Effect of Temperature on Phase Equilibrium of the Mixed-Solvent System of (2,2,2-Trifluoroethanol + Methanol + Cyclohexane)[†]

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An experimental study was carried out to construct a type II phase diagram of the liquid−liquid equilibrium of the mixed solvents of (2,2,2-trifluoroethanol + methanol + cyclohexane) at the temperatures $T = (283.15, 293.15, 303.15, \text{ and } 313.15)$ K, and under atmospheric pressure of 101.2 kPa. Gas−liquid chromatography was used to obtain the mole fractions of the tie line ends of the two liquid phases at equilibrium. The NRTL and UNIQUAC equations reproduced satisfactorily all the measured data with an average root-mean-square deviation in phase-mole fractions equal to 1.04 %. The binary intermolecular interactions governing the mixture of unlike molecules were estimated by means of the same equations. The temperature effect on the system miscibility is slightly more significant on the cyclohexane-rich phase than on the (trifluoroethanol + methanol)-rich phase.

Introduction

Clean fuels from materials which have thermal and storage stability are a necessity to reduce climate change that threatens and endangers the natural environment and resources. The use of natural gas as a vehicular fuel is environmentally advantageous. Nonetheless, the storage and transportation of natural gas for such application need careful attention. The use of methanol as an energy-storage medium and as a fuel receives attention due to its availability, low cost, clean-burning characteristics, and high octane rating. Methanol also plays a critical role in the production of biodiesel. Even so, methanol is a hazardous chemical that is highly flammable and toxic and must be properly stored and transported. Methanol is also an efficient antifreeze material and antigas hydrate former in natural gas pipelines, including gas storage and transportation facilities. Recently, hydrocarbon mixtures such as (methanol + cyclohexane) are proposed to dissolve natural gas at moderate temperatures and pressures.[1]

Pure solvent and solvent mixtures of 2,2,2-trifluoroethanol demonstrate chemical and thermal stability, and they find a wide range of technical applications.[2−5] Solutions containing 2,2,2-trifluoroethanol, methanol, and cyclohexane are good reacting media.[6]

We have previously studied the volumetric properties of (2,2,2-trifluoroethanol + methanol)[7] and the phase behavior of binary mixtures of 2,2,2-trifluoroethanol.[8−10] In this work, gas−liquid chromatography was used to investigate the liquid−liquid phase behavior of the ternary mixed solvents of (2,2,2-trifluoroethanol + methanol + cyclohexane) at four temperatures from (283.15 to 313.15) K and atmospheric pressure of 101.2 kPa. The system presents a type II phase diagram of the liquid−liquid equilibrium (LLE). The experimental, NRTL, and UNQUAC correlated data were found to agree reasonably well, with an average root-mean-square deviation (rmsd) equal to 1.04 %. The obtained data might contribute to the understanding of the ternary mixed solvents containing 2,2,2-trifluoroethanol.

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

		ρ(298.15 K)/(kg·m^{-3})		UNIQUAC[14]	
component	100 w	exptl	lit.	r	q
heptane	99.5	680.0	679.5[12]	4.5000	3.860
methanol	99.7	787.0	786.4[12]	1.4311	1.432
2-propanol	99.5	781.4	781.3[12]	2.7791	1.972
cyclohexane	99.8	774.0	774.0[12]	4.0464	3.240
2,2,2-trifluoroethanol	99.2	1382.4	1381.8[13]	2.6100	2.504

Experimental

Cyclohexane was purchased from Panreac; heptane, methanol, and 2,2,2-trifluoroethanol were purchased from Fluka; and 2-propanol was purchased from Labosi. The chemicals were stored over A3 molecular sieves and were analyzed for purity by gas−liquid chromatography. Densities of pure liquids were measured at the temperature $T = (298.150 \pm 0.003)$ K using an Anton-Paar vibrating-tube densimeter DMA5000 with an accuracy of $\pm$ 0.03 kg·m^{-3}. The observed density data agreed with literature values to $\pm$ 0.5 kg·m^{-3}.

The equipment and liquid−liquid equilibrium measuring procedures were as previously reported.[8,11]

Feed heterogeneous mixtures with known mole fractions were prepared by mass using an OHAUS balance (model: Explorer) with a precision of $\pm$ 0.1 mg. The uncertainty in the mole fraction of the prepared mixtures was estimated to be $\pm 3 \cdot 10^{-4}$.

