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Study of Vapor−Liquid Equilibrium for Binary Mixtures (Chloroform + 2,2,2-Trifluoroethanol) and (α,α,α-Trifluorotoluene + 2,2,2-Trifluoroethanol) at Pressure 102 kPa

Zadjia Atik*

Faculty of Chemistry, University of Sciences and Technology Houari Boumediene, P.O. Box 32 El-Alia,
16112 Bab-Ezzouar, Algiers, Algeria

Vapor−liquid equilibria (VLE) of binary mixtures of (chloroform + 2,2,2-trifluoroethanol) and (α,α,α-trifluorotoluene + 2,2,2-trifluoroethanol) were determined at the pressure 102 kPa using the dynamic ebulliometry method. The measured activity coefficients of the equilibrium mixtures satisfied the thermodynamic consistency area test of Redlich−Kister to ≤ 3 % and were adequately correlated by means of NRTL and UNIQUAC thermodynamic models. The two systems are low-boiling azeotropes, with maximum excess Gibbs energies of 1238 $J\cdot mol^{-1}$ for the former and 1226 $J\cdot mol^{-1}$ for the latter. The azeotrope formation is attributed to different types of hydrogen bonding dominating the mixtures.

Introduction

Novel and clean sources of energetic fluids and technical mixture solvents are taking an important part in chemical engineering research and unit development. α,α,α-Trifluorotoluene (TFT) and 2,2,2-trifuoroethanol (TFE) are non-ozone-depleting and non-flammable solvents and are excellent substitutes of chlorinated solvents.

TFT is suitable as a component of liquid−crystalline media in display devices. Since it has good chemical and thermal stability, it also shows characteristics of solvation, which makes it particularly interesting to carry out organic chemistry reactions. Whereas, TFE and its mixture solvents have been proposed as organic working fluids in high-temperature absorption heat pumps and in Rankine engines for terrestrial and space applications.

As part of our studies devoted to the thermodynamic behavior of liquid mixtures containing TFE and TFT,[1−4] we present in this work experimental measurements of vapor−liquid equilibrium (VLE) of binary mixtures of (chloroform + TFE) and (TFT + TFE) at atmospheric pressure. The liquid components are highly polar, and the conjugate binary mixtures exhibit strong deviation from the ideal behavior leading to the formation of low-boiling azeotropes. We aim to provide new quantitative information with respect to molecular interactions in such binary mixtures in order to improve recovery of TFE by azeotropic distillation.

Experimental Section

TFE and TFT were supplied by Fluka A.G. (x > 99.7 %), and chloroform was from Prolabo (x > 99.5 %). The physicochemical properties of pure components and the corresponding constants needed for VLE data reduction are assembled in Tables 1 and 2 with literature values.[5−7]

The isobaric VLE measurements were carried out in a glass recirculation equilibrium still,[8] with a 100 cm^3 mixing cell. The equipment and measuring procedure have been outlined in ref 9. The uncertainties in measurements were 0.2 kPa for pressure, 0.1 K for temperature, and 0.002 for mole fraction of liquid and vapor phases.

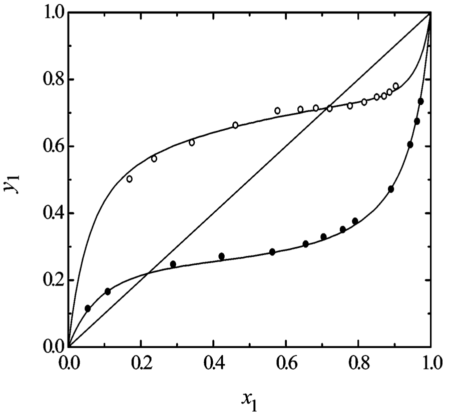

Figure 1. Vapor−liquid diagram $(y_1, x_1)_p$: ○, ($x_1CHCl_3 + x_2CF_3CH_2OH$); ●, ($x_1C_7H_5F_3 + x_2CF_3CH_2OH$); −, UNIQUAC equation.

