Solubilities and Phase Equilibria for Ternary Solutions of α,α,α-Trifluorotoluene, Water, and 2-Propanol at Three Temperatures and Pressure of 101.2 kPa

Zadjia Atik* and Malika Chaou

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

Solubility and liquid−liquid equilibrium (LLE) data of water + 2-propanol + α,α,α-trifluorotoluene are determined at three temperatures T = (288.15, 298.15, and 308.15) K and pressure p = 101.2 kPa. The measured solubility and LLE results are correlated quantitatively by empirical equations, NRTL model, and UNIQUAC model. The correlated plait-point compositions of the solutions agree with the measured values. The effect of temperature upon the miscibility of the ternary systems is small. The literature data for these systems are quasi-nonexistent.

Introduction

The mutual solubility of a pair of partially miscible liquids is generally affected by the presence of a third component and, consequently, changes to their solubilities arise. The use of liquid−liquid equilibrium (LLE) studies in chemical engineering and production units is fundamentally important to a wide range of industrial applications, contributing directly to the development of tools used for the synthesis and separation processes applied in solvent absorption and extraction units through water removal and dehydration of chemical substances to high-purity valuable compounds. As a solvent or diluent, propanol has found key applications in medicine, clearing of electronic devices, purification of natural products such as oils, perfume manufacturing, and antiseptic for cosmetics.

Owing to the high ionization energy of fluorine element and its low polarizability, the chemical C−F bond existing in organic compounds greatly influences their chemical and physical properties when compared to their non-fluorine homologue hydrocarbons, leading to molecules and mixtures of highly desirable properties applied from life science to material industries. Fluorinated hydrocarbons are nontoxic, less aggressive for the ozone layer, and excellent substitutes of chlorinated solvents. Unfortunately, the solubility and LLE data of aqueous solutions containing fluorinated hydrocarbons are very scarce.[1] This work reports new data on the solubilities and liquid−liquid phase diagrams of solutions of (water + 2-propanol + α,α,α-trifluorotoluene) at temperatures of (288.15, 298.15, and 308.15) K and pressure of 101.2 kPa. The solubility and LLE data are correlated satisfactorily using empirical equations and thermodynamic models.

Experimental Section

The chemical substances and their mole fraction purities are 2-propanol and α,α,α-trifluotoluene (Fluka AG, 0.995), 2-propanol (Merck, > 0.998) and were used as received from the suppliers. The chemical purities were confirmed by gas−liquid chromatographic analysis. Triple-distilled water was used throughout the study. Solutions were prepared by mass using an OHAUS balance (model: Explorer) with a precision of ± 0.1 mg. The error in mole fractions of the prepared solutions was estimated to be $\pm\, 3\cdot10^{-4}$.

Densities of pure components were determined with Anton-Paar vibrating-tube densimeter DMA5000 with a precision of $\pm\, 2\cdot10^{-5}\ \mathrm{g\cdot cm^{-3}}$ at a temperature controlled to ± 2 mK, which was calibrated with triple-distilled and dry air. The measured densities at 298.15 K compared to $\pm\, 5\cdot10^{-4}\ \mathrm{cm^3\cdot mol^{-1}}$ with the literature values.[2] The atmospheric pressure was determined to ± 0.1 kPa with a mercury barometer (Prolabo: Fortin, no. 02025008). The continuous visual-titration method was used to construct the solubility curves (binodals).

At a constant temperature (T ± 0.03 K), the solubility and tie line measurements of the ternary solutions (water + 2-propanol + α,α,α-trifluorotoluene) were performed as previously described.[1] The uncertainties in component mole fractions of the solution were better than ± 0.005. For tie line phase separation, the synthesized heterogeneous solutions were left to settle in stopped ampoules for 4 to 7 days inside the cryostat bath at the desired temperature till both phases became transparent. Samples of the upper and lower layers were collected using glass syringes with 15 cm long needles and then analyzed directly with a Perkin-Elmer gas chromatograph (model: Clarus 500) run by Total Chrom software (column: Porapak P, 0.6 m, Q80/100 mesh, TCD; temperatures: column = 423.15 K, detector = 473.15 K, injector = 513.15 K, nitrogen flow rate = 20 mL/min, sample injection: 0.2 μL; retention time/min: water = 0.492, ethanol =1.621, 2-propanol = 2.845, α,α,α-trifluorotoluene = 15.645).

Ethanol was used as a solvent for the gas chromatograph internal standard calibration. Three composition analyses were performed for each sample, and a mean error of 0.003 in mole fractions was achieved.

