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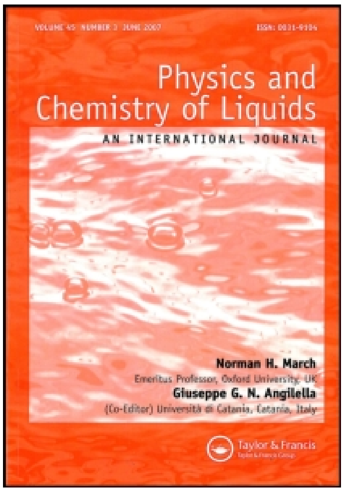

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Ternary liquid–liquid equilibria for mixtures of (ethanol + toluene + *n*-decane)

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The data on the liquid–liquid equilibrium in (ethanol + toluene + *n*-decane) have been measured at three temperatures 298.15, 303.15 and 313.15 K and ambient pressure. Gas liquid chromatography has been employed, to determine the composition of the substances in liquid phases. The measured tie-line data are presented. The experimental ternary liquid–liquid equilibrium data have been correlated, using the universal quasi chemical (UNIQUAC) and non-random tow-liquid (NRTL) activity coefficient models to obtain the binary interaction parameters of these components. Both the UNIQUAC and NRTL models, satisfactorily predict the equilibrium compositions. The partition coefficients and the selectivity factor of the toluene extraction from *n*-decane mixtures were calculated and presented.

Keywords: Ternary mixture; Ethanol; Toluene; *n*-decane; Solvent extraction; Tie-line; Activity model

1. Introduction

The separation of pure aromatic hydrocarbons and alkanes from their mixtures is an important goal in chemical operations [1,2]. From a practical and economical point of view, solvent extraction is an attractive process for this separation. Therefore, there is currently a considerable interest in using suitable solvents for extracting aromatic hydrocarbons from alkane mixtures in different chemical and petrochemical industries [3,4].

By considering the important role of the liquid–liquid equilibrium (LLE) data in the design of any industrial extraction process, it is worth while to study the LLE of ternary and quaternary mixtures of [(single-solvent or mixed-solvent) + aromatic hydrocarbons + alkanes] [5]. Many solvents have been tried to improve such separations [5,6]. Due to practical and environmental aspects, light alcohols may be considered as the suitable solvents in the recovery of aromatic hydrocarbons from refinery process stream [1,5]. Unfortunately, the experimental data extraction of aromatic hydrocarbons, by the

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solvent alcohol, such as methanol and ethanol, are scarce. Therefore, the objective of this article is to study the LLE of (ethanol + toluene + *n*-decane) ternary mixtures.

The measured LLE results for the ternary mixture of (ethanol + toluene + *n*-decane) have been reported at three temperatures, 298.15, 303.15 and 313.15 K. The results were successfully correlated by the UNIQUAC [7] and NRTL [8] activity coefficient models, and the parameters of the models, were evaluated and reported. The results of this study can lead to evaluate the selectivity factors and distribution coefficients for the extraction of toluene from *n*-decane mixtures. The comparison of the calculated selectivity factors and distribution coefficients at different temperatures, indicate that ethanol can be considered as a potential solvent, for extraction of toluene from *n*-decane mixtures at room temperature.

2. Experimental

Pure grade compounds toluene, *n*-decane and ethanol, were supplied by Merck Co. Inc., Germany. However, the purity of each compound, was checked by gas chromatography, and the results confirmed that the mass fraction purity was higher than 0.99.

The experimental procedure is described in the previous work [5]. Only the operating conditions of gas liquid chromatography measurements were different, which is given in table 1.

3. Results and discussion

The mole fractions of each component in the two liquid phases at equilibrium of the studied ternary mixtures are presented in table 2. Also in this table, the partition coefficient K_i and selectivity factor S are reported.

The dissolving capacity or the distribution coefficient (K_i) that refers to the equilibrium partitioning of the toluene between two phases is defined in the following form [9,10]:

$$K_i = \frac{x_i^e}{x_i^d}, \tag{1}$$

where the superscript e and d indicates the ethanol-rich phase and decane-rich phase respectively.

Table 1. Operating condition for gas–liquid chromatographic analysis.

Column size	$2\,\text{m} \times 2.2\,\text{mm}$
Column packing	OV-17 Csorb WHP 100–200 mesh
Detector temperature	523.15 K
Injector temperature	523.15 K
Oven temperature	$333.15\,\text{K}$ (isotime = 1 min) $\xrightarrow{298.15\,\text{K min}^{-1}}$ $463.15\,\text{K}$
Carrier gas	Nitrogen
Flow rate	$25\,\text{cm}^3\,\text{min}^{-1}$

The selectivity factor, which is a convenient measure of the separation power of the solvent for the extraction of the toluene from *n*-decane mixtures is defined as [10]:

$$S = \frac{K_2}{K_3}, \tag{2}$$

According to the experimental selectivity factor reported in table 2, the minimum selectivity factor is 1.31, which means that the extraction of toluene by the whole used solvents is possible. The experimental values of K in this study are presented in tables 2 and 3.

