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Experimental Isobaric Vapor−Liquid Equilibria of Binary Mixtures of 2,2,2-Trifluoroethanol with Benzene or Toluene

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Vapor−liquid equilibrium of binary mixtures of (benzene + 2,2,2-trifluoroethanol) and (toluene + 2,2,2-trifluoroethanol) were measured in a dynamic recirculation still at pressure 102 kPa. The experimental results were tested for thermodynamic consistency and were well-represented by the NRTL and UNIQUAC equations. The two systems are azeotropic.

Introduction

Nowadays scientists are keenly devoted to provide new solvent mixtures and energy fluids with clean and safe characteristics. With this in mind, 2,2,2-trifluoroethanol (commercially called fluorinol) and its solvent mixtures have been proposed and tested as organic working fluids in high-temperature absorption heat pumps and heat transformers. They have also been used in Rankine engines for terrestrial and space applications. In bioengineering, 2,2,2-trifluoroethanol is a commonly used cosolvent. Unfortunately, fluorinol is an expensive chemical reagent.

As part of our study of thermodynamic properties of 2,2,2-trifuoroethanol,[1−3] we now present experimental data of vapor−liquid equilibrium (VLE) of binary mixtures of (benzene + 2,2,2-trifluoroethanol) and (toluene + 2,2,2-trifluoroethanol) at atmospheric pressure. The solvents used in this work are chosen for their various applications, where they are used in petroleum, perfumes, and pharmaceutical industries.

The realistic applications of the data provide helpful information for understanding molecular interactions in such binary mixtures and hopefully will improve recovery and reduce the cost of 2,2,2-trifluorethanol. Apart from the study of the (2,2,2-trifluoroethanol + benzene) system at 298.15 K,[4] no literature data on thermodynamic phase behavior for these systems is available.

Experimental Section

The liquid substances used for this work were all of the highest commercially available purity from Fluka A.G., with stated mole fraction purities of 0.999 for benzene and toluene and of 0.997 for 2,2,2-trifluoroethanol. They were used as received from the supplier.

The physicochemical properties of pure components of this study are listed in Tables 1 and 2 and are compared with literature data.[2,5−7] The VLE measurements were carried out in a continuous dilution recirculation still; Eckert-Gmehling type.[8] The vapor phase was condensed at 263 K using a Lauda cryostat (model RCS). Equilibrium temperatures were measured using a calibrated digital thermometer (thermistor: YSI-400, Cole-Parmer, model 8502) with resolution of 0.05 K. Atmospheric pressure was determined by a mercury barometer (Prolabo: Fortin 0202500). A steady state was established within the

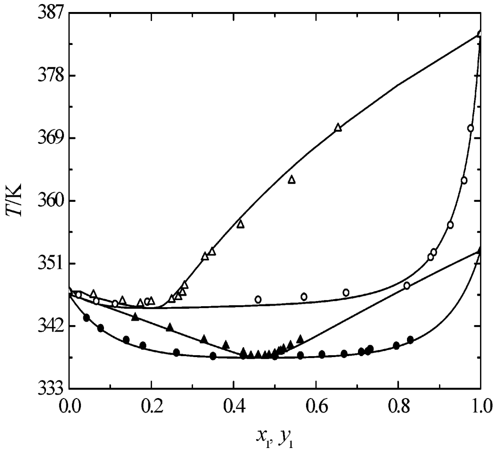

Figure 1. Vapor−liquid composition, temperature equilibrium diagram: ●, ▲, ($x_1C_6H_6 + x_2CF_3CH_2OH$); ○, △, ($x_1C_7H_8 + x_2CF_3CH_2OH$); −, NRTL equation.

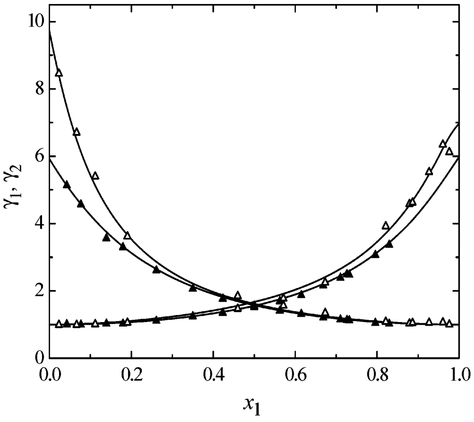

Figure 2. Activity coefficient, composition diagram: ▲, ($x_1C_6H_6 + x_2CF_3CH_2OH$); △, ($x_1C_7H_8 + x_2CF_3CH_2OH$); −, NRTL equation.

Table 1. Refractive Index n, Density ρ Values at 298.15 K, and Normal Boiling Point T_b of Pure Liquids

	n		ρ/g·cm^{-3}		T_b/K	
component	expt.	lit.[5]	expt.	lit.[2,5]	expt.	lit.[5]
benzene	1.4974	1.4978	0.8735	0.8736	353.0	353.3
toluene	1.4936	1.4941	0.8622	0.8622	383.6	383.8
2,2,2-trifluoroethanol	na	na	1.3824	1.3821	347.4	347.2

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Table 2. Critical Temperature T^C, Critical Pressure p^C, Acentric Factor w, Antoine Constants (mmHg, °C), and UNIQUAC Structural Parameters (r, q) of Pure Liquids

				Antoine constants			UNIQUAC	
component	T^C/K	p^C/kPa	w	A	B	C	r	q
benzene	562.2	4898.1	0.212	6.880	1196.8	219.16	3.188	2.400
toluene	591.8	4113.8	0.257	6.951	1342.3	219.19	3.923	2.968
2,2,2-trifluoroethanol	499.3	4870	0.635	8.008	1494.7	217.85	2.610	2.504
reference	5,6			5,6			7	

Table 3. Experimental Vapor−Liquid Equilibrium Data for Binary Systems at Pressure 102 kPa

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
				($x_1C_6H_6 + x_2CF_3CH_2OH$)					
343.2	0.043	0.161	5.238	1.030	337.8	0.562	0.486	1.436	1.735
341.7	0.077	0.245	4.659	1.023	337.9	0.615	0.499	1.344	1.914
340.0	0.139	0.328	3.634	1.050	338.0	0.669	0.500	1.235	2.211
339.2	0.180	0.381	3.364	1.049	338.3	0.710	0.510	1.173	2.448
338.2	0.261	0.424	2.660	1.133	338.4	0.726	0.515	1.154	2.553
337.7	0.350	0.442	2.107	1.273	338.7	0.732	0.522	1.149	2.538
337.8	0.423	0.460	1.805	1.384	339.2	0.796	0.538	1.073	3.140
337.7	0.500	0.476	1.589	1.554	340.0	0.829	0.562	1.045	3.451
				($x_1C_7H_8 + x_2CF_3CH_2OH$)					
346.5	0.023	0.059	8.451	0.988	347.8	0.821	0.281	1.083	3.919
345.6	0.067	0.130	6.702	0.992	351.9	0.879	0.331	1.032	4.577
345.2	0.112	0.174	5.397	1.007	352.6	0.887	0.348	1.050	4.627
345.5	0.190	0.200	3.613	1.056	356.5	0.927	0.417	1.054	5.528
345.8	0.460	0.249	1.847	1.467	362.9	0.961	0.541	1.068	6.347
346.2	0.571	0.266	1.563	1.778	370.4	0.976	0.653	1.001	6.123
346.8	0.673	0.276	1.346	2.246					

circulating still in 20 min. The equilibrium mole fractions of liquid and vapor phases of the binary mixtures were determined at 298.2 K by measuring their refractive indices using an Abbe-type refractometer with uncertainty of $3 \cdot 10^{-4}$. The uncertainties in measurements of pressure, temperature and mole fraction were 0.2 kPa, 0.1 K, and $2 \cdot 10^{-3}$, respectively.

Results and Discussion

The vapor−liquid equilibrium state of a real solution is described by the thermodynamic equations:

$$\phi_i^v y_i p = \gamma_i x_i p_i^\sigma \phi_i^\sigma \exp(PE)_i \tag{1}$$

and

$$\phi_i^v y_i = \phi_i^l x_i \tag{2}$$

where x_i and y_i are the equilibrium liquid and vapor compositions; γ_i, ϕ_i^l, and ϕ_i^v are the activity and fugacity coefficients of component i in a liquid or vapor mixture, respectively; and $(PE)_i$ is the Poynting effect. The fugacity coefficient, ϕ_i^l or ϕ_i^v, was calculated from the Redlich−Soave−Kwong equation of state.[9] The saturated vapor pressure p_i^σ of pure component i was calculated from the Antoine equation. The experimental VLE data are given in Table 3. The activity coefficients for each binary mixture were correlated with non-random two-liquid (NRTL)[10] and universal quasi-chemical (UNIQUAC)[11] equations. The binary molecular interaction parameters for the NRTL and UNIQUAC models were evaluated by minimizing the objective function (eq 3) using the nonlinear regression method of Nedler−Mead:

$$F = \sum_i^n \{(\gamma_{1,\mathrm{expt}} - \gamma_{1,\mathrm{calc}})_i^2 + (\gamma_{2,\mathrm{expt}} - \gamma_{2,\mathrm{calc}})_i^2\} \tag{3}$$

where the subscripts calc and expt refer to calculated and experimental values. Both correlation equations represent the experimental data satisfactorily.

The studied systems exhibit strong real behavior leading to the formation of low boiling azeotropes. Table 4 lists values of the binary interaction parameters for the NRTL and UNIQUAC models, the azeotropes, and the mean deviations between experimental and correlated equilibrium temperatures and vapor mole fractions ($\overline{\Delta T}$,$\overline{\Delta y_1}$). The experimental and correlated data of the two systems are shown in Figures 1 to 4.