Ternary feed mixtures of different mole fractions, of approximately 8 cm^3 volume in 20 cm^3 stoppered ampoules, were vigorously stirred for 8 h, and the ampoules were then submerged in the cryostat bath and allowed to attain phase equilibrium for three days at the temperature ($T \pm 0.03$) K, until the solution phases became entirely clear. Samples were then taken from each phase using glass hypodermic syringes. A Perkin-Elmer gas chromatograph (model: Clarus 500) was

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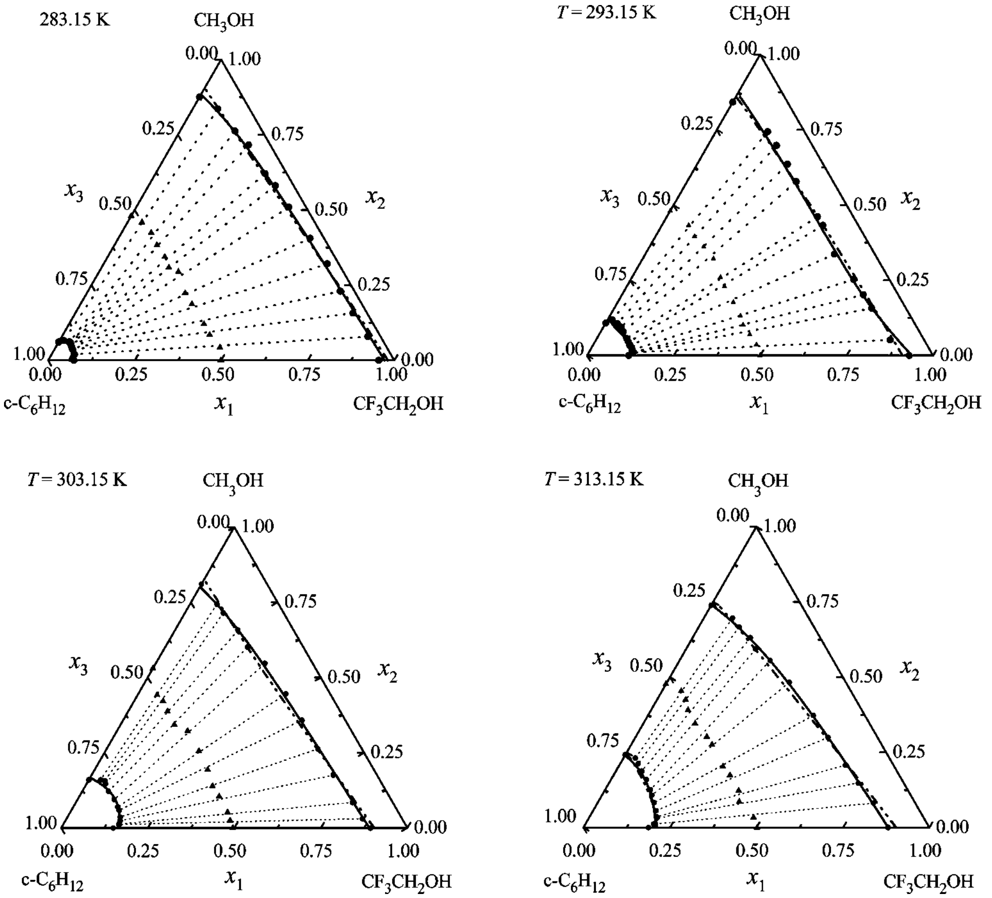

Figure 1. Liquid−liquid equilibrium for 2,2,2-trifluoroethanol (1) + methanol (2) + cyclohexane (3): ▲, feed mixture; ●, LLE point; ..., tie line; −•−, NRTL; −, UNIQUAC.

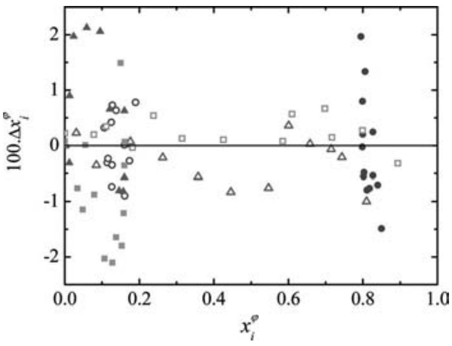

Figure 2. Deviations for predicting the liquid−liquid equilibrium data for 2,2,2-trifluoroethanol (1) + methanol (2) + cyclohexane (3) at $T = 303.15$ K using the UNIQUAC equation. Solid symbols, cyclohexane-rich phase; open symbols, (trifluoroethanol + methanol)-rich phase: ■, □, trifluoroethanol; ▲, △, methanol; ●, ○, cyclohexane.