The UNIQUAC and NRTL models were used to correlate the experimental data. The NRTL model and the activity coefficient for the component i are expressed as follows:

$$\ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ji} x_j G_{ji}}{\sum_{k=1}^{n} x_k G_{ki}} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{m=1}^{n} \tau_{mj} x_m G_{mj}}{\sum_{k=1}^{n} x_k G_{kj}} \right) \tag{3}$$

where,

$$\tau_{ij} = \frac{(g_{ij} - g_{jj})}{RT}, \quad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}), \quad \alpha_{ij} = \alpha_{ji} \tag{4}$$

In the equation above, g_{ij} and α_{ij} are the interaction parameters of the NRTL model, where, x is the mole fraction and T is the equilibrium temperature. The calculated NRTL parameters (τ_{ij} and α_{ij}) are presented in table 3.

Table 2. Experimental LLE data for ternary mixtures [ethanol (1) + toluene (2) + *n*-decane (3)],where x is the mole fraction. The subscripts indicate the compound, and the superscripts d and e indicate the *n*-decane and ethanol rich-phases, respectively. The symbol S and K_2 represent the selectivity and distribution coefficients of toluene, respectively.

x_1^d	x_2^d	x_3^d	x_1^e	x_2^e	x_3^e	S	K_2
[Ethanol (1) + toluene (2) + *n*-decane (3)] at $T = 298.15$ K							
0.2951	0.3432	0.3617	0.7266	0.1553	0.1181	1.38	0.45
0.2637	0.2792	0.4571	0.767	0.1202	0.1128	1.74	0.43
0.2592	0.2506	0.4902	0.7916	0.1072	0.1012	2.07	0.43
0.2471	0.1737	0.5792	0.8331	0.0833	0.0836	3.32	0.47
0.2446	0.1318	0.6236	0.8462	0.0731	0.0807	4.34	0.53
[Ethanol (1) + toluene (2) + *n*-decane (3)] at $T = 303.15$ K							
0.3220	0.3309	0.3471	0.6977	0.1682	0.1341	1.31	0.51
0.3088	0.2631	0.4281	0.7464	0.1247	0.1289	1.57	0.48
0.3048	0.2351	0.4601	0.7756	0.1105	0.1139	1.89	0.47
0.2792	0.1527	0.5681	0.8263	0.0774	0.0963	2.75	0.46
0.2777	0.1192	0.6041	0.8559	0.0639	0.0802	4.03	0.52
[Ethanol (1) + toluene (2) + *n*-decane (3)] at $T = 313.15$ K							
0.3691	0.2353	0.3956	0.7073	0.1365	0.1562	1.40	0.58
0.3631	0.2136	0.4233	0.7317	0.1217	0.1466	1.65	0.57
0.3412	0.1627	0.4961	0.7778	0.0941	0.1281	2.24	0.57
0.3303	0.1456	0.5241	0.8135	0.0781	0.1084	2.60	0.53
0.2950	0.1228	0.5822	0.8405	0.0652	0.0943	3.23	0.53

The equations for the UNIQUAC model are given below:

$$\ln \gamma_i = \ln\left(\frac{\Phi_i}{x_i}\right) + 0.5Zq_i \ln\left(\frac{\theta_i}{\Phi_i}\right) + L_i - \left(\frac{\Phi_i}{x_i}\right)\sum_{j=1}^{n} L_j x_j + q_i\left(1.0 - \ln\sum_{j=1}^{n}\theta_j \tau_{ji}\right) - q_i\sum_{j=1}^{n}\left(\frac{\theta_j \tau_{ij}}{\sum_{k=1}^{n}\theta_k \tau_{kj}}\right) \tag{5}$$

where,

$$L_j = 0.5Z(r_j - q_j) - r_j + 1, \quad \theta_i = \frac{q_i x_i}{\sum_{j=1}^{m} q_j x_j}, \quad \Phi_i = \frac{r_i x_i}{\sum_{j=1}^{m} r_j x_j} \quad \tau_{ij} = \exp\left(-\frac{a_{ij} + b_{ij}T}{RT}\right) \tag{6}$$

where τ_{ij}, r and q are the interaction, the volume and the surface area parameters, respectively. As usual in the UNIQUAC model, the lattice coordination number Z, was assumed to be equal to ten. The parameters r and q depend on molecular interactions, molecular size and molecular external surface areas [9]. The volume and surface area parameters (r and q) are listed in table 4. The interaction parameters τ_{ij} are calculated and presented in table 5.

