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Liquid−Liquid Equilibrium for 2,2,2-Trifluoroethanol + Ethanol + Cyclohexane from (288.15 to 308.15) K

Zadjia Atik* and Amina Kritli

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

Binodal and tie line points (LLE) for the 2,2,2-trifluoroethanol + ethanol + cyclohexane system were determined at the temperatures T = (288.15, 298.15, and 308.15) K and atmospheric pressure. Consistent liquid−liquid equilibrium data and plait points were attained using Hand, Othmer−Tobias, NRTL, and UNIQUAC equations. The strength of the binary intermolecular interaction governing the unlike molecules was evaluated. For alcohol-rich solutions, molecular cluster formation by a variety of hydrogen-bonding configurations between ethanol and trifluoroethanol hydroxyl groups and fluorine atoms results in a moderate temperature effect on the phase behavior of the partially miscible system.

1. Introduction

Conventional refrigerants and fossil fuels have negative environmental and climate impact, by both direct and indirect contributions to global warming. As the chemical industries are increasingly facing strict environmental regulations, new technologies and fluids are becoming necessary. Ethanol is a natural biodegradable substance and is an alternative to petroleum and coal fuels. It is largely used as a single fuel for combustion engines that cut poisonous gas emissions and greenhouse gases. Cyclohexane occurs naturally in crude oil and has large industrial applications: nylon and rubber manufacture, varnish and paint remover, and a dehydrating solvent for alcohols whether obtained from fermentation or synthetic processes. Organic mixtures of ethanol and cyclohexane find usage in varnish solvents and glossy coatings of surfaces which comprise a copolymer.

2,2,2-Trifluoroethanol (TFE) is an environmentally friendly novel and clean energetic fluid source with good chemical and thermal stability and shows characteristics of solvation, which makes it particularly interesting for synthetic chemistry and separation processes. Trifluoroethanol forms technical mixture solvents which are taking an important branch in chemical engineering research and unit development, as organic working fluids for thermal engines and heat pumps for terrestrial and space applications.

Cyclohexane is virtually insoluble in 2,2,2-trifluoroethanol. In continuation of our study of the phase diagram behavior of 2,2,2-trifluoroethanol mixtures,[1,2] we report new experimental data on the solubilities and liquid−liquid phase diagrams of the system (2,2,2-trifluoroethanol + ethanol + cyclohexane) at the temperatures T = (288.15, 298.15, and 308.15) K and atmospheric pressure, (101.2 ± 0.1) kPa. The tie lines and plait points of each system were favorably correlated using Hand, Othmer−Tobias, NRTL, and UNIQUAC equations.

For most industrial and fuel uses, the ethanol must be purified. This study reveals the high capacity of 2,2,2-trifluoroethanol to extract alcohol from binary cyclohexane/ethanol solutions and that ethanol may further be purified using a process free of chemical residues which render the alcohol unfit for human consumption.

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

	ρ(298.15 K)/(kg·m^{-3})		UNIQUAC[5]	
component	exptl	lit.	r	q
ethanol	785.2	784.9[3]	2.1055	1.972
2-propanol	781.4	781.3[3]	2.7791	2.508
cyclohexane	774.0	774.0[3]	4.0464	3.240
2,2,2-trifluoroethanol	1382.4	1381.8[4]	2.6100	2.504

Table 2. Binodal Points for 2,2,2-Trifluoroethanol (1) + Ethanol (2) + Cyclohexane (3) from (288.15 to 308.15) K at p = 0.1 MPa

x_1	x_2	x_1	x_2	x_1	x_2
T = 288.15 K		T = 298.15 K		T = 308.15 K	
0.116	0.329	0.037	0.173	0.172	0.255
0.142	0.394	0.060	0.223	0.201	0.294
0.168	0.424	0.081	0.279	0.220	0.310
0.200	0.452	0.111	0.342	0.248	0.334
0.249	0.472	0.146	0.382	0.274	0.355
0.284	0.475	0.184	0.420	0.296	0.368
0.309	0.473	0.216	0.437	0.326	0.372
0.337	0.472	0.265	0.441	0.368	0.376
0.392	0.444	0.305	0.436	0.402	0.369
0.459	0.413	0.342	0.430	0.448	0.356
0.532	0.370	0.386	0.407	0.563	0.294
0.587	0.333	0.453	0.367	0.607	0.271
0.644	0.283	0.508	0.338	0.655	0.238
0.746	0.205	0.593	0.281	0.712	0.194
0.785	0.165	0.662	0.261	0.764	0.158
0.819	0.148	0.720	0.213	0.832	0.102

2. Experimental

Cyclohexane was supplied by Panneac, ethanol by Merck, 2,2,2-trifluoroethanol by Fluka, and 2-propanol by Labosi. The chemical purities were confirmed by gas−liquid chromatography, with mole fractions higher than 0.998 for the first two substances, 0.992 for TFE, and 0.995 for the latter. Water, triple-distilled in a homemade glass apparatus, was used to calculate the electronic densimeter. Solutions of 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 solutions is estimated to be ± $3 \cdot 10^{-4}$.

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

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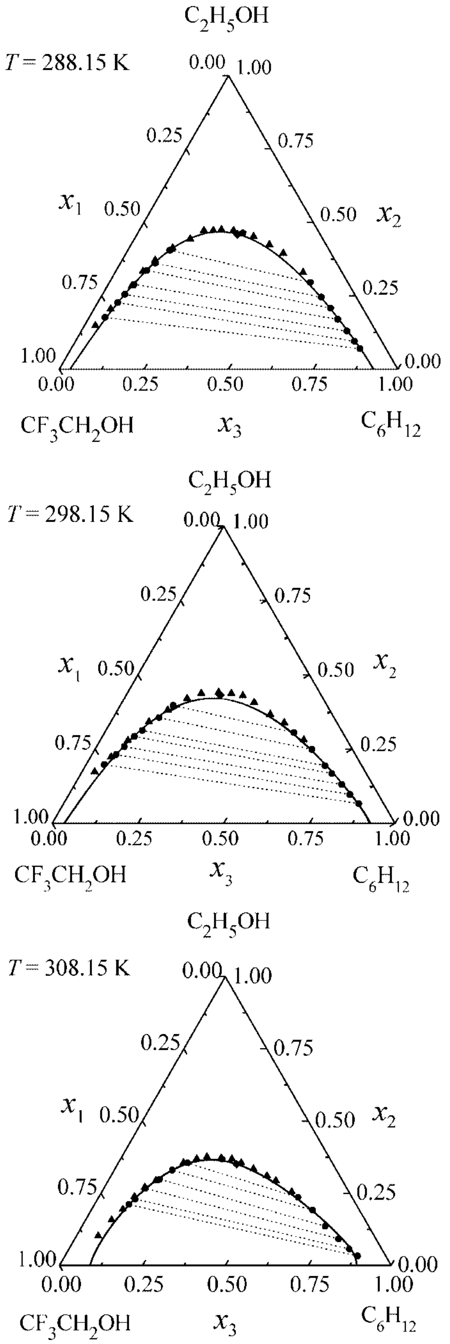

Figure 1. Binodal curve and liquid−liquid equilibrium for 2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3): ▲, solubility; ●, liquid−liquid equilibrium point; ♦, plait point; −, NRTL;···, tie line.

Densities of pure liquids were measured at the temperature 298.15 K with an Anton-Paar vibrating-tube densimeter DMA5000 and agreed within ± 0.5 $kg \cdot m^{-3}$ with the literature values[3,4] and are shown in Table 1,together with the van der Waals molecular parameters (r, q).[5]

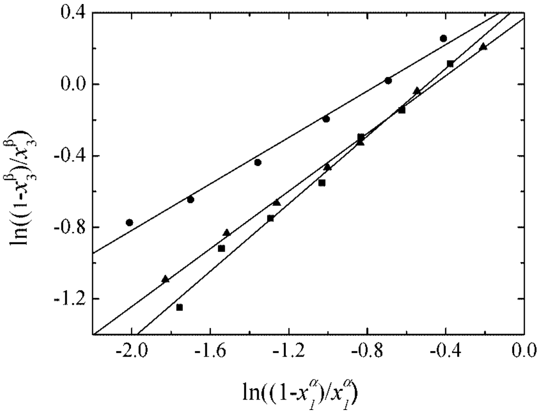

Figure 2. Othmer−Tobias correlation of LLE data for 2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3) at T = (■, 288.15; ▲, 298.15; ●, 308.15) K; −, eq 2.

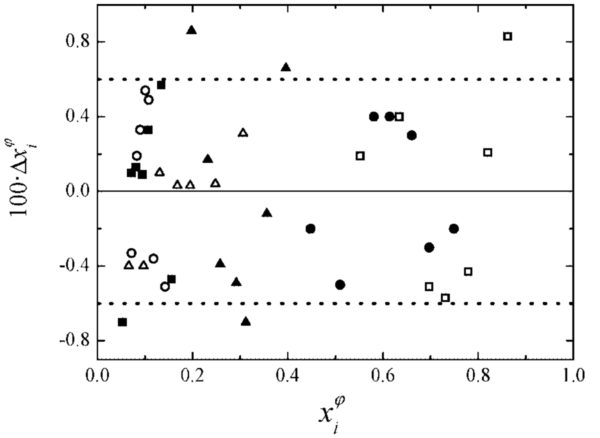

Figure 3. Deviations for predicting the liquid−liquid equilibrium data for 2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3) at T = 298.15 K using the UNIQUAC equation. Solid symbols, trifluoroethanol-rich phase; open symbols, cyclohexane-rich phase: ●,○, trifluoroethanol; ▲, Δ, ethanol; ■, □, cyclohexane; . . ., $2 \cdot \sigma(x_i^\varphi)$ from the UNIQUAC correlation.

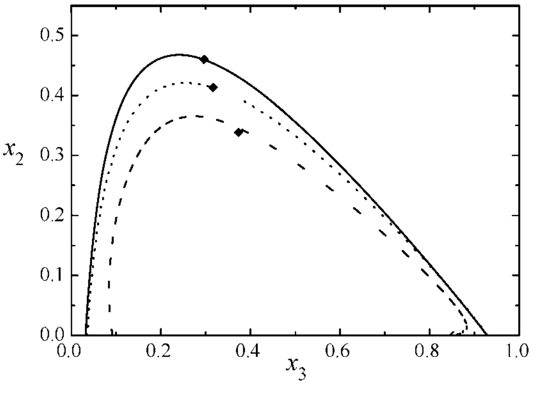

Figure 4. Temperature effect on liquid−liquid equilibrium for 2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3) by UNIQUAC correlation: −, 288.15 K; •••, 298.15 K; ---, 308.15 K; ♦, plait point.

The binodal curve and tie-line measurements of solutions of ethanol, 2,2,2-trifluoroethanol, and cyclohexane were performed at constant temperature controlled within ± 0.03 K as previously described.[6] For the determination of tie-lines, the feed solutions were stirred for 6 h and left to settle in stoppered ampoules for up to seven days inside the cryostat bath at the desired temperature until the bottles were clear. Samples of the upper and lower liquid layers were collected and then analyzed by means of a Perkin-Elmer gas chromatograph (model: Clarus 500) run by Total Chrom software using a packed column (Perkin-Elmer 6' × 1/8'' OD SS, packing material: Carbopack B 80/100 mesh, 5 % Carboix 20M) and TCD detector. The chromatographic setting conditions for sample analysis were: temperatures (K); injector = 523.2; column = 373.2; detector = 473.2; nitrogen flow rate = 20 $mL \cdot mn^{-1}$; sample injection 0.2 μL. The component retention times (min) were: ethanol = 2.46; 2-propanol = 3.75; cyclohexane = 6.52; trifluoroethanol = 9.29.

Table 3. Liquid−Liquid Equilibrium Data for 2,2,2-Trifluoroethanol (1) + Ethanol (2) + Cyclohexane (3) from (288.15 to 308.15) K at p = 0.1 MPa

	feed composition		trifluoroethanol-rich phase		cyclohexane-rich phase	
T/K	x_1	x_2	x_1^α	x_2^α	x_1^β	x_2^β
288.15	0.343	0.354	0.471	0.405	0.111	0.295
	0.368	0.309	0.536	0.361	0.104	0.245
	0.390	0.275	0.573	0.336	0.095	0.208
	0.411	0.240	0.635	0.289	0.093	0.170
	0.428	0.202	0.679	0.255	0.086	0.129
	0.450	0.166	0.715	0.227	0.081	0.095
	0.469	0.132	0.777	0.176	0.077	0.070
298.15	0.343	0.353	0.448	0.396	0.142	0.306
	0.367	0.314	0.510	0.356	0.118	0.248
	0.389	0.280	0.581	0.312	0.108	0.195
	0.413	0.242	0.614	0.292	0.101	0.168
	0.434	0.198	0.661	0.258	0.090	0.131
	0.450	0.166	0.697	0.232	0.083	0.097
	0.471	0.130	0.749	0.198	0.072	0.066
308.15	0.383	0.324	0.436	0.355	0.163	0.236
	0.437	0.201	0.495	0.330	0.141	0.192
	0.422	0.234	0.549	0.298	0.131	0.136
	0.398	0.279	0.608	0.267	0.113	0.092
	0.460	0.168	0.656	0.230	0.097	0.057
	0.471	0.146	0.685	0.211	0.086	0.033

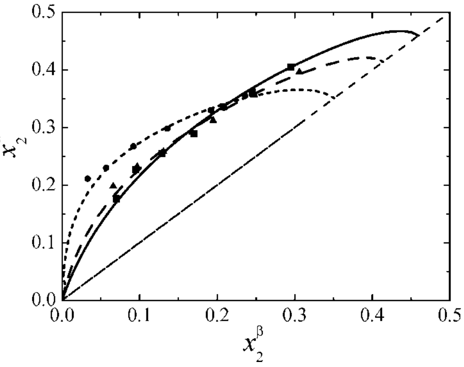

Figure 5. Distribution of ethanol in trifluoroethanol and organic phases for 2,2,2-tifluoroethanol (1) + ethanol (2) + cyclohexane (3). Exptl/NRTL: ■/−, 288.15 K; ▲/- - -, 298.15 K; •/. . ., 308.15 K.

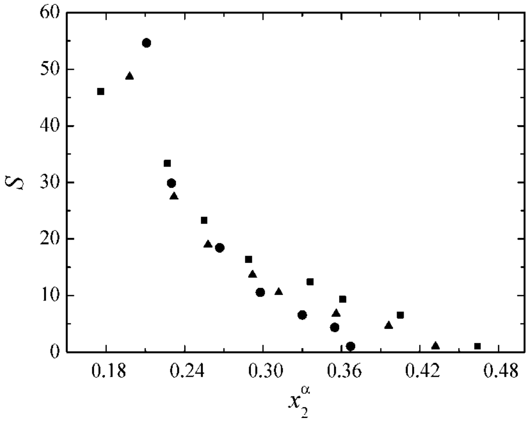

Figure 6. Selectivity s of trifluoroethanol for ethanol from liquid−liquid equilibrium of 2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3): T = (■, 288.15; ▲, 298.15; ●, 308.15) K.

Synthesized solutions corresponding to the binodal curve data for a measuring temperature were used to calibrate the gas chromatograph in the mole fraction range of interest, with 2-propanol as a solute. The duplicate analysis of solution mole fractions was reproducable within ± 0.003. The densities at T = 298.15 K and the UNIQUAC structural parameters[6] of the pure substances are given in Table 1.