used to determine the sample mole fractions. The chromatograph was equipped with a thermal conductivity detector and a packed column (Perkin-Elmer 6 × 1/2 OD SS; packing material: Carbopack B 80/100 mesh, 5 % Carboix 20M). All samples were examined under the following conditions: 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. The chromatograph working temperatures were estimated to be accurate to ± 0.5 K. The gas chromatograph was calibrated by means of standard mixtures of the three components of interest: the internal standard was 2-propanol, and heptane was added to homogenize the standard mixtures which were partially miscible. The liquid−liquid equilibrium observed data had uncertainties of ± 0.003 in phase mole fractions. The purity, observed, and reported density values,[12,13] together with the UNIQUAC structural parameters[14] of the pure chemicals are given in Table 1.

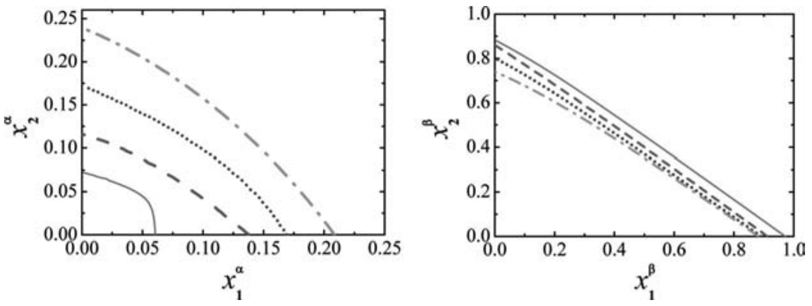

Figure 3. Effect of temperature on the liquid−liquid equilibrium for 2,2,2-trifluoroethanol (1) + methanol (2) + cyclohexane (3) from the UNIQUAC equation: −, $T = 283.15$ K; - - -, $T = 293.15$ K; ....., $T = 303.15$ K; −•−, $T = 313.15$ K.

Table 2. Liquid−Liquid Equilibrium for 2,2,2-Trifluoroethanol (1) + Methanol (2) + Cyclohexane (3) at $p = 0.1$ MPa

