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Liquid−Liquid Equilibrium for the Ternary Systems Nonane + Dimethyl Carbonate + