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Short communication

Liquid–liquid equilibria for mixtures of (ethylene carbonate + aromatic hydrocarbon + cyclohexane)

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Abstract

Liquid–liquid equilibrium data for mixtures of (ethylene carbonate + benzene + cyclohexane) at temperatures 303.15 and 313.15 K and (ethylene carbonate + BTX + cyclohexane) at temperature 313.15 K are reported, where the BTX is benzene, toluene and *m*-xylene. The compositions of liquid phases at equilibrium were determined by gas liquid chromatography. The selectivity factors and partition coefficients of ethylene carbonate for the extraction of benzene, toluene and *m*-xylene from (ethylene carbonate + BTX + cyclohexane) are calculated and presented. The obtained results are compared with the selectivity factors and partition coefficients of ethylene carbonate for the extraction of benzene from (ethylene carbonate + benzene + cyclohexane). The liquid–liquid equilibrium data were correlated with the UNIQUAC and NRTL activity coefficient models. The phase diagrams for the studied mixtures are presented and the correlated tie line results have been compared with the experimental data. The comparisons indicate the applicability of the UNIQUAC and NRTL activity coefficients model for liquid–liquid equilibrium calculations of the studied mixtures. The tie line data of the studied mixtures also were correlated using the Hand method.

Keywords: Ethylene carbonate; Cyclohexane; LLE data; Solvent extraction; Aromatic hydrocarbon; NRTL; UNIQUAC

1. Introduction

There are a great number of industrial solvent extraction processes containing aromatics (benzene, toluene, *m*-xylene, etc.) and saturated hydrocarbons (hexane, heptane, octane cyclohexane, etc.) [1,2].

Previous work shows that ethylene carbonate can be used as a suitable solvent in the recovery of aromatics, such as toluene, and *m*-xylene from alkane mixtures [3].

This work reports liquid–liquid equilibrium (LLE) results for the mixtures {ethylene carbonate (1) + benzene (2) + cyclohexane (3)} at 303.15 and 313.15 K and (ethylene carbonate + BTX + cyclohexane) at 313.15 K, where BTX is the mixture of benzene, toluene and *m*-xylene.

Thermodynamic models can be used for simulation and design of extraction processes. Activity coefficient models, such as non-random two-liquid models (NRTL) [4] and the universal quasichemical model (UNIQUAC) [5] have been successfully applied to correlate LLE data [6]. The accurate correlation of LLE data by using NRTL and UNIQUAC activity coefficient models depend on experimentally optimized interaction parameters. The experimental and correlated results are compared and reported. According to these comparisons the UNIQUAC and NRTL activity coefficient models are applicable for LLE calculations of the studied mixtures.

2. Experimental

2.1. Chemicals

All materials (purity of 99%) ethylene carbonate, cyclohexane, benzene, toluene, *m*-xylene supplied by Merck. The purity of each of the components was checked by gas chromatography, and the results confirmed the mass fraction purity was higher than 0.99. All compounds were used without further purification and were stored in a desiccator with a drying agent before the use.

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Table 1
Experimental LLE data for ternary system ethylene carbonate (1) + benzene (2) + cyclohexane (3)

Feed		Cyclohexane-rich phase		Ethylene carbonate-rich phase		S	K
w_1	w_2	w_1	w_2	w_1	w_2		
{ethylene carbonate (1) + benzene (2) + cyclohexane (3)} at 313.15 K							
0.2000	0.5700	0.0935	0.6281	0.7060	0.2647	4.00	0.42
0.2900	0.5100	0.0785	0.6222	0.7486	0.2272	4.50	0.36
0.1900	0.4000	0.0249	0.4621	0.7953	0.1763	6.88	0.38
0.4000	0.2700	0.0130	0.3986	0.8444	0.1326	8.51	0.33
{ethylene carbonate (1) + benzene (2) + cyclohexane (3)} at 303.15 K							
0.2400	0.5000	0.0358	0.5996	0.6590	0.2958	3.92	0.49
0.3750	0.4000	0.0296	0.5607	0.7186	0.2435	4.69	0.43
0.2300	0.4100	0.0168	0.4709	0.7367	0.2252	7.20	0.48
0.4000	0.2900	0.0084	0.4268	0.7948	0.1752	7.73	0.41
0.3300	0.3050	0.0074	0.3994	0.8439	0.1346	9.30	0.34

Table 2
LLE of ternary mixture {(ethylene carbonate (1) + BTX (2) + cyclohexane (3)} at 313.15 K