Results and Discussion

α,α,α-Trifluorotoluene has a very wide miscibility gap in water. The experimental solubility and LLE data of the investigated ternary aqueous systems were given in Tables 1 and 2, respectively. The solubility curves and tie lines for the ternary phase equilibrium were well-fitted by the empirical equation:[3]

$$x_2 = a + bx_3^{1/2} + cx_3 + dx_3^{2} + ex_3^{3} \qquad (1)$$

---

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

10.1021/je600526x CCC: $37.00

Table 1. Experimental Solubilities for Water (1) + 2-Propanol (2) + α,α,α-Trifluorotoluene (3) at 101.2 kPa

x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
			$T = 288.15$ K				
0.0460	0.1781	0.1897	0.3621	0.3945	0.3835	0.6507	0.2762
0.0795	0.2635	0.2235	0.3744	0.4367	0.3741	0.6989	0.2475
0.1042	0.2839	0.2707	0.3870	0.4802	0.3601	0.7405	0.2220
0.1075	0.2912	0.3093	0.3962	0.5297	0.3412	0.7585	0.2151
0.1520	0.3355	0.3562	0.3893	0.5903	0.3105	0.7906	0.1917
			$T = 298.15$ K				
0.0754	0.2199	0.3335	0.3680	0.5358	0.3104	0.7837	0.1793
0.1148	0.2698	0.3726	0.3630	0.5811	0.2902	0.8151	0.1605
0.1648	0.3173	0.4137	0.3540	0.6328	0.2623	0.8358	0.1481
0.2206	0.3489	0.4510	0.3434	0.6883	0.2323	0.0486	0.1759
0.2933	0.3671	0.4922	0.3277	0.7415	0.2036		
			$T = 308.15$ K				
0.0693	0.0801	0.1675	0.2675	0.4592	0.2864	0.8170	0.1143
0.0912	0.1378	0.1903	0.2805	0.5380	0.2573	0.8795	0.0768
0.1178	0.2162	0.2241	0.2929	0.6157	0.2235	0.9058	0.0617
0.1203	0.2290	0.2712	0.3107	0.6914	0.1841	0.3901	0.3043
0.1405	0.2500	0.3317	0.3144	0.7604	0.1462		

Table 2. Experimental Liquid−Liquid Equilibrium and Plait Point for Water (1) + 2-Propanol (2) + α,α,α-Trifluorotoluene (3) at 101.2 kPa

total composition		aqueous phase		organic phase	
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}
		$T = 288.15$ K			
0.4752	0.3249	0.8265	0.1636	0.3079	0.3929
0.5562	0.3082	0.7684	0.2030	0.3623	0.3890
0.4959	0.2732	0.8850	0.1073	0.2476	0.3812
0.5226	0.2301	0.9200	0.0780	0.1972	0.3691
0.5719	0.1756	0.9562	0.0428	0.1347	0.3218
0.6087	0.1217	0.9785	0.0215	0.0768	0.2660
0.6475	0.0718	0.9858	0.0142	0.0270	0.1813
x^{cs}		0.5147	0.3504	0.5147	0.3504
		$T = 298.15$ K			
0.5969	0.2559	0.8456	0.1408	0.3692	0.3642
0.4631	0.3017	0.8856	0.1052	0.3291	0.3697
0.4213	0.2999	0.9197	0.0730	0.2876	0.3692
0.4176	0.2888	0.9415	0.0528	0.2496	0.3652
0.4480	0.2454	0.9616	0.0349	0.2164	0.3506
0.4842	0.1887	0.9732	0.0268	0.1401	0.3038
0.5075	0.1574	0.9800	0.0200	0.1053	0.2751
0.7405	0.0321	0.9831	0.0169	0.0136	0.0765
x^{cs}		0.5479	0.3038	0.5479	0.3038
		$T = 308.15$ K			
0.4867	0.2478	0.7259	0.1600	0.2965	0.3175
0.5041	0.2227	0.7847	0.1323	0.2442	0.3008
0.5261	0.1859	0.8430	0.0999	0.1715	0.2730
0.5462	0.1569	0.8650	0.0848	0.1480	0.2501
0.5880	0.0908	0.9251	0.0456	0.0900	0.1610
0.5936	0.0644	0.9500	0.0300	0.0699	0.1191
x^{cs}		0.5287	0.2618	0.5287	0.2618

where x_2 and x_3 are the compositions of 2-propanol and α,α,α-trifluorotoluene, respectively.