3. Results and Data Correlation

The experimental solubility and LLE data for 2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3) are given in Tables 2 and 3, respectively, and are shown in Figure 1. The consistency of the liquid−liquid equilibrium data of this work was confirmed by the Hand correlation equation[7]

$$\ln\left(x_2^\beta / x_3^\beta\right) = A + B \ln\left(x_2^\alpha / x_1^\alpha\right) \tag{1}$$

and the Othmer−Tobias correlation equation[8]

$$\ln\{(1 - x_3^\beta)/x_3^\beta\} = A_1 + B_1 \ln\{(1 - x_1^\alpha)/x_1^\alpha\} \tag{2}$$

where x_i^ϕ denotes the observed mole fraction of component i in the liquid phase ϕ (α, is the trifluoroethanol-rich phase; β, is the cyclohexane-rich phase). The fitting parameters (A, B) of eq 1 and (A_1, B_1) of eq 2 were determined using a linear least-squares method, and the values are reported in Table 4 along with the correlation coefficients R^2. Figure 2 outlines the temperature dependence of the Othmer−Tobias correlation for the systems.

The critical solution mole fractions (x_1^{cs}, x_2^{cs}) of the ternary solutions of 2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3) were estimated by the method of Othmer−Tobias:[8] (0.311, 0.464) at 288.15 K; (0.274, 0.432) at 298.15 K; (0.307, 0.367) at 308.15 K.

For partially miscible systems, the thermodynamic liquid−liquid equilibrium state (at constant temperature and pressure) is described by

$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta \tag{3}$$

where γ_i^ϕ and x_i^ϕ are the activity coefficient and mole fraction of component i in liquid phase ϕ, respectively.

The measured liquid−liquid equilibrium data were correlated with the activity coefficient models of nonrandom two liquid (NRTL)[9] and universal quasi chemical (UNIQUAC).[10] The model parameters were estimated by minimizing the objective function

$$F(x) = \left[\sum_{l}^{N} \min\left\{\sum_{i}^{3}\sum_{\phi}^{2}\left(x_i^\phi - x_i^{\phi,\mathrm{calcd}}\right)^2\right\}\right] \tag{4}$$

where x_i^ϕ and $x_i^{\phi,\mathrm{calcd}}$ denote the experimental and correlated mole fraction of component i, in phase ϕ for l tie-line number,

Table 4. Hand and Othmer−Tobias Parameters for 2,2,2-Trifluoroethanol (1) + Ethanol (2) + Cyclohexane (3) from (288.15 to 308.15) K at $p = 0.1$ MPa

	Hand: eq 1			Othmer−Tobias: eq 2		
T/K	A	B	R^2	A_1	B_1	R^2
288.15	0.312	0.709	0.992	0.464	0.944	0.992
298.15	0.195	0.611	0.996	0.370	0.807	0.998
308.15	0.124	0.417	0.989	0.481	0.649	0.992

Table 5. Correlated Parameters for NRTL and UNIQUAC from LLE Data and Deviation Values in Plait Points, Δx_i^{cs}, for 2,2,2-Trifluoroethanol (1) + Ethanol (2) + Cyclohexane (3)

		NRTL		UNIQUAC	
components		Δg_{ij}	Δg_{ji}	Δu_{ij}	Δu_{ji}
i, j	α_{ij}	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}
		T/K = 288.15			
1, 2	0.2	−5311.5	−3414.7	−410.7	−640.2
1, 3		6286.0	1420.2	170.8	1661.4
2, 3		3726.8	−11.3	−1.4	−2107.3
Δx_1^{cs}, Δx_2^{cs}		0.067	0.004	0.067	0.004
		T/K = 298.15			
1, 2	0.2	−4816.4	−291.2	−454.5	−820.0
1, 3		6202.7	444.6	1355.5	1699.5
2, 3		3874.0	−633.2	144.7	288.0
Δx_1^{cs}, Δx_2^{cs}		0.003	0.018	0.005	0.019
		T/K = 308.15			
1, 2	0.2	−570.3	−928.4	−4522.7	−3297.6
1, 3		5139.9	340.9	945.9	1453.0
2, 3		10789.9	−639.9	757.9	−4360.5
Δx_1^{cs}, Δx_2^{cs}		0.016	0.016	0.019	0.028
		288.15 ≤ T/K ≤ 308.15			
1, 2	0.2	−3068.7	−3601.6	819.8	470.6
1, 3		5187.1	3876.8	1711.0	1864.0
2, 3		7801.0	−5610.3	−1052.6	4275.1