Feed				Cyclohexane-rich phase				Ethylene carbonate-rich phase				S	K
w_1	BTX			w_1	BTX			w_1	BTX				
	w_B	w_T	w_X		w_B	w_T	w_X		w_B	w_T	w_X		
{ethylene carbonate (1) + BTX (2) + cyclohexane (3)} at 313.15 K													
0.6000	0.1280	0.1262	0.1256	0.1514	0.2111	0.2624	0.3126	0.6250	0.1218	0.1190	0.1170	1.66	0.46
0.5500	0.1347	0.1329	0.1322	0.0828	0.2120	0.2472	0.2785	0.6923	0.1076	0.0954	0.0873	4.05	0.40
0.4100	0.1516	0.1495	0.1488	0.0452	0.2075	0.2311	0.2547	0.8060	0.0752	0.0581	0.0460	4.58	0.26
0.1900	0.1751	0.1728	0.1719	0.0249	0.1869	0.2056	0.2218	0.8389	0.0641	0.0467	0.0346	5.48	0.24
0.2000	0.1516	0.1495	0.1488	0.0174	0.1702	0.1820	0.1939	0.8720	0.0514	0.0356	0.0252	5.50	0.20
0.2200	0.1381	0.1362	0.1355	0.0140	0.1552	0.1636	0.1743	0.8924	0.0434	0.0292	0.0204	6.34	0.19

2.2. *Procedure*

The experimental LLE data were determined by using a glass cell with a water jacket to maintain a constant temperature (±0.1 °C). The solutions were made by mass using Sartorius analytical balance (Model A200S, accurate to 0.0001 g). The mixtures were prepared inside the cell and vigorously agitated with a magnetic stirrer for 2 h, and then left to settle for at least 12 h. Samples of both liquid phases were collected and analyzed by methods described in previous work [3]. The reproducibility of the measured concentration of LLE was smaller than 0.3%, and the absolute error for each mass fraction, w should be less than 0.01.

3. Results and discussion

The experimental LLE data for mixtures of {ethylene carbonate (1) + benzene (2) + cyclohexane (3)} at two different temperature, 303.15 and 313.15 K are reported in Table 1. The compositions are reported in mass fraction, with the symbol w_i^{E} indicating the mass fraction of constituent i in the ethylene carbonate-rich phase and w_i^{C} indicating the mass fraction of constituent i in the cyclohexane-rich phase. Table 2 shows the obtained LLE data for mixtures of {(ethylene carbonate (1) + BTX (2) + cyclohexane (3)} at 313.15 K. The UNIQUAC and NRTL models were used to correlate the experimental data by minimizing the following objective function [1,7]:

$$\mathrm{OF} = \sum_i \sum_j \sum_k (w_{ijk}^{\mathrm{exp}} - w_{ijk}^{\mathrm{cal}})^2 \qquad (1)$$

where w^{exp} and w^{cal} are the experimental and calculated mass fractions and the subscripts i, j and k, respectively designate, the component, the phase and the tie line. 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 [3]:

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

where M is the total number of tie lines. The RMSD values are listed in Table 3. The results of RMSD calculations by both models, UNIQUAC and NRTL indicate good agreement

Table 3
The root-mean-square deviation percent (RMSD) values for the studied mixtures

Mixture	T/K	RMSD	
		NRTL	UNIQUAC
Ethylene carbonate + benzene + cyclohexane	303.15	0.0512	0.0221
Ethylene carbonate + benzene + cyclohexane	313.15	0.0443	0.0285
Ethylene carbonate + BTX + cyclohexane	313.15	0.0642	0.0253

Table 4
The calculated UNIQUAC structural parameters

Component	*r*	*q*
Cyclohexane	4.0464	3.2400
Benzene	2.4000	3.1878
m-xylene	4.6578	3.5360
Toluene	3.9228	2.9680
Ethylene carbonate	1.3532	1.0800

with experimental data as shown in Table 3. The calculated volume parameter (r) and surface area parameter (q) of UNIQUAC model are listed in Table 4.

The effectiveness of extraction of aromatic compounds by ethylene carbonate by their selectivity (S), as a measure of the ability of ethylene carbonate to separate aromatics from cyclohexane is [2]:

$$S = \left(\frac{w_2^{\mathrm{E}}}{w_2^{\mathrm{C}}}\right)\left(\frac{w_3^{\mathrm{C}}}{w_3^{\mathrm{E}}}\right) \tag{3}$$

where the subscript 2 represents benzene or BTX (benzene, toluene or *m*-xylene) and 3 represents cyclohexane. This quantity is not constant over the whole two-phase region. The experimental values of S are listed in Tables 1 and 2. Selectivity in all cases is greater than 1, and this means that extraction is possible.

The capacity or dissolving ability of a solvent as the measure of the ratio of solvent to the feed required for the desired recovery of aromatics is in the following form:

$$K = \frac{w_2^{\mathrm{E}}}{w_2^{\mathrm{C}}}. \tag{4}$$

The experimental values of K in this study were also presented in Tables 1 and 2.

