}, \quad \xi_i = \frac{x_i q_i}{\sum_j x_j q_j} \qquad (i \text{ and } j = 1, 2) \tag{5}$$

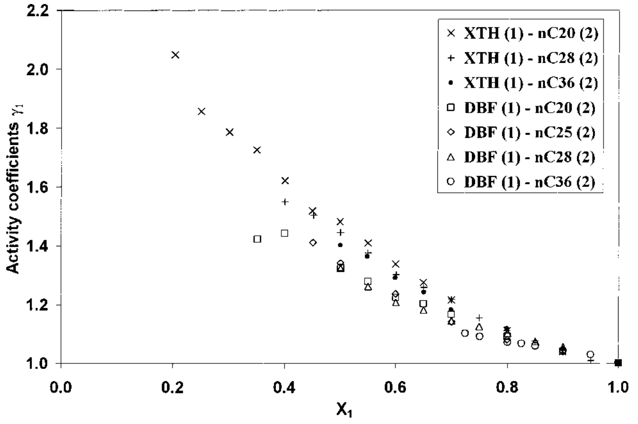

Figure 2. Activity coefficients of DBF and XTH (γ_1) in solutions with *n*-alkanes.

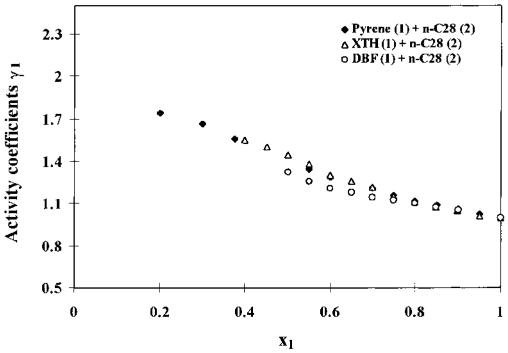

Figure 3. Activity coefficients of pyrene (Mahmoud et al., 1998), DBF, and XTH (γ_1) in solution with octacosane.

In this model interactions between two groups are characterized with parameters $h°$ and $g°$, which have to be adjusted with experimental data. Three groups are necessary to represent all compounds considered: "aliphatic carbon", "aromatic carbon", and "oxygen". Calculations performed to establish interaction parameters of these groups and to obtain a good representation of all data considered failed. Therefore, in further calculations we considered "DBF" and "XTH" as the separate groups. Interaction parameters $h°$ and $g°$ between the DBF group and the aliphatic carbon group and between the XTH group and the aliphatic carbon group were separately determined by minimizing respectively F_H and F_G objective functions defined as follows:

$$F_H = \left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{H^E_{i,\mathrm{exp}} - H^E_{i,\mathrm{cal}}}{H^E_{i,\mathrm{exp}}}\right)^2\right]^{1/2} \tag{6}$$

and

$$F_G = \left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\gamma_{i,\mathrm{exp}} - \gamma_{i,\mathrm{cal}}}{\gamma_{i,\mathrm{exp}}}\right)^2\right]^{1/2} \tag{7}$$

using the simplex procedure of Nelder and Mead (1965). In eqs 6 and 7, n represents the number of experimental points and the subscripts cal and exp are relative to experimental and calculated values of molar excess enthalpies and activity coefficients, γ, of component 1 or 2. Values of parameters $g°$ and $h°$ are reported in Table 4 together with mean relative deviations on activity coefficients and excess enthalpies. Activity coefficients of both aromatics are well represented. More important deviations

Table 4. Representation of SLE and H^M Experimental Data Using the Group Contribution Lattice Model (Kehiahian et al., 1978)[a]

	mean relative deviations on activity coefficients and excess enthalpies (%)			interaction parameters	
system	δH^M	$\delta\gamma_1$	$\delta\gamma_2$	$g°/(J\cdot mol^{-1})$	$h°/(J\cdot mol^{-1})$
XTH + *n*-C20	12.1	1.9	5.7	550.6	720.3
XTH + *n*-C28					
XTH + *n*-C36					
DBF + *n*-C20	20.5	2.4	7.9	540.7	683.1
DBF + *n*-C25					
DBF + *n*-C28					
DBF + *n*-C36					

[a] Values of interaction parameters and results of activity coefficients and enthalpy of mixing calculation.

are found with activity coefficients of *n*-alkanes. Recently, Mahmoud et al. (1998) analyzed activity coefficients of long-chain *n*-alkanes calculated from SLE data and concluded that their evolution with concentration cannot be well represented using current thermodynamic models. The enthalpy of mixing is poorly represented. This is partly due to a greater experimental uncertainty observed with systems containing *n*-hexatriacontane.

The inspection of Table 4 shows that parameters *h*° and *g*° corresponding to interactions between the DBF group and the aliphatic carbon group and those concerning the XTH group and the aliphatic carbon group are very close and that thermodynamic data of systems containing both polyaromatics can be well represented using one set of parameters only.

Conclusions

In this paper SLE and H^E data of the systems {DBF + eicosane, $C_{20}H_{42}$}, {DBF + pentacosane, $C_{25}H_{52}$}, {DBF + octacosane, $C_{28}H_{58}$}, {DBF + hexatriacontane, $C_{36}H_{74}$}, {xanthene + eicosane}, {xanthene + octacosane}, and {xanthene + hexatriacontane} were studied and correlated using the group contribution model based on the lattice theory (Kehiahian et al., 1978). Thermodynamic properties of two series of systems are very close. Interactions of *n*-alkanes with DBF are almost identical with those of the XTH group despite the fact that the number of carbon atoms of these compounds is not the same. Moreover, these interactions are very close to those between *n*-alkanes and polyaromatic hydrocarbons, as demonstrated in Figure 3 with activity coefficients of pyrene in the {pyrene + octacosane} system. It could be tentatively suggested that that the introduction of an oxygen atom into the ether position of a polyaromatic structure does not modify significantly thermodynamic properties.

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