Table 6. Deviations for Predicting the Liquid−Liquid Equilibrium Data for 2,2,2-Trifluoroethanol (1) + Ethanol (2) + Cyclohexane (3) at $T = 298.15$ K Using the UNIQUAC Equation

trifluoroethanol-rich phase			cyclohexane-rich phase		
Δx_1^{α}	Δx_2^{α}	Δx_3^{α}	Δx_1^{β}	Δx_2^{β}	Δx_3^{β}
−0.002	0.007	−0.005	−0.005	0.003	0.002
−0.005	−0.001	0.006	−0.004	0.000	0.004
0.004	−0.007	0.003	0.005	0.000	−0.005
0.004	−0.005	0.001	0.005	0.000	−0.006
0.003	−0.004	0.001	0.003	0.001	−0.004
−0.003	0.002	0.001	0.002	−0.004	0.002
−0.002	0.009	−0.007	−0.003	−0.004	0.008

respectively. For a ternary solution, seven binary interaction parameters between components i and j (Δg_{ij}, Δg_{ji}, α_{ij}) were obtained for the NRTL equation, and six parameters (Δu_{ij}, Δu_{ji}) were obtained for the UNIQUAC equation. As the studied systems exhibit a large miscibility gap, the nonrandomness parameter α_{ij} for the NRTL equation was fixed to 0.2. The standard deviation of the data fitting is estimated from the equation

$$\sigma(x_i^{\phi}) = \left[\sum_{l}^{N}\left\{\sum_{i}^{3}\sum_{\phi}^{2}\frac{\left(x_i^{\phi} - x_i^{\phi,\mathrm{calcd}}\right)^2}{6N}\right\}\right]^{0.5} \tag{5}$$

The standard deviation in phase mole fraction $\sigma(x_i^{\phi})$ is smaller than $3 \cdot 10^{-3}$ for both phases by the two models' predictions. The correlated parameters for NRTL and UNIQUAC equations are listed in Table 5 along with the differences between the experimental and correlated mole fractions of the critical solutions ($\Delta x_i^{\mathrm{cs}} = x_i^{\mathrm{cs}} - x_i^{\mathrm{cs,calcd}}$). Table 6 lists deviations for predicting the liquid−liquid equilibrium data for 2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3) at $T = 298.15$ K using the UNIQUAC equation, and they are illustrated in Figure 3.

To represent the phase equilibrium behavior in the temperature range of the study, a simultaneous correlation of the three data sets was performed to give a common set of parameters for the models; even so, the residuals obtained are larger. The correlated liquid−liquid equilibrium data resulting from the UNIQUAC model are plotted in Figure 4. The distributions of ethanol in the fluoroalcohol and organic phases for the systems are illustrated in Figure 5. The capacity of 2,2,2-trifluoroethanol to extract ethanol from its cyclohexane solutions is high, with selectivity equal to: $s = (x_2^{\alpha}x_3^{\beta}/x_2^{\beta}x_3^{\alpha})$. Selectivity values for the three temperatures are found to be within the range $4 \le S \le 56$, which encourages efficient extraction at low temperatures. The selectivity values are exposed in Figure 6.

The cluster formation involving molecular like−like and like−dislike hydrogen bonding interactions between ethanol and trifluoroethanol hydroxyl groups and fluorine atoms results in a moderate temperature effect on the phase behavior of the alcohol-rich region of the partially miscible solutions.

4. Conclusion

New solubility and liquid−liquid equilibrium data are reported for (2,2,2-trifluoroethanol + ethanol + cyclohexane) at three temperatures and atmospheric pressure. The LLE data are well represented by thermodynamic models. The correlated binodal curves and plait points by NRTL and UNIQUAC models compare favorably with the measured values. In view of the specific intermolecular interactions governing the systems, the temperature effect on the system miscibility is fairly reasonable. Ethanol can effectively be recovered from its cyclohexane solutions by adding trifluorethanol, an environmentally friendly solvent.

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