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Liquid−Liquid Equilibrium of (Cyclohexane + 2,2,2-Trifluoroethanol) and (Cyclohexane + Methanol) from (278.15 to 318.15) K

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Tie-line points (LLE) for binary systems of cyclohexane + methanol and cyclohexane + 2,2,2-trifluoroethanol were determined at temperatures from $T = (278.15 \text{ to } 318.15)$ K and at atmospheric pressure. The NRTL and UNIQUAC activity coefficient models with temperature-dependent parameters correlated from experimental data gave a good reconstruction of the phase envelope for the two systems. The temperature effect on the 2,2,2-trifluoroethanol system is quite significant, with the predicted critical solution point by means of NRTL equation equal to: $T^{\text{cs}} = 335.1$ K, $x_{\text{TFE}}^{\text{cs}} = 0.548$.

Introduction

2,2,2-Trifluoroethanol (TFE) is an environmentally friendly solvent with good chemical and thermal stability. Cyclohexane is partially soluble in 2,2,2-trifluoroethanol. Previously, we have published studies on 2,2,2-trifluoroethanol mixtures.[1–3] Here we report data on the liquid−liquid phase diagram of the binary systems cyclohexane + methanol and cyclohexane + 2,2,2-trifluoroethanol at atmospheric pressure. The tie-lines of the two systems were favorably correlated using NRTL and UNIQUAC equations. To our knowledge, the LLE literature data for the (cyclohexane + 2,2,2-trifluoroethanol) system are inexistent.

Experimental

Cyclohexane was purchased from Panneac; heptane, methanol, and 2,2,2-trifluoroethanol from Fluka; and 2-propanol from Labosi. The chemicals were stored over A3 molecular sieves and were analyzed for purity by gas−liquid chromatography. Feed heterogeneous mixtures with known mole fractions were prepared by mass using an OHAUS balance (model: Explorer) with a precision of ± 0.1 mg. The uncertainty in the mole fraction of the prepared mixtures was estimated to be $\pm 3 \cdot 10^{-4}$. Densities of pure liquids were measured at the temperature $T = 298.15$ K with an Anton-Paar vibrating-tube densimeter DMA5000 and agreed within $\pm 0.5 \text{ kg} \cdot \text{m}^{-3}$ with the literature values.[4,5] The densities and the UNIQUAC structural parameters[6] of the pure chemicals are given in Table 1.

The equipments and liquid−liquid equilibrium measuring procedures were as previously reported.[7] Binary heterogeneous mixtures of different mole fractions, of approximately 6 cm^3 volume, were prepared by mass in stoppered ampoules. The mixtures were stirred for 8 h, and the ampoules were then submerged in the cryostat bath which controls the temperature to ± 0.03 K and allowed to attain phase equilibrium for three days at the desired temperature until the solution phases become entirely clear. Samples were taken from each phase using glass hypodermic syringes with 15 cm long needles. They were then analyzed by means of a Perkin-Elmer gas chromatograph (model: Clarus 500) for component compositions: packed column (Perkin-Elmer 6′ × 1/2″ OD SS; packing material: Carbopack B 80/100 mesh, 5 % Carboix 20M), and thermal conductivity detector; temperatures: injector = 513.2 K; column = 393.2 K; detector = 473.2 K, nitrogen flow rate = 20 $\text{mL} \cdot \text{min}^{-1}$, sample injection: 0.2 μL.

Table 1. Component Purity (*w* %), Density *ρ*, and the van der Waals Molecular Parameters (*r*, *q*)

		ρ(298.15 K)/($\text{kg} \cdot \text{m}^{-3}$)		UNIQUAC[6]	
component	100 *w*	exptl	lit.	*r*	*q*
heptane	99.5	680.0	679.5[4]	4.5000	3.860
methanol	99.7	787.0	786.4[4]	1.4311	1.432
2-propanol	99.5	781.4	781.3[4]	2.7791	1.972
cyclohexane	99.8	774.0	774.0[4]	4.0464	3.240
2,2,2-trifluoroethanol	99.2	1382.4	1381.8[5]	2.6100	2.504

The chromatograph was calibrated with known mixtures containing four components, cylohexane, methanol or trifluoroethanol, 2-propanol, and heptane, with 2-propanol used as solute, and heptane was added to homogenize the prepared standard mixtures which were partially miscible. The component retention times were: methanol = 1.135 min; 2-propanol = 2.164 min; cyclohexane = 3.528 min; 2,2,2-trifluoroethanol = 5.032 min. The mixture mole fractions were reproducable within ± 0.003.