feed mixture			cyclohexane-rich phase			(TFE + MeOH)-rich phase		
x_1	x_2	x_3	x_1^{α}	x_2^{α}	x_3^{α}	x_1^{β}	x_2^{β}	x_3^{β}
$T = 283.15$ K								
0.500[a]	0.000	0.500	0.075	0.000	0.925	0.955	0.000	0.045
0.000[a]	0.480	0.520	0.000	0.061	0.939	0.000	0.875	0.125
0.042	0.459	0.499	0.013	0.066	0.922	0.072	0.836	0.092
0.475	0.043	0.482	0.066	0.020	0.914	0.884	0.079	0.037
0.424	0.085	0.491	0.053	0.036	0.911	0.802	0.157	0.041
0.390	0.121	0.489	0.049	0.040	0.911	0.729	0.230	0.041
0.322	0.187	0.491	0.045	0.046	0.910	0.646	0.321	0.033
0.284	0.224	0.492	0.042	0.049	0.909	0.554	0.406	0.040
0.229	0.295	0.476	0.040	0.052	0.908	0.442	0.509	0.050
0.086	0.424	0.490	0.031	0.061	0.908	0.160	0.762	0.079
0.123	0.383	0.494	0.035	0.058	0.907	0.221	0.716	0.063
0.194	0.309	0.497	0.038	0.055	0.907	0.367	0.581	0.053
0.165	0.344	0.491	0.034	0.060	0.906	0.317	0.621	0.063
$T = 293.15$ K								
0.500[a]	0.000	0.500	0.120	0.000	0.880	0.931	0.000	0.069
0.000[a]	0.481	0.519	0.000	0.108	0.892	0.000	0.842	0.158
0.077	0.433	0.490	0.125	0.010	0.865	0.850	0.052	0.098
0.471	0.036	0.493	0.127	0.009	0.864	0.744	0.157	0.099
0.400	0.102	0.498	0.120	0.019	0.861	0.643	0.253	0.104
0.435	0.070	0.495	0.129	0.011	0.860	0.697	0.202	0.101
0.156	0.362	0.482	0.034	0.106	0.860	0.198	0.698	0.104
0.377	0.132	0.491	0.107	0.033	0.860	0.546	0.337	0.117
0.334	0.177	0.489	0.097	0.045	0.858	0.465	0.432	0.103
0.282	0.230	0.488	0.086	0.057	0.857	0.435	0.461	0.104
0.255	0.260	0.485	0.065	0.079	0.856	0.315	0.578	0.107
0.204	0.322	0.474	0.046	0.095	0.859	0.261	0.636	0.103
0.112	0.396	0.492	0.013	0.119	0.868	0.150	0.744	0.106
$T = 303.15$ K								
0.496[a]	0.000	0.504	0.150	0.000	0.850	0.894	0.000	0.106
0.000[a]	0.530	0.470	0.000	0.160	0.840	0.000	0.810	0.190
0.475	0.025	0.500	0.161	0.012	0.827	0.855	0.031	0.114
0.455	0.052	0.493	0.160	0.013	0.827	0.799	0.085	0.116
0.404	0.105	0.491	0.158	0.024	0.818	0.698	0.176	0.126
0.368	0.139	0.493	0.153	0.036	0.811	0.610	0.263	0.127
0.327	0.193	0.480	0.138	0.059	0.803	0.517	0.358	0.125
0.270	0.256	0.474	0.129	0.070	0.802	0.426	0.446	0.128
0.204	0.322	0.474	0.106	0.095	0.799	0.315	0.547	0.138
0.155	0.343	0.502	0.079	0.121	0.800	0.238	0.601	0.161
0.113	0.388	0.499	0.055	0.146	0.799	0.182	0.658	0.160
0.084	0.421	0.495	0.034	0.160	0.806	0.078	0.744	0.178
0.056	0.442	0.502	0.048	0.157	0.795	0.111	0.715	0.174
$T = 313.15$ K								
0.502[a]	0.000	0.498	0.188	0.000	0.812	0.881	0.000	0.119
0.000[a]	0.477	0.523	0.000	0.242	0.758	0.000	0.739	0.261
0.475	0.034	0.491	0.197	0.012	0.791	0.797	0.082	0.121
0.408	0.086	0.506	0.197	0.032	0.771	0.721	0.148	0.131
0.387	0.123	0.490	0.194	0.036	0.770	0.654	0.207	0.139
0.337	0.174	0.489	0.182	0.056	0.762	0.557	0.300	0.143
0.302	0.203	0.495	0.163	0.083	0.754	0.478	0.373	0.149
0.234	0.276	0.490	0.144	0.108	0.748	0.354	0.483	0.163
0.206	0.302	0.492	0.131	0.126	0.743	0.262	0.556	0.183
0.150	0.346	0.504	0.102	0.160	0.738	0.201	0.594	0.205
0.107	0.391	0.502	0.075	0.188	0.737	0.167	0.631	0.202
0.083	0.425	0.492	0.052	0.212	0.736	0.117	0.667	0.216
0.056	0.454	0.490	0.035	0.231	0.734	0.083	0.697	0.220

[a] Binary LLE data taken from ref 8.

Results and Data Correlation

The studied system of 2,2,2-trifluoroethanol (1) + methanol (2) + cyclohexane (3) exhibits a type II liquid−liquid phase diagram, with phase α being rich in cyclohexane and phase β being rich in (trifluoroethanol + methanol). The observed tie-line values at the temperatures (283.15, 293.15, 303.15, and 313.15) K and pressure of 101.2 kPa are given in Table 2, and they are shown in Figure 1. The liquid−liquid equilibrium data were correlated with the activity coefficient models of nonrandom two liquid (NRTL)[15] and the universal quasi chemical (UNIQUAC).[16] The models' binary interaction parameters were estimated by minimizing the objective function

$$F = \sum_{l}^{M} \sum_{i}^{3} \sum_{\varphi}^{2} (\Delta x_i^{\varphi})^2 \qquad (1)$$

with $\Delta x_i^{\varphi} = x_{i,\text{exptl}}^{\varphi} - x_{i,\text{calcd}}^{\varphi}$, where $x_{i,\text{exptl}}^{\varphi}$ and $x_{i,\text{calcd}}^{\varphi}$ denote the experimental and correlated mole fraction of component i, in phase φ for l tie-line number, respectively.

