Solubilities and liquid–liquid equilibria of (water + ethanol + α,α,α-trifluorotoluene) at temperatures $T = (288.15, 298.15, \text{ and } 308.15)$ K and pressure $p = 101.2$ kPa

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Abstract

New solubility and liquid–liquid equilibrium (LLE) data of solutions of (water + ethanol + α,α,α-trifluorotoluene) are determined at three temperatures (288.15, 298.15, and 308.15) K and atmospheric pressure. The solubility and LLE data are correlated quantitatively by empirical equations, NRTL, and UNIQUAC models. The effect of temperature upon miscibility of the ternary systems is small. Practically, α,α,α-trifluorotoluene is capable to extract efficiently ethanol from its dilute aqueous solutions to obtain absolute alcohol.
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1. 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 wide industrial applications. Fluorinated hydrocarbons HFC's are non-toxic, non-polluting, and environmentally accepted chemicals. Unfortunately, a survey of the literature indicates that the amount of data available of their non-ideal solutions [1,2] is significantly small to date.

The solubility and liquid–liquid equilibrium data of aqueous solutions containing fluorinated hydrocarbons are to our knowledge inexistent. α,α,α-Trifluorotoluene has a very wide miscibility gap in water and the water content that may be contained in the pure product has a negligible influence on the LLE phase diagram. This work reports new data on the solubilities and liquid–liquid phase diagrams of solutions of (water + ethanol + 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 NRTL and UNIQUAC models, respectively.

The measurement and correlation of liquid–liquid phase equilibrium properties are important for a precise description of the real behaviour of solutions in the heterogeneous region, thus 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 from aqueous solutions to high purity valuable compounds.

2. Experimental

The chemical substances and their mole-fraction purities are ethanol and α,α,α-trifluorotoluene (Fluka AG, 0.995),

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2-propanol (Merck, >0.998), and are used as received from the suppliers. The chemical purities are confirmed by gas-liquid chromatographic analysis. Triple-distilled water is used through out the study. Solutions are prepared by mass using an OHAUS balance (Model: Explorer) with a precision of ±0.1 mg. The error in the compositions (mole fractions) of the prepared solutions is estimated to be ±3 · 10^{-4}.

Densities of pure components are measured at the temperature 298.15 K with Anton-Paar vibrating-tube densimeter DMA5000 ($\delta\rho = \pm 2 \cdot 10^{-5}$ g · cm^{-3}, $\delta T = \pm 2 \cdot 10^{-3}$ K), which is calibrated with triple distilled water ($\rho = 0.997047$ g · cm^{-3}, $T = 298.15$ K) [3] and dry air. The densities of pure liquids measured at temperature 298.15 K compared to ±5 · 10^{-4} cm^3 · mol^{-1} with the literature values [3]. The atmospheric pressure is determined to ±0.1 kPa with a mercury barometer (Prolabo: Fortin, No. 02025008).

The solubility measurements of the ternary solutions are performed visually in a Pyrex jacketed equilibrium cell (70 cm^3) equipped with an inlet arm fitted with a screw-cap.

A constant temperature in the cell is achieved by a Lauda cryostat (model: RC6CP-Edition 2000), which controls the temperature to ±0.01 K. The circulating-cooling fluid is distilled water which temperature is measured with a calibrated digital thermistor-thermometer (Cole-Parmer Instrument, model: 8502-16, thermistor: YSI-400) with precision better than ±0.03 K. The continuous visual-titration method is used to construct the solubility (binodal) curves, where ethanol is injected through the inlet arm septum progressively to a stirred heterogeneous solution of (water + ethanol + α,α,α-trifluorotoluene) until the homogeneity is established for more than 10 mn. At the very dilute water zones, the water molecules are present at the top of organic phase and a longer time is needed to stabilize the system into the heterogeneous zone.

The tie-line compositions of ternary solutions within a heterogeneous zone are prepared by mass in 10 cm^3 Pyrex ampoules with tight stoppers, stirred vigorously for more than 6 h, and are left to settle for 36 h inside the cryostat bath at the desired temperature until both phases became transparent. Samples of the upper and lower layers are collected using glass hypodermic syringes with 15 cm long needles. The samples are analysed directly with a Perkin–Elmer gas chromatograph (Model: Clarus 500) run by a 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/mn, sample injection: 0.2 μl, α,α,α-trifluorotoluene residence time = 16.01 mn). 2-Propanol is used as a solvent for the internal standard calibration. Three composition analyses are performed for each sample and a mean error of less than ±0.003 is achieved.

To check on our experimental techniques, a test system of (water (1) + ethanol (2) + benzene (3)) is carried out at the temperature 303.15 K and atmospheric pressure and gave the plait point composition: ($x_1 = 0.298$, $x_2 = 0.380$)

that compares favourably with the estimated literature data ($x_1 = 0.282$, $x_2 = 0.365$) [4].

3. Results and discussion

The experimental solubility and liquid–liquid equilibrium data of the investigated ternary systems are given in tables 1 and 2, respectively. We modified Mistry *et al.* equation [5] to fit best the measured solubilities for the ternary phase equilibrium:

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

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

The reliability and consistency of the liquid–liquid equilibrium data obtained in this investigation are checked satisfactorily by the methods of Hand and Othmer–Tobias.

TABLE 1

Experimental solubilities for the system (water (1) + ethanol (2) + α,α,α-trifluorotoluene (3))

x_1	x_2	x_1	x_2
	$T = 298.15$ K		
0.0108	0.0116	0.3146	0.4371
0.0908	0.2831	0.3460	0.4431
0.1109	0.3074	0.3828	0.4438
0.1314	0.3320	0.4227	0.4401
0.1597	0.3607	0.4693	0.4276
0.1992	0.3889	0.5226	0.4050
0.2298	0.4029	0.5721	0.3786
0.2440	0.4079	0.6146	0.3508
0.2701	0.4182	0.6464	0.3295
0.2873	0.4253		
	$T = 288.15$ K		
0.0797	0.2489	0.3839	0.4292
0.0903	0.2666	0.4154	0.4298
0.1023	0.2854	0.4430	0.4273
0.1165	0.3026	0.4722	0.4196
0.1327	0.3206	0.5029	0.4079
0.1515	0.3397	0.5297	0.3964
0.1740	0.3566	0.5577	0.3817
0.2000	0.3743	0.5867	0.3634
0.2581	0.4017	0.6148	0.3444
0.2832	0.4121	0.6383	0.3286
0.3030	0.4184	0.6619	0.3112
0.3245	0.4226	0.6857	0.2931
0.3388	0.4283	0.7001	0.2836
0.3599	0.4286		
	$T = 308.15$ K		
0.0604	0.1732	0.3544	0.3864
0.0981	0.2440	0.4067	0.3881
0.1257	0.2731	0.4626	0.3757
0.1762	0.3276	0.5172	0.3568
0.1900	0.3331	0.5789	0.3235
0.1890	0.3345	0.6445	0.2820
0.2369	0.3661	0.7012	0.2444
0.2597	0.3702	0.7593	0.2008
0.3033	0.3824	0.8160	0.1547
0.3179	0.3839	0.8863	0.0962