The phase diagrams for the studied ternary mixtures, are presented in figures 1–3. The experimental selectivity data for the mixtures of [ethanol (1) + toluene (2) + n-decane (3)] at three temperatures 298.15, 303.15 and 313.15 K, are presented in figure 4. According to these figures, the selectivity is higher at lower temperatures, and therefore, it is better to perform the extraction at lower temperatures. However, considering the economical and practical aspects, for an efficient extraction, the room temperature may be considered.

Table 3. Binary interaction parameters for the NRTL model, in the mixture of [ethanol (1) + toluene (2) + n-decane (3)] at different temperatures.

T/K	$i-j$	τ_{ij}	τ_{ji}	α_{ij}
298.15	1–2	1.9193	0.6687	0.293
	1–3	0.4650	2.3092	0.200
	2–3	−0.7673	0.7246	0.200
303.15	1–2	1.8877	0.6577	0.293
	1–3	0.4573	2.2711	0.200
	2–3	−0.7547	0.7126	0.200
313.15	1–2	1.8274	0.6367	0.293
	1–3	0.4427	2.1986	0.200
	2–3	−0.7306	0.6899	0.200

Table 4. The calculated UNIQUAC structural parameters.

Component	r	q
Decane	7.1974	6.0160
Toluene	3.9228	2.9680
Ethanol	2.5755	2.5880

Table 5. Binary interaction parameters for the UNIQUAC model, in the mixture of [ethanol (1) + toluene (2) + *n*-decane (3)] at different temperatures.

T/K_i	$i-j$	τ_{ij}	τ_{ji}
298.15	1–2	0.2089	1.3261
	1–3	0.2636	1.1251
	2–3	1.2592	0.7882
303.15	1–2	0.2144	1.3200
	1–3	0.2694	1.1229
	2–3	1.2544	0.7913
313.15	1–2	0.2252	1.3083
	1–3	0.2810	1.1187
	2–3	1.2453	0.7973

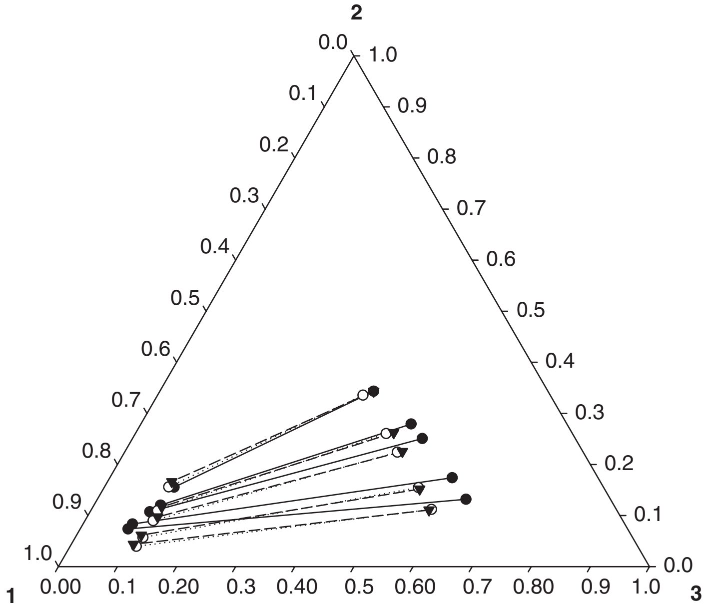

Figure 1. LLE data for [ethanol (1) + toluene (2) + *n*-decane (3)] at $T = 298.15$ K: (●) experimental tie-line data; (○) NRTL model; (▶) UNIQUAC model.

The root-mean-square deviation (RMSD) is a measure of the agreement, between the experimental data and the calculated values. The RMSD value is defined as follows [5]:

$$\mathrm{RMSD} = \left[\sum_i \sum_j \sum_k \left(x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{cal}} \right)^2 / 6M \right]^{1/2}, \qquad (7)$$

where, M is the total number of tie lines, x^{exp} and x^{cal} are the experimental and calculated mole fractions, and the subscripts i, j and k, respectively designate, the component, the phase and the tie line. The results of RMSD calculations by using both models, UNIQUAC and NRTL indicate good agreements with experimental data as shown in table 6.

