Measurements and Calculation of Vapor−Liquid Equilibria for the Binary Mixtures of Fluorobenzene and Alkanes at a Pressure of 101.4 kPa

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Vapor−liquid equilibria (VLE) of binary mixtures of (hexane + fluorobenzene) and (heptane + fluorobenzene) were measured over the whole composition range in a dynamic recirculation ebulliometer at the pressure 101.4 kPa. The experimental results were well calculated by means of the NRTL and UNIQUAC thermodynamic models. The former system exhibits a shallow azeotrope in the fluorobenzene-rich zone, whereas the azeotrope lies in the heptane-rich zone for the latter one. Remarkably, the influence of the fluorine atom of the fluorobenzene molecule on the azeotrope, relative volatility, and distribution factors for both systems is found to be trivial in comparison with the homologue hydrocarbon mixtures of benzene with hexane and heptane.

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1. Introduction

Hydrofluorocarbons (HFCs) are a new “green” generation of fluids. Many HFC mixtures reveal strong nonideal behavior with low boiling azeotropes.

Fluorobenzene is used for the development of lower boiling fuel to meet cold conditions, reduce emissions as well as fuel costs, and protect the environment. It is actually used to control carbon content in steel manufacturing, as a common starting reagent for fluorinating pharmaceuticals and agrochemicals, as pesticides−insecticide, and for plastic and resin polymers.

Following previous studies devoted to the thermodynamic phase equilibrium behavior of liquid mixtures containing fluorinated hydrocarbons,[1−6] this work explores the vapor−liquid equilibrium behavior of binary mixtures of (hexane + fluorobenzene) and (heptane + fluorobenzene) at a pressure of 101.4 kPa. The chemical substances used in this work are chosen for their industrial applications, where they are used in petroleum, perfume, and pharmaceutical industries.

Reliable liquid−vapor equilibrium data of multicomponent systems are required by chemical engineers for better performance of separation processes, throughout purification and recovery of valuable materials. At present, very few measurements on thermodynamic phase behavior have been reported for these systems, and this study is a contribution to the enhancement of literature records of fluorinated hydrocarbon mixtures.

2. Experimental Section

The liquid substances used for this work were commercially available from Fluka A. G., with stated mole fraction purities of 0.999 for benzene and heptane and of 0.997 for fluorobenzene, and were used as received. The physicochemical properties of pure components[7] are listed in Table 1.

The vapor−liquid equilibrium measurements were performed using a recirculation still with operating techniques as described previously.[4] The measurement uncertainties in equilibrium temperature, phase mole fractions, and atmospheric pressure were 0.2 K, 0.002, and 0.2 kPa, respectively.

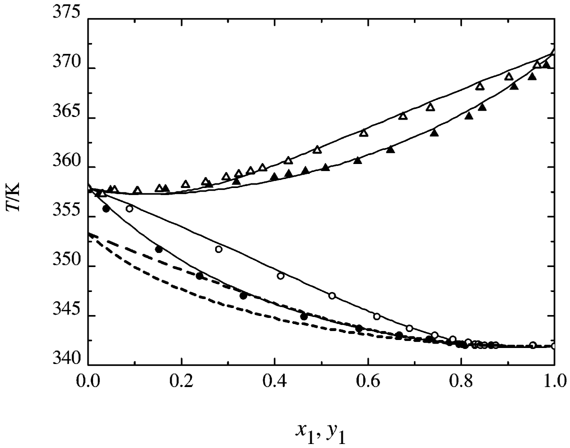

Figure 1. Vapor−liquid equilibrium diagram (T, x_1, y_1): ●, ○, ($x_1C_6H_{14}$ + $x_2C_6H_5F$); ▲, △, ($x_1C_7H_{16}$ + $x_2C_6H_5F$); —, NRTL eq; ····, UNIQUAC eq for ($x_1C_6H_{14}$ + $x_2C_6H_6$) from ref 13.

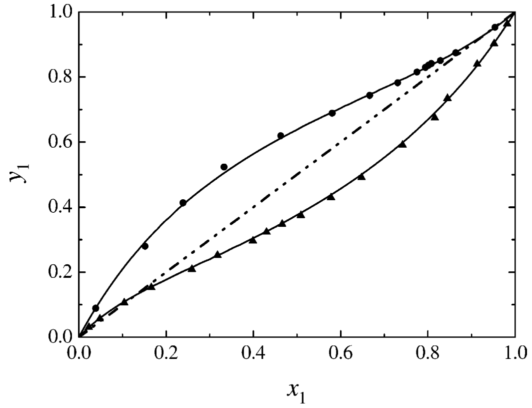

Figure 2. Equilibrium compositions diagram (y_1, x_1): ●, ($x_1C_6H_{14}$ + $x_2C_6H_5F$); ▲, ($x_1C_7H_{16}$ + $x_2C_6H_5F$); —, UNIQUAC eq.