In order to correlate the tie line data, the following equation was used [8]:

$$\frac{w_2^{\mathrm{C}}}{w_3^{\mathrm{C}}} = a\left(\frac{w_2^{\mathrm{E}}}{w_1^{\mathrm{E}}}\right)^{b}. \tag{5}$$

Eq. (5) represents a linear dependency of the ratio $w_2^{\mathrm{C}}/w_3^{\mathrm{C}}$ on the ratio $w_2^{\mathrm{E}}/w_1^{\mathrm{E}}$ in logarithmic coordinates. For studied mixtures parameters a and b are listed in Table 5.

Fig. 1 shows the selectivity of ethylene carbonate for the extraction of benzene, toluene and *m*-xylene from (BTX + cyclohexane). Fig. 2 shows the comparison of the obtained experimental selectivity data for (ethylene carbonate + benzene + cyclohexane) mixture at 313.15 K with that obtained for (ethylene carbonate + *m*-xylene + cyclohexane) and (ethylene carbonate + toluene + cyclohexane) mixtures from the previous work [3].

Table 5
Parameters of the Eq. (5) for the studied mixtures

Mixture	*T*	*a*	*b*	R^2
Ethylene carbonate + benzene + cyclohexane	303.15	3.563	0.943	0.998
Ethylene carbonate + benzene + cyclohexane	313.15	10.34	1.463	0.989
Ethylene carbonate + BTX + cyclohexane	313.15	19.05	1.34	0.972

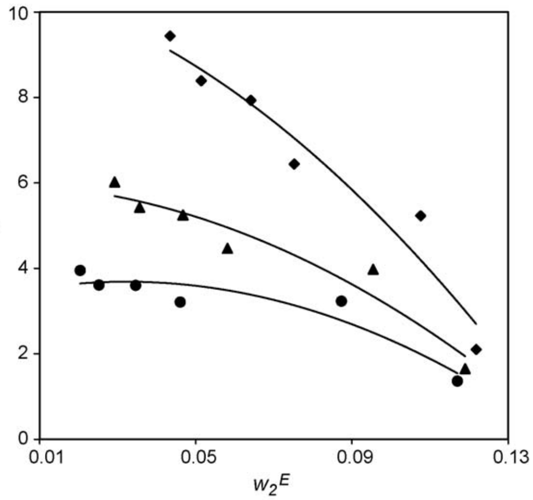

Fig. 1. Experimental selectivity data for: (♦) benzene, (▲) toluene and (●) *m*-xylene in {ethylene carbonate (1) + BTX (2) + cyclohexane (3)} mixture at 313.15 K.

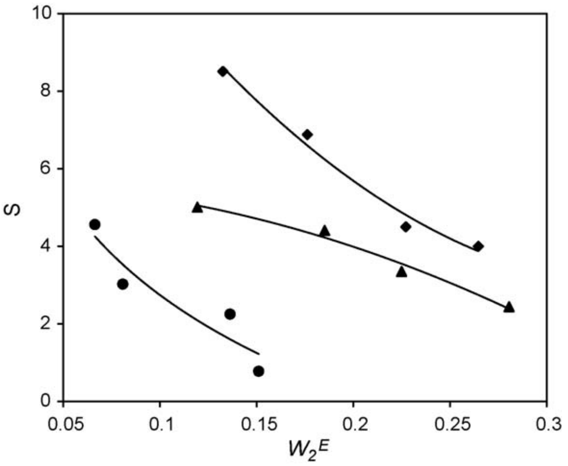

Fig. 2. Experimental selectivity data for: (●) {ethylene carbonate (1) + *m*-xylene (2) + cyclohexane (3)}, (▲) {ethylene carbonate (1) + toluene (2) + cyclohexane (3)}, (♦) {ethylene carbonate (1) + benzene (2) + cyclohexane (3)}mixtures at 313.15 K.

4. Conclusions

The obtained LLE results for the mixture (ethylene carbonate + benzene + cyclohexane) at 303.15 and 313.15 K show that the selectivity and distribution coefficient of ethylene carbonate for extraction of benzene from (benzene + cyclohexane) mixtures decreases with increasing temperature. Therefore the extraction is more efficient at the low temperature. The comparison of the calculated selectivity of ethylene carbonate for extraction of benzene, toluene and *m*-xylene from (BTX + cyclohexane) mixture indicates that the extraction efficiency of benzene is greater than toluene and *m*-xylene. The measured selectivity of ethylene carbonate for the extraction of benzene from (benzene + cyclohexane) mixture at 313.15 K is compared with that previously obtained for the extraction of toluene and *m*-xylene from (toluene + cyclohexane) and (*m*-xylene + cyclohexane) mixtures, respectively. These comparisons indicate that ethylene carbonate is more efficient for the extraction of benzene than toluene and *m*-xylene. The selectivity of ethylene carbonate for the extraction of benzene from (benzene + cyclohexane) is compared with that obtained for the extraction of benzene from (benzene + BTX) at 313.15 K. According to this comparison benzene may be extracted from (benzene + cyclohexane) mixture easier than (BTX + cyclohexane) mixture.

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