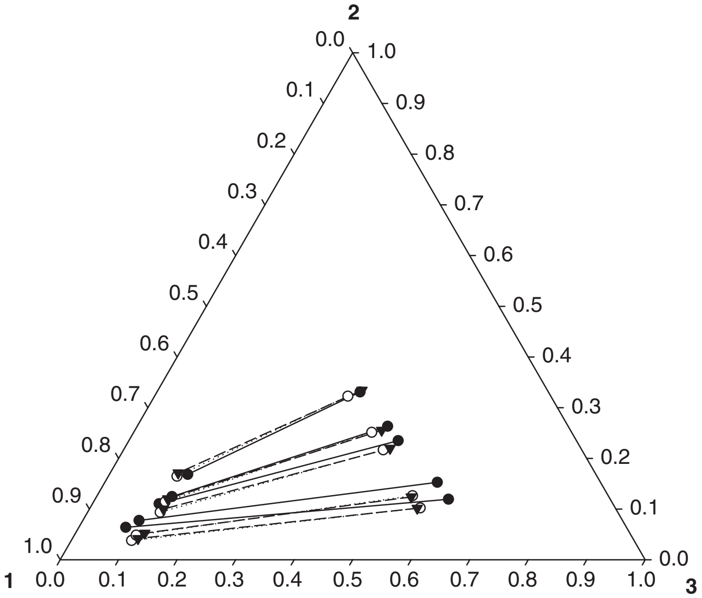

Figure 2. LLE data for [ethanol (1) + toluene (2) + *n*-decane (3)] at $T = 303.15\,\mathrm{K}$: (●) experimental tie-line data; (○) NRTL model; (▶) UNIQUAC model.

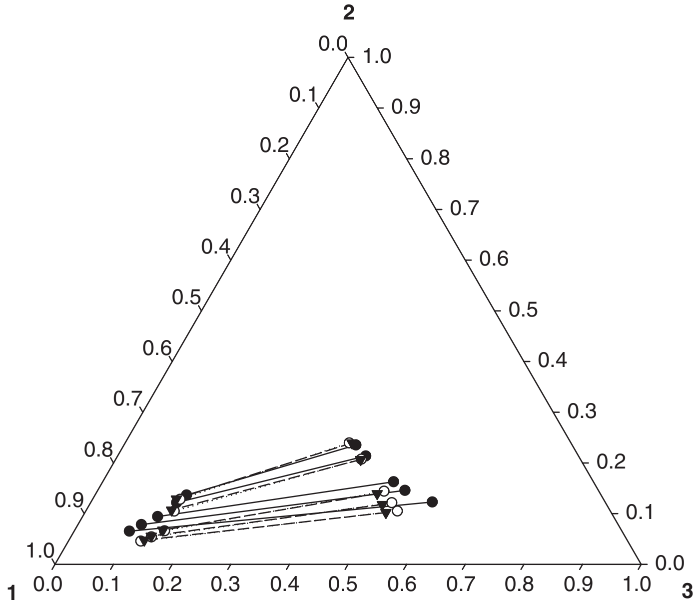

Figure 3. LLE data for [ethanol (1) + toluene (2) + *n*-decane (3)] at $T = 313.15\,\mathrm{K}$: (●) experimental tie-line data; (○) NRTL model; (▶) UNIQUAC model.

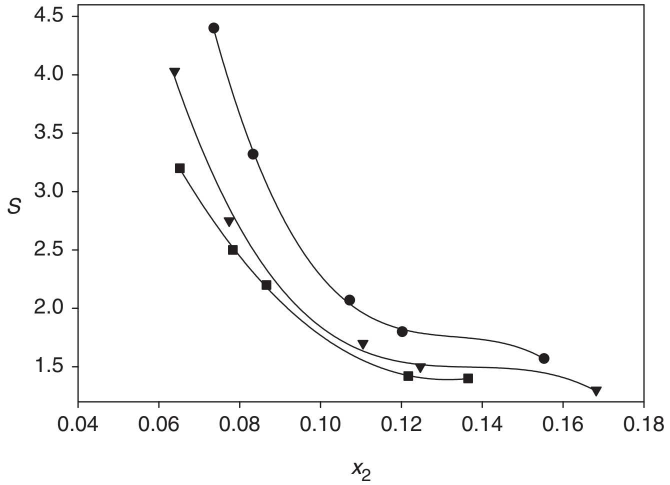

Figure 4. Experimental selectivity data for [ethanol (1) + toluene (2) + *n*-decane (3)] mixtures at (●) 298.15 K, (▶) 303.15 K, (■) 313.15 K.

Table 6. The root-mean-square deviation percent (RMSD) values for the studied ternary mixtures.

RMSD					
298.15 K		303.15 K		313.15 K	
NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC
0.0314	0.0125	0.0278	0.0163	0.0288	0.0127

4. Conclusions

Data on liquid–liquid equilibrium in (ethanol + toluene + *n*-decane) were presented at three temperatures 298.15, 303.15 and 313.15 K. The NRTL and UNIQUAC models were used to correlate the experimental results. The selectivity and distribution coefficient of the used solvent were compared in the studied ternary mixtures.

The effect of temperature in the extraction of toluene from *n*-decane as shown in table 2, indicates that at lower temperature, *S* is higher. Therefore, by considering the economical and environmental aspects, toluene may be extracted from *n*-decane at room temperature.

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