Results and Discussion

The liquid−liquid equilibrium between two liquid phases (α and β) is established when

$$(\gamma_i x_i)^{\alpha} = (\gamma_i x_i)^{\beta}$$
$$\sum_i x_i^{\alpha} = \sum_i x_i^{\beta} = 1.0 \qquad (i = 1, 2, ..., N; T, p, \text{constant}) \quad (1)$$

where x_i and γ_i are the mole fraction and activity coefficient of component *i*, respectively.

The calculation of liquid−liquid equilibrium mole fractions x_i^{ϕ} was performed by solving the thermodynamic eq 1 for each phase simultaneously provided the activity coefficient values γ_i^{ϕ} are given. The activity coefficients γ_i^{ϕ} in eq 1 were expressed by NRTL[8] and UNIQUAC[9] equations and were used to correlate the LLE data of (cyclohexane + methanol) and (cyclohexane + 2,2,2-trifluoroethanol) systems, for which the temperature-

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Table 2. Experimental Liquid−Liquid Equilibrium and UNIQUAC Data for Cyclohexane (1) + Methanol (2) at $p = 0.1$ MPa

	feed mixture		cyclohexane-rich phase		methanol-rich phase	
T/K	x_1	x_2	x_1^{α}	$x_1^{\alpha,\text{calcd}}$	x_1^{β}	$x_1^{\beta,\text{calcd}}$
278.15	0.502	0.498	0.942	0.946	0.104	0.110
283.15	0.520	0.480	0.939	0.934	0.125	0.123
288.15	0.510	0.490	0.922	0.918	0.135	0.135
293.15	0.519	0.481	0.892	0.896	0.158	0.155
298.15	0.496	0.504	0.876	0.875	0.177	0.173
303.15	0.530	0.470	0.841	0.845	0.190	0.193
308.15	0.516	0.484	0.812	0.805	0.218	0.220
313.15	0.523	0.477	0.758	0.756	0.261	0.262
316.15	0.520	0.480	0.702	0.712	0.301	0.298

Table 3. Experimental Liquid−liquid Equilibrium and NRTL Data for Cyclohexane (1) + 2,2,2-Trifluoroethanol (2) at $p = 0.1$ MPa

	feed mixture		cyclohexane-rich phase		trifluoroethanol-rich phase	
T/K	x_1	x_2	x_1^{α}	$x_1^{\alpha,\text{calcd}}$	x_1^{β}	$x_1^{\beta,\text{calcd}}$
283.15	0.501	0.499	0.925	0.925	0.045	0.045
288.15	0.500	0.500	0.899	0.904	0.054	0.057
293.15	0.500	0.500	0.880	0.889	0.069	0.067
298.15	0.499	0.501	0.865	0.873	0.088	0.079
303.15	0.496	0.504	0.850	0.854	0.106	0.094
308.15	0.503	0.497	0.837	0.830	0.111	0.112
313.15	0.498	0.502	0.812	0.803	0.119	0.134
316.15	0.502	0.498	0.786	0.783	0.144	0.150
318.15	0.499	0.501	0.767	0.769	0.167	0.161

Table 4. Interaction Parameters, $A_{ij} = a_{ij} + b_{ij}T$, for NRTL and UNIQUAC Equations

	NRTL			UNIQUAC	
components ij	α_{ij}	a_{ij}/K	b_{ji}	a_{ij}/K	b_{ji}
cyclohexane (1) + methanol (2)					
1,2	0.2	2512.31	−6.668	1620.90	−3.288
2,1		34.05	1.070	169.93	−0.540
cyclohexane (1) + 2,2,2-trifluoroethanol (2)					
1,2	0.2	1126.75	−2.538	352.93	−0.514
2,1		1493.01	−2.982	483.02	−1.238

dependent binary interaction parameters, $A_{ij} = a_{ij} + b_{ij}T$, between components i and j were obtained by minimizing the objective function

$$F = \sum_{l}^{M}\sum_{\phi}^{2}(x_i^{\phi} - x_{i,\text{calcd}}^{\phi})^2 \tag{2}$$

where x_i^{ϕ} and $x_{i,\text{calcd}}^{\phi}$ denote the experimental and correlated mole fraction of component i, in phase ϕ, and l is the number of tie-lines, respectively. The nonrandomness parameter αij value for NRTL equations was held constant at 0.2. The standard deviation σ_s in the phase mole fraction was estimated from the equation

$$\sigma_s = 100\cdot\left[\sum_{l}^{M}\sum_{\phi}^{2}(x_i^{\phi} - x_{i,\text{calcd}}^{\phi})^2/(2M-4)\right]^{0.5} \tag{3}$$

In this work, the measured tie-lines were well fitted with σ_s equal to 0.5 % for each correlating equation and are given in Tables 2 and 3 for (cyclohexane + methanol) and (cyclohexane + 2,2,2-trifluoroethanol), respectively, compared with calculated data. The measured values of the cyclohexane + methanol system compared satisfactorily with the literature data.[10]

The adjusted interaction parameters for NRTL and UNIQUAC equations are listed in Table 4. Figure 1 shows a comparison of the measured (T, x_1) diagram and UNIQUAC data for the cyclohexane (1) + methanol (2) system together with literature values.[10] Whereas, the observed and NRTL-correlated LLE diagram for cyclohexane (1) + 2,2,2-trifluoroethanol (2) system is shown in Figure 2. Deviations for correlating the LLE data for cyclohexane (1) + 2,2,2-trifluoroethanol (2) using the UNIQUAC equation are illustrated in Figure 3. The predicted critical solution point for the 2,2,2-trifluoroethanol system by means of the NRTL equation was: $T^{\text{cs}} = 335.1$ K, $x_{\text{TFE}}^{\text{cs}} = 0.548$.

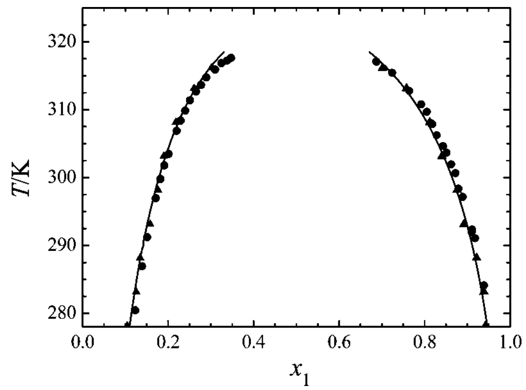

Figure 1. Comparison of observed and correlated LLE data for cyclohexane (1) + methanol (2): ▲, this work; ●, from ref 10; −, UNIQUAC eq.

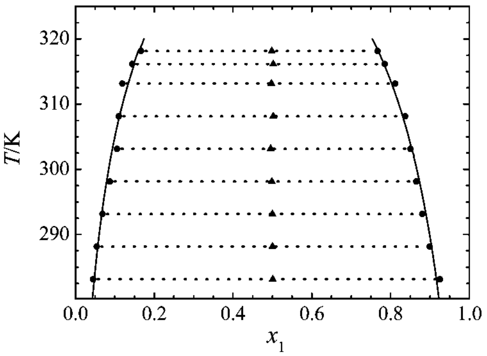

Figure 2. Liquid−liquid equilibrium for cyclohexane (1) + 2,2,2-trifluoroethanol (2): ●, LLE point; ▲, feed mixture;..., tie line; −, NRTL eq.

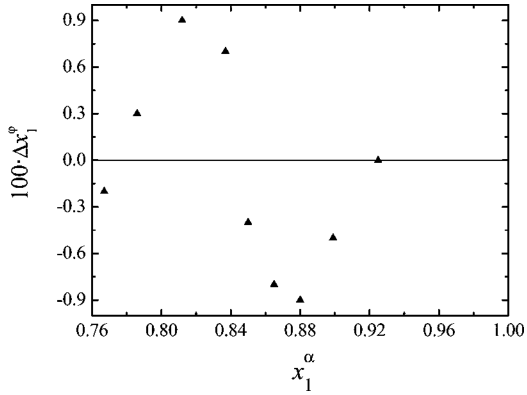

Figure 3. Deviations in phase mole fractions from the UNIQUAC correlation for cyclohexane (1) + 2,2,2-trifluoroethanol (2).

Conclusion

New liquid−liquid equilibrium data are reported for (cyclohexane + 2,2,2-trifluoroethanol) at atmospheric pressure and at temperatures beneath the critical solution. The correlated LLE curves by NRTL and UNIQUAC models compare favorably with the measured values. The temperature effect on this system is quite significant.

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