3. Results and Discussion

The present systems exhibit strong nonideal behavior leading to the formation of low boiling azeotropes. The fugacity coefficients of component i in the liquid and vapor phases (ϕ_i^l, ϕ_i^v) were calculated according to Soave.[9] The saturated vapor

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Table 1. Physicochemical Properties of Pure Constituents:[7] Normal Boiling Temperature, Critical Temperature and Pressure, Acentric Factor, Antoine Constants, and UNIQUAC Structural Parameters

	T_b/K					Antoine constants (mmHg, °C)			UNIQUAC[8]	
component	exptl	lit.	T_c/K	p_c/kPa	w	A	B	C	r	q
hexane	341.7	341.9	507.7	3034.8	0.298	6.878	1171.5	224.37	4.500	3.856
heptane	371.8	371.6	540.7	2775.0	0.351	6.894	1264.4	216.64	4.500	3.860
fluorobenzene	357.5	357.9	560.1	4550.5	0.245	7.413	1509.2	248.19	3.404	2.572

Table 2. Experimental Vapor−Liquid Equilibrium Data for Binary Systems at a Pressure of 101.4 kPa

x_1	y_1	T/K	γ_1	γ_2	x_1	y_1	T/K	γ_1	γ_2
				($x_1C_6H_{14} + x_2C_6H_5F$)					
0.039	0.089	355.8	1.506	1.017	0.775	0.815	342.3	1.040	1.379
0.152	0.280	351.7	1.369	1.039	0.795	0.829	342.1	1.038	1.408
0.239	0.413	349.0	1.392	1.031	0.802	0.836	342.1	1.037	1.398
0.333	0.523	347.0	1.344	1.022	0.808	0.841	342.0	1.039	1.403
0.463	0.619	344.9	1.219	1.088	0.829	0.850	342.0	1.023	1.486
0.581	0.689	343.7	1.123	1.186	0.864	0.874	342.0	1.010	1.570
0.667	0.743	343.0	1.078	1.263	0.954	0.953	342.0	0.997	1.731
0.731	0.782	342.6	1.048	1.345					
				($x_1C_7H_{16} + x_2C_6H_5F$)					
0.023	0.031	357.3	2.094	1.014	0.509	0.374	359.9	1.050	1.202
0.048	0.057	357.7	1.821	1.000	0.578	0.429	360.6	1.038	1.249
0.104	0.106	357.6	1.568	1.011	0.648	0.491	361.7	1.024	1.290
0.166	0.153	357.8	1.409	1.022	0.742	0.591	363.4	1.021	1.343
0.259	0.209	358.2	1.218	1.061	0.816	0.675	365.1	1.006	1.421
0.318	0.252	358.5	1.184	1.080	0.845	0.734	366.0	1.028	1.344
0.399	0.296	359.0	1.091	1.136	0.913	0.840	368.1	1.022	1.353
0.430	0.323	359.3	1.095	1.141	0.952	0.902	369.1	1.021	1.459
0.466	0.348	359.6	1.078	1.162	0.982	0.963	370.3	1.020	1.418

Table 3. Summary of VLE Data Reduction Values for Binary Systems at 101.4 kPa

NRTL				UNIQUAC			
$\Delta\lambda_{12}$	$\Delta\lambda_{12}$			Δu_{12}	Δu_{21}		
J·mol^{-1}	J·mol^{-1}	$\sigma(\Delta y_1)$	$\sigma(\Delta T$/K)	J·mol^{-1}	J·mol^{-1}	$\sigma(\Delta y_1)$	$\sigma(\Delta T$/K)
			($x_1C_6H_{14} + x_2C_6H_5F$) ($x_{1,az} = 0.933$, $T_{az} = 341.8$ K)				
$\alpha = 0.2983$							
2608.7	−712.0	0.005	0.3	2467.4	−1407.9	0.005	0.2
			($x_1C_7H_{16} + x_2C_6H_5F$) ($x_{1,az} = 0.133$, $T_{az} = 357.3$ K)				
$\alpha = 0.2981$							
−1900.7	4536.7	0.006	0.5	−953.3	1649.6	0.006	0.5

pressure, p_i^σ, of pure component i was calculated from the Antoine equation. The measured vapor−liquid equilibrium data at a pressure of 101.4 kPa were thermodynamically consistent and are listed in Table 2. Data reduction of the activity coefficient of the liquid-phase mixtures was performed by means of the nonrandom two-liquid (NRTL)[10] and the universal quasichemical (UNIQUAC)[11] equations. The structural parameters for the UNIQUAC equation are given in Table 3. The molecular energy parameters for the above thermodynamic models were evaluated by minimizing the square deviations of experimental data from calculated values of activity coefficients using the Simplex−Nelder−Mead method.[12] Table 3 summarizes the energy parameter values for the NRTL and UNIQUAC equations together with the standard deviations in vapor mole fraction and equilibrium temperature: $\sigma(\Delta y_1)$, $\sigma(\Delta T)$.

The measured and calculated vapor−liquid equilibrium diagrams, (T, x_1, y_1) and (y_1, x_1), are illustrated in Figures 1 and 2, respectively. The differences between calculated equilibrium temperatures and vapor mole fractions and the experimental equilibrium values, ΔT and Δy_1, are plotted against liquid mole fraction x_1 in Figure 3. The relative volatility as calculated from the expression $\alpha_{ij} = (\gamma_i p_i^\sigma \phi_j^v / \gamma_j p_j^\sigma \phi_i^v)$ varies within $0.98 \leq \alpha_{ij} \leq 2.41$ and $0.48 \leq \alpha_{ij} \leq 1.36$ for the hexane and heptane mixtures, respectively.

Alkanes are nonpolar and fairly unreactive molecules and are present in petroleum. In contrast, the fluorobenzene molecule has more electron-accepting abilities than benzene, giving extra stabilization energy to it; nonetheless, both substances present shallow azeotropes with alkanes. The calculated azeotropes are given in Table 3. This study indicates that the influence of the fluorine atom on the azeotrope, relative volatility α_{ij}, and distribution factor K for both systems is found to be trivial in comparison with the homologue hydrocarbon mixtures of benzene with hexane and heptane,[13,14] as can be seen in Figure 1.

4. Conclusion

This study reports experimental vapor−liquid equilibrium data for (hexane + fluorobenzene) and (heptane + fluorobenzene)

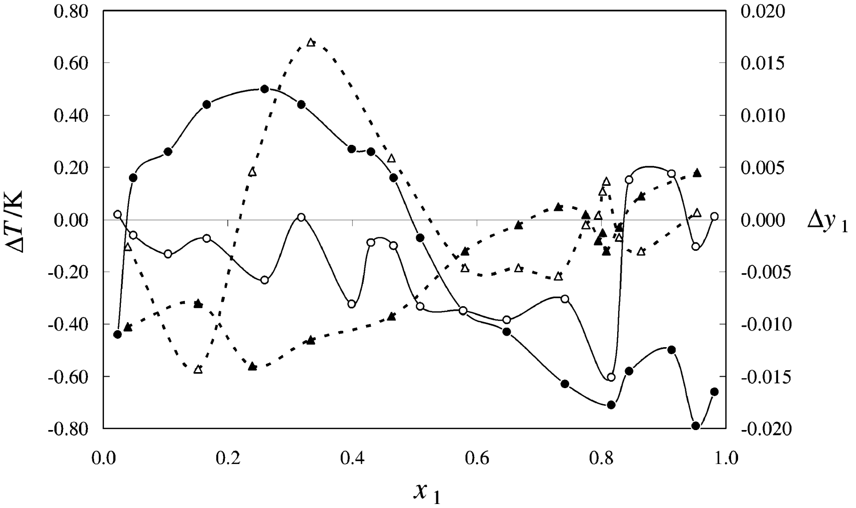

Figure 3. Deviations of experimental vapor−liquid equilibrium data from calculated values by UNIQUAC: ○/△, Δy_1; ●/▲, ΔT; —, ($x_1C_6H_{14} + x_2C_6H_5F$); ····, ($x_1C_7H_{16} + x_2C_6H_5F$).

at a pressure of 101.4 kPa. The data are well calculated with the NRTL and UNIQUAC equations. Values of binary interaction parameters are given. The two systems reveal azeotropes. When mixing, the strength and polarity of the carbon−fluorine bond in the fluorobenzene molecule gave rise to a fair inductive energy effect on the alkane molecules to form shallow azeotropes.

Acknowledgment

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