Results and Discussion

The present activity coefficients of the equilibrium mixtures satisfied the Gibbs Duhem equation represented by the area test of Redlich-Kister:

$$D = \int_{x_1=0}^{x_1=1} \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 \cong 0 \tag{1}$$

Hence, they are considered to be thermodynamically consistent with $D = |(A_p - A_n)/(A_p + A_n)|\cdot 100 \leq 3$ %, where A_p and A_n are the positive and negative areas, respectively.

The measured vapor−liquid data are given in Table 3. The saturated vapor pressure of pure components is determined from the Antoine equation. The fugacity coefficients of the liquid and vapor phases were obtained using the Redlich−Soave−Kwong equation of state.[10]

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* E-mail: atik_zadjia@yahoo.fr. Fax: +213 21247311.

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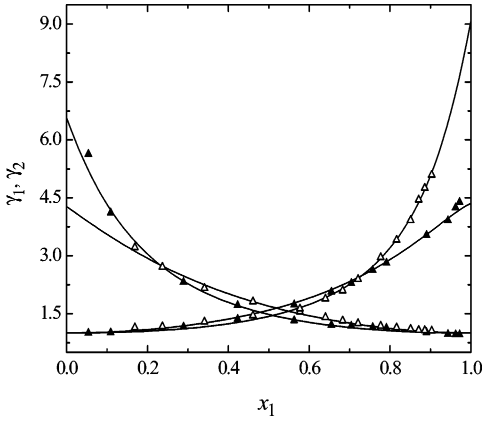

Figure 2. Activity coefficient diagram ($(\gamma_i, x_1)_p$): △, ($x_1CHCl_3 + x_2CF_3CH_2OH$); ▲, ($x_1C_7H_5F_3 + x_2CF_3CH_2OH$); —, UNIQUAC equation.

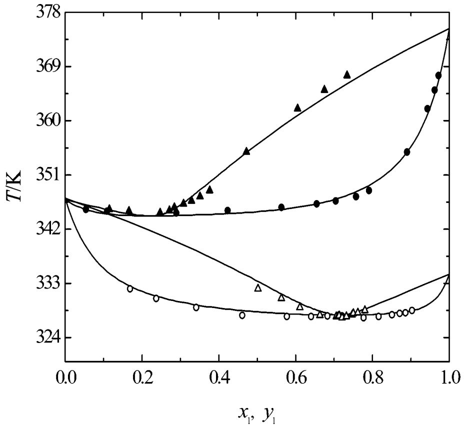

Figure 3. Phase diagram ($(T, x_1, y_1)_p$): ○, △, ($x_1CHCl_3 + x_2CF_3CH_2OH$); ●, ▲, ($x_1C_7H_5F_3 + x_2CF_3CH_2OH$); —, NRTL equation.

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.	expt.	lit.[5]
chloroform	1.4429	1.4429	1.4773	1.4797[a]	334.1	334.3
α,α,α-trifluorotoluene	1.4132	1.4122	1.1822	1.1813[a]	375.7	375.3
2,2,2-trifluoroethanol	na	na	1.3824	1.3821[b]	347.4	347.2

[a] From ref 5. [b] From ref 6.

The activity coefficients of mixtures were calculated by means of the nonrandom two-liquid (NRTL)[11] and the universal quasi-chemical (UNIQUAC)[12] equations. The molecular energy parameters for the above equations were evaluated by minimizing the objective function (eq 2) using the Simplex−Nedler−Mead method:[13]

$$F(\Delta g_{ij}, \Delta g_{ji}, \alpha_{ij}) = \sum_{i}^{n} \{(\gamma_{1,\mathrm{expt}} - \gamma_{1,\mathrm{calc}})_i^2 + (\gamma_{2,\mathrm{expt}} - \gamma_{2,\mathrm{calc}})_i^2\} \cong \min \quad (2)$$

where calc and expt refer to calculated and experimental values. The standard deviations of correlation are $\sigma_T = 0.5$ K and $\sigma_y = 0.01$. Table 4 lists values of the energy parameters for the NRTL and UNIQUAC equations, the azeotrope, the mean deviation between experimental and correlated equilibrium temperature and vapor mole fraction ($\overline{\Delta T}$, $\overline{\Delta y_1}$), and the limiting activity coefficient γ_i^∞. The experimental and correlated VLE curves of the two systems are shown in Figures 1 to 5. It is observed that the deviations of experimental quantities from calculated values are nonrandomly distributed; this may be due to impurities from the injection and sampling septa, which are less resistant to fluorinated hydrocarbons at boiling temperatures. The relative volatilities α_{ij} of the mixtures are calculated from the expression: $\alpha_{ij} = (x_i y_j / y_i x_j)$ where *x* and *y* are the mole fraction of liquid phase and of vapor phase, respectively. The relative volatility at infinite dilution α_{ij}^∞ for chloroform in TFE is equal to 6.13 and that for TFT in TFE is equal to 2.85.

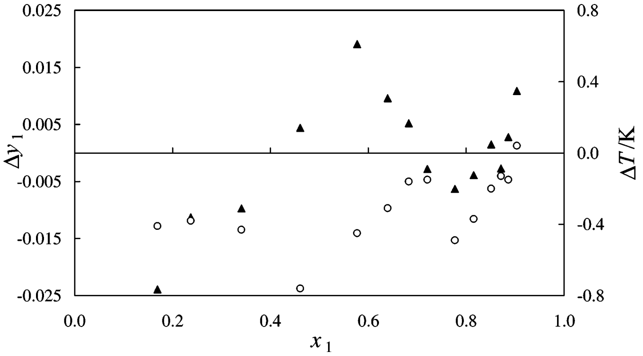

Figure 4. Deviations of experimental vapor-phase temperatures and compositions from calculated values by NRTL for ($x_1CHCl_3 + x_2CF_3CH_2OH$): ▲, Δy_1; ○, ΔT.

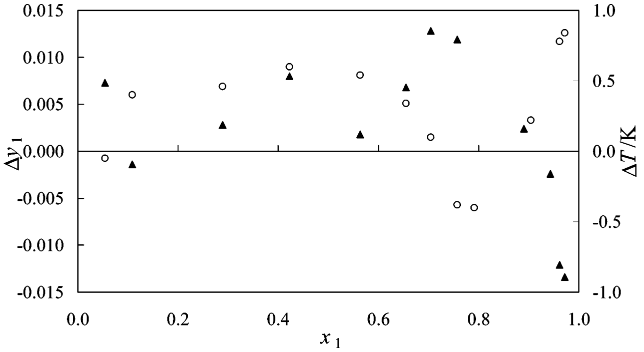

Figure 5. Deviations of experimental vapor−liquid equilibrium data from calculated values by NRTL for ($x_1C_7H_5F_3 + x_2CF_3CH_2OH$): ▲, Δy_1; ○, *T*.

Chloroform and TFT are electron-acceptor molecules, while TFE is a proton-donor molecule in which the hydroxyl protons endure fair intermolecular exchange as a result of autoprotolysis. Thus, the strong real behavior of the present mixtures is the outcome of different hydrogen bonds: Cl···H, F···H, and O···H, giving rise to molecular aggregates of various sizes and shapes to form eventually a low-boiling azeotrope. Also, the extent of self-association of TFE molecules is enhanced by mixing as compared to the pure state. Consequently, both mixtures have almost symmetric (G_m^E/RT, *x*) curves with maximum excess Gibbs energies: $\{x_1 = 0.55, G_m^E = 1238$ J·mol$^{-1}\}$ for (chloroform (1) + 2,2,2-trifluoroethanol (2)), and $\{x_1 = 0.5, G_m^E = 1226$ J·mol$^{-1}\}$ for (TFT (1) + TFE (2)). Besides, our measurement on the mixing of TFE with halogenated molecules reveals at 298.15 K a reasonable molecular expansion with maximum excess volumes: $\{x_1 = 0.428, V_m^E = 1.022$ cm^3·mol$^{-1}\}$ for (chloroform (1) + TFE (2)) and $\{x_1 = 0.496, V_m^E = 0.594$ cm^3·mol$^{-1}\}$ for (TFT (1) + TFE (2)).[1] So far, no literature