The LLE results of this investigation are represented satisfactorily by the method of Othmer−Tobias:[4]

$$\ln\{(1 - x_{33})/x_{33}\} = A + B \ln\{(1 - x_{11})/x_{11}\} \qquad (2)$$

where x_{i1} and x_{i3} are the compositions of component i in the aqueous phase and the organic phase, respectively. The fitting parameters of eqs 1 and 2 were determined using a linear-least-squares method, with standard deviations: $\sigma_s < 10^{-4}$ for eq 1 and $\sigma_s < 4 \cdot 10^{-2}$ for eq 2, and the fitting parameter values are reported in Table 3.

The plait-point compositions of the ternary systems (x_i^{cs}, x_j^{cs}) at each temperature are estimated by the Othmer−Tobias methods and are reported in Table 2. The solubility and LLE data at the three temperatures are plotted in Figure 1 and in Figure 2 for Othmer-Tobias correlation.

Table 3. Fitting Parameters of Solubility and Liquid−Liquid Equilibrium Data for Water (1) + 2-Propanol (2) + α,α,α-Trifluorotoluene (3)

eq 1					eq 2	
a	b	c	d	e	A	B
			$T = 288.15$ K			
0.0185	1.2892	−1.0365	−0.2756		1.9012	0.6704
			$T = 298.15$ K			
0.0094	0.9902	−0.4728	−0.5598		1.8476	0.4923
			$T = 308.15$ K			
−0.0225	0.1862	1.4502	−2.6797	1.0404	1.4419	0.9937

Table 4. Values of Molecular Interaction Parameters for NRTL and UNIQUAC from Liquid−Liquid Equilibrium Data for Water (1) + 2-Propanol (2) + α,α,α-Trifluorotoluene (3)

	NRTL (α = 0.2)		UNIQUAC	
	$\Delta\lambda_{ij}$	$\Delta\lambda_{ji}$	Δu_{ij}	Δu_{ji}
component *i-j*	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}
		$T = 288.15$ K		
1-2	−2160.8	−3311.1	−1552.7	583.1
1-3	8548.0	8728.5	−121.2	10887.7
2-3	−7581.8	−10729.7	−3145.7	−91.1
		$T = 298.15$ K		
1-2	1504.7	−3986.9	−1281.5	351.6
1-3	6868.9	8296.6	−894.0	11292.6
2-3	−9916.6	−8923.0	−4668.0	579.3
		$T = 308.15$ K		
1-2	−717.2	3552.2	−611.7	3904.5
1-3	5843.3	6016.6	−1063.8	7481.9
2-3	−6547.8	6806.1	740.7	207.1

Structural Parameters for UNIQUAC Model[7]

	r	q
water	0.920	1.400
2-propanol	2.779	2.508
α,α,α-trifluorotoluene	4.428	3.512

Two thermodynamic activity coefficient models are used to correlate the LLE data at each temperature: non random two liquid (NRTL)[5] and the universal quasi chemical (UNIQUAC).[6] The structural molecular parameters for the UNIQUAC model, (r, q), are computed using refer 7. The value of α, the nonrandomness parameter for the NRTL model, was set equal to 0.2. The binary molecular interaction parameters for NRTL ($\Delta\lambda_{ij}$, $\Delta\lambda_{ji}$) and UNIQUAC (Δu_{ij}, Δu_{ji}) were determined by minimizing the objective function:

$$F(x) = \sum_i \sum_l \sum_\varphi (x_{il\varphi} - \dot{x}_{il\varphi})^2 \qquad (3)$$

where x_i and $\dot{x}_i$ denote the experimental and correlated composition of component i, respectively; φ is the liquid phase; and l is the numbers of tie lines. The standard deviation of the fit for NRTL and UNIQUAC models was estimated from

$$\sigma_s = \{\sum_i \sum_l \sum_\varphi (x_{il\varphi} - \dot{x}_{il\varphi})^2/6l\}^{1/2} \qquad (4)$$

Both models correlate the experimental LLE data satisfactorily with standard deviations σ_s less than 0.003. The molecular energy interaction parameters for NRTL and UNIQUAC models are listed in Table 4 together with UNIQUAC structural parameters. A comparison between the experimental and correlated compositions of the critical solutions, $\Delta x_i^{cs} = (x_{i,calc}^{cs} -$