Due to the strong electronegative induction effects of the three fluorine atoms, the extent of self-association of 2,2,2-trifluoroethanol molecules in the pure liquid or in solution in aprotic solvent is higher than the homologue hydrocarbon alcohols. Accordingly, the mixing feature of (2,2,2-trifluoroethanol + aromatic hydrocarbon) systems is indicated by a significant aggregation and rehabilitation of the hydrogen bond networks of 2,2,2-trifluoroethanol molecules in the mixtures prevailing large and positive excess enthalpies and excess heat capacities.[4,12] Moreover, The effect of molecular size and shape on the volumetric mixing behavior of 2,2,2-trifluoroethanol with

Table 4. Molecular Interaction Parameters of NRTL and UNIQUAC and Correlated Azeotrope Data, Mean Deviations in Temperature, and Vapor-Mole Fraction ($\overline{\Delta T}$, $\overline{\Delta y_1}$), and the Limiting Activity Coefficients γ_i^∞

	NRTL					UNIQUAC			
	$\Delta\lambda_{12}$/J·mol^{-1}	$\Delta\lambda_{12}$/J·mol^{-1}	$x_{1,}$az	T_{az}/K		Δu_{12}/J·mol^{-1}	Δu_{21}/J·mol^{-1}	$x_{1,}$az	T_{az}/K
				($x_1C_6H_6 + x_2CF_3CH_2OH$)					
$\alpha_{12} = 0.294$	3100.3	2878.3	0.469	337.7		908.0	908.5	0.469	337.7
$\overline{\Delta T}$/K	0.1				$\overline{\Delta T}$/K		0.1		
$\overline{\Delta y_1}$	0.004				$\overline{\Delta y_1}$		0.005		
γ_1^∞	5.98				γ_1^∞		5.81		
γ_2^∞	5.93				γ_2^∞		5.83		
				($x_1C_7H_8 + x_2CF_3CH_2OH$)					
$\alpha_{12} = 0.442$	3801.1	4447.5	0.198	344.6		1552.3	529.3	0.216	344.6
$\overline{\Delta T}$/K	0.6				$\overline{\Delta T}$/K		0.8		
$\overline{\Delta y_1}$	0.012				$\overline{\Delta y_1}$		0.012		
γ_1^∞	9.73				γ_1^∞		8.47		
γ_2^∞	6.97				γ_2^∞		6.38		

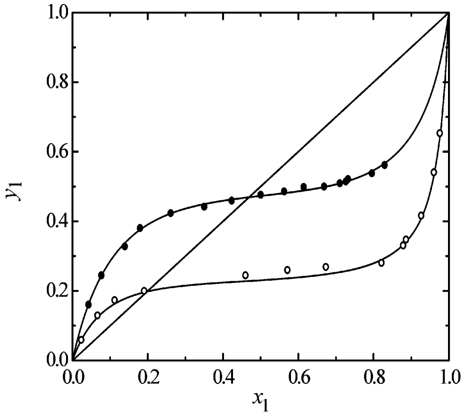

Figure 3. Vapor−liquid composition diagram: ●, ($x_1C_6H_6$ + $x_2CF_3CH_2OH$); ○, ($x_1C_7H_8$ + $x_2CF_3CH_2OH$); −, NRTL equation.

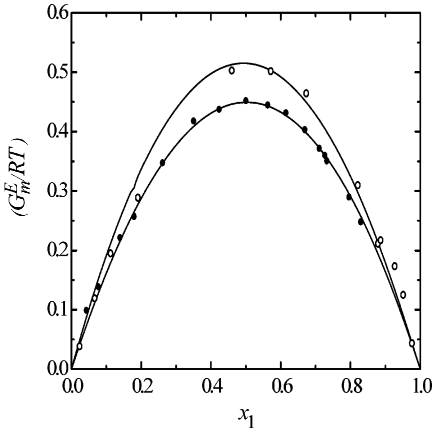

Figure 4. Molar excess Gibbs function diagram: ●, ($x_1C_6H_6$ + $x_2CF_3CH_2OH$); ○, ($x_1C_7H_8$ + $x_2CF_3CH_2OH$); −, NRTL equation.

aromatic or fluoro-aromatic molecules reveals at 298.15 K weak cross-molecular associations with extreme mixing values of 1.15 $cm^3 \cdot mol^{-1}$ for (2,2,2-trifluoroethanol + benzene)[4] and 0.82 $cm^3 \cdot mol^{-1}$ for (2,2,2-trifluoroethanol + fluorobenzene).[3]

Conclusions

Experimental VLE data are reported for the systems of (benzene + 2,2,2-trifluoroethanol) and (toluene + 2,2,2-trifluoroethanol) at pressure 102 kPa. The reported data are thermodynamically consistent and are satisfactorily correlated with NRTL and UNIQUAC thermodynamic models. The two systems are azeotropic.

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