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
chloroform	536.6	5329	0.216	6.955	1171.0	226.23	2.870	2.410
α,α,α-trifluorotoluene	562.0	3559	0.282	7.214	1458.2	234.27	4.428	3.512
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

x_1	y_1	T/K	γ_1	γ_2	x_1	y_1	T/K	γ_1	γ_2
				$x_1CHCL_3 + x_2CF_3CH_2OH$					
0.1692	0.5015	332.1	3.213	1.139	0.7207	0.7134	327.6	1.249	2.392
0.2374	0.5630	330.5	2.712	1.169	0.7768	0.7207	327.3	1.183	2.958
0.3409	0.6112	329.0	2.157	1.289	0.8155	0.7316	327.5	1.136	3.406
0.4610	0.6629	327.7	1.808	1.451	0.8508	0.7467	327.8	1.100	3.920
0.5769	0.7062	327.5	1.550	1.626	0.8713	0.7498	328.0	1.071	4.448
0.6396	0.7100	327.5	1.405	1.884	0.8859	0.7618	328.1	1.067	4.754
0.6828	0.7142	327.6	1.320	2.100	0.9033	0.7798	328.5	1.056	5.091
				$x_1C_7H_5F_3 + x_2CF_3CH_2OH$					
0.054	0.115	345.3	5.630	1.001	0.757	0.351	347.4	1.145	2.624
0.109	0.166	345.0	4.115	1.012	0.791	0.376	348.4	1.134	2.818
0.289	0.247	344.7	2.321	1.161	0.890	0.472	354.8	1.015	3.533
0.423	0.271	345.1	1.720	1.360	0.904	0.509	357.5	0.985	3.393
0.563	0.284	345.6	1.325	1.733	0.943	0.605	362.0	0.968	3.915
0.655	0.308	346.2	1.210	2.069	0.962	0.675	365.1	0.961	4.247
0.704	0.329	346.7	1.182	2.292	0.972	0.734	367.5	0.958	4.390

Table 4. Energy Parameters for NRTL and UNIQUAC Equations, Correlated Azeotrope, Mean Deviation in Vapor-Mole Fraction and Temperature ($\overline{\Delta y_1}$, $\overline{\Delta T}$), and Limiting Activity Coefficient γ_i^∞

NRTL				UNIQUAC			
$\Delta\lambda_{12}$	$\Delta\lambda_{21}$		T_{az}	Δu_{12}	Δu_{21}		T_{az}
J·mol^{-1}	J·mol^{-1}	$x_{1,az}$	K	J·mol^{-1}	J·mol^{-1}	$x_{1,az}$	K
			$x_1CHCl_3 + x_2CF_3CH_2OH$				
α = 0.568							
5362.1	3552.8	0.715	327.8	3225.1	15.1	0.705	327.9
$\overline{\Delta T}$/K	0.3			$\overline{\Delta T}$/K	0.6		
$\overline{\Delta y_1}$	0.008			$\overline{\Delta y_1}$	0.011		
γ_1^∞	6.53			γ_1^∞	4.27		
γ_2^∞	12.74			γ_2^∞	9.09		
			$x_1C_7H_5F_3 + x_2CF_3CH_2OH$				
α = 0.296							
2035.4	3845.1	0.230	344.2	1531.1	215.0	0.232	344.2
$\overline{\Delta T}$/K		0.5		$\overline{\Delta T}$/K	0.5		
$\overline{\Delta y_1}$		0.007		$\overline{\Delta y_1}$	0.008		
γ_1^∞		6.71		γ_1^∞	6.54		
γ_2^∞		4.51		γ_2^∞	4.43		

values are found in literature for an exact comparison with our data.

Conclusions

New VLE data were obtained for the systems of TFE with chloroform or TFT at 102 kPa pressure and were thermodynamically consistent. The measured data were correlated with NRTL and UNIQUAC thermodynamic models. Both systems are low-boiling azeotropes.

Acknowledgment

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