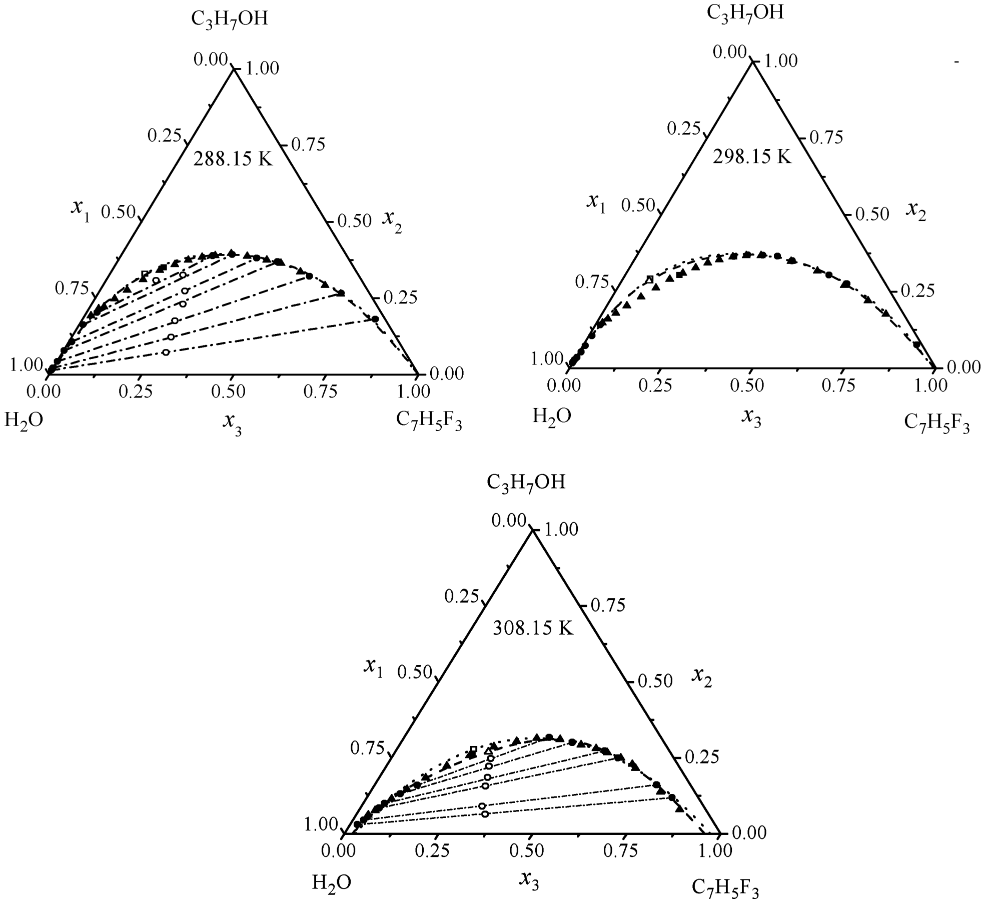

Figure 1. Solubility and liquid−liquid equilibrium data for water (1) + 2-propanol (2) + α,α,α-trifluorotoluene (3) as function of temperature: ▲, solubility point; ●, LLE point; ○, total point; ■, plait point; □, plait point-NRTL; △, plait point-UNIQUAC; - • -, tie line; •••, NRTL; - - -, UNIQUAC.

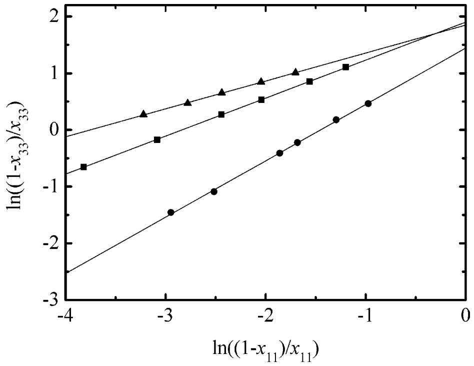

Figure 2. Othmer−Tobias correlation of liquid−liquid equilibrium data for water (1) + 2-propanol (2) + α,α,α-trifluorotoluene (3). T = ■, 288.15 K; ▲, 298.15 K; ●, 308.15 K; −, eq 2.

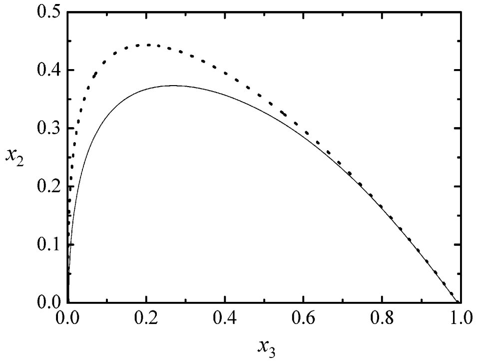

Figure 3. Binodal curves from NRTL data at 298.15 K: −, water (1) + 2-propanol (2) + α,α,α-trifluorotoluene (3); •••, water (1) + ethanol (2) + α,α,α-trifluorotoluene (3) from ref 1.

$x_{\mathrm{i,expt}}^{\mathrm{cs}}$), gives at 308.15 K: NRTL, ($\Delta x_1^{\mathrm{cs}} = -0.012$, $\Delta x_2^{\mathrm{cs}} = 0.017$); UNIQUAC, ($\Delta x_1^{\mathrm{cs}} = -0.047$, $\Delta x_2^{\mathrm{cs}} = 0.008$).

The selectivity, S, of α,α,α-trifluorotoluene to extract 2-propanol from its aqueous solutions is equal to $s = (x_{11}x_{23}/x_{21}x_{13})$. Selectivity increases considerably with increasing composition of water in the aqueous layer and decreases with increasing temperature: S (2 → 87 at 288.15 K; 2 → 69 at 298.15 K; 2 → 25 at 308.15 K). High selectivity of a solvent would minimize the number of stages and reflux ratios required for a practical extraction process.

2-Propanol and water forms a minimum boiling azeotrope[8] at $T_{\mathrm{az}} = 353.3$ K and $x_{\mathrm{az}}(\mathrm{PrOH}) = 0.689$. In aqueous solutions, hydrophobic interaction undergoes between water and propanol to form hydrate, resulting in a slight reduction of the hydrogen bond forces among water and alcohol molecules,[9] in favor of the C−F•••HO− and the π•••C−F interactions in the α,α,α-trifluorotoluene solutions, where the organic phase is richer in 2-propanol.

The effect of temperature on the miscibility gap of the system (water + 2-propanol + α,α,α-trifluorotoluene) is small and becomes moderately important at 308.15 K where the area of the two-phase region becomes smaller, in which the cross-associative dispersion forces enhance slightly the mutual solubility of the solution components. At the same temperature, the α,α,α-trifluorotoluene molecules are better dissolved in the presence of propanol hydrate toward the water-rich region of the ternary solutions rather than in ethanol[1] as illustrate in Figure 3.

Conclusion

New solubility and LLE data are measured for the system (water + 2-propanol + α,α,α-trifluorotoluene) at temperatures of (288.15, 298.15, and 308.15) K and pressure of 101.2 kPa. The LLE data are correlated by empirical equations and thermodynamic models. The effect of temperature on the miscibility gap is negligible as temperatures are increased from (288.15 to 298.15) K and becomes moderately significant at 308.15 K.

The determined data showed good internal consistencies and are well-correlated by empirical expressions. Practically, α,α,α-trifluorotoluene is capable to extract efficiently 2-propanol from its dilute aqueous solutions to obtain absolute alcohol.

Literature Cited

(1) Atik, Z.; Chaou, M. Solubilities and liquid−liquid equilibria of (water + ethanol + α,α,α-trifuorotoluene) at temperatures $T = (288.15, 298.15, \text{and } 308.15)$ K and pressure $p = 101.2$ kPa. *J. Chem. Thermodyn.* **2006**, doi:10.1016/j.jct.2006.09.004

(2) Riddick, J. A.; Bunger, W. B.; Sakano, Physical, T. K. *Properties and Methods of Purification, Vol. II, Organic Solvents*; Wiley: New York, 1986; pp 74, 192, 196, 461.

(3) Mistry, S. L.; Kaul, A.; Merchuk, J. C.; Asenjo, J. A. Mathematical modelling and computer simulation of aqueous two-phase continuous protein extraction. *J. Chromatogr.* **1996**, *A741*, 151−163.

(4) Othmer, D. F.; Tobias, P. E. Tie line correlation. *Ind. Eng. Chem.* **1942**, *34*, 693−696.

(5) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135−144.

(6) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J*. **1975**, *21*, 116−128.

(7) Poling, B. E.; Prausnitz, J. M.; O'Connell, J.P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2000.

(8) Al-Rub, F. A.; Datta, R. Separation of 2-propanol−water mixture with capillary porous plates. *Sep. Sci. Technol.* **1999**, *34*, 725−741.

(9) Max, J-J.; Daneault, S.; Chapados, C. 1-Propanol hydrate by IR spectroscopy. *Can. J. Chem.* **2002**, *80*, 113−123.

Received for review November 19, 2006. Accepted January 14, 2007. We thank L'Agence Nationale pour le Développement de la Recherche Universitaire, A.N.D.R.U. (Algeria), Project AU19908, for partial support of this work.

JE600526X