The nonrandomness parameter α_{ij} for the NRTL equation was fixed to 0.2. The root-mean-square deviation (rmsd) of the LLE data fitting was estimated from the equation

$$\text{rmsd} = \left[\sum_{l}^{M} \sum_{i}^{3} \sum_{\varphi}^{2} (\Delta x_i^{\varphi})^2 / 6M \right]^{0.5} \qquad (2)$$

The values of rmsd (Δx_i^{φ}) for correlated phase mole fractions were smaller than 2 % for the phases (α and β) by the two correlative models, with an average value of rmsd equal to 1.04 %. The correlated parameters for NRTL and UNIQUAC equations are listed in Table 3. Deviations for predicting the liquid−liquid equilibrium data for 2,2,2-trifluoroethanol (1) + methanol (2) + cyclohexane (3) at $T = 303.15$ K calculated by the UNIQUAC equation are listed in Table 4, and they are illustrated in Figure 2.

The cyclohexane-apolar molecules and temperature increase weaken the macrocluster stability of the self- and cross-associations formed by hydrogen bonding in pure and mixed trifluoroethanol and methanol molecules. Consequently, the effect of temperature on the system miscibility is slightly more significant on the cyclohexane-rich phase than on the (trifluo-

Table 3. Binary Interaction Parameters from NRTL and UNIQUAC for 2,2,2-Trifluoroethanol (1) + Methanol (2) + Cyclohexane (3) at $p = 0.1$ MPa

	NRTL ($\alpha_{ij} = 0.20$)			UNIQUAC		
i/j	Δg_{i1}/K	Δg_{i2}/K	Δg_{i3}/K	Δu_{i1}/K	Δu_{i2}/K	Δu_{i3}/K
$T = 283.15$ K						
1	0.0	401.71	878.24	0.00	470.26	215.02
2	−55.28	0.0	424.39	−75.25	0.0	670.23
3	398.27	548.84	0.0	166.42	21.80	0.0
$T = 293.15$ K						
1	0.0	1082.2	671.01	0.0	91.271	194.5
2	−573.64	0.0	434.96	−36.53	0.0	21.055
3	327.23	327.23	0.0	105.72	623.23	0.0
$T = 303.15$ K						
1	0.0	89.07	509.56	0.0	293.01	100.26
2	46.38	0.0	379.91	−81.69	0.0	6.92
3	298.25	515.25	0.0	193.24	613.42	0.0
$T = 313.15$ K						
1	0.0	371.77	692.80	0.00	208.54	117.51
2	−256.72	0.0	408.79	−74.20	0.0	0.76
3	244.28	387.06	0.0	167.98	595.09	0.0

Table 4. rmsd % of Correlation for the Liquid−Liquid Equilibrium of 2,2,2-Trifluoroethanol (1) + Methanol (2) + Cyclohexane (3) at $p = 0.1$ MPa

	cyclohexane-rich phase			(TFE + MeOH)-rich phase			
equation	Δx_1^{α}	Δx_2^{α}	Δx_3^{α}	Δx_1^{β}	Δx_2^{β}	Δx_3^{β}	correlation
$T = 283.15$ K							
NRTL	0.72	0.68	0.57	0.62	0.83	1.44	0.86
UNIQUAC	0.77	0.64	0.58	0.32	0.43	0.75	0.60
$T = 293.15$ K							
NRTL	0.93	1.30	1.01	0.56	0.69	1.21	0.99
UNIQUAC	1.20	1.23	0.65	0.82	0.57	1.26	1.00
$T = 303.15$ K							
NRTL	1.65	1.49	1.08	0.45	0.83	1.14	1.18
UNIQUAC	1.27	1.52	0.93	0.34	0.47	0.52	0.95
$T = 313.15$ K							
NRTL	2.25	1.91	1.10	0.80	1.08	1.21	1.48
UNIQUAC	1.91	1.96	0.86	0.60	0.52	0.49	1.23

roethanol + methanol)-rich phase, as seen in the UNIQUAC (x_2^{φ}, x_1^{φ}) graphs represented in Figure 3.

Conclusion

New liquid−liquid equilibrium data are reported for (2,2,2-trifluoroethanol + methanol + cyclohexane) at four temperatures and atmospheric pressure. The mole fractions of the tie-lines end are obtained by gas chromatography. The system presents type II liquid−liquid equilibrium. The LLE data are correlated by means of the NRTL and UNIQUAC models, and only small deviations from observed data were found. The immiscibility region of the system decreases slightly with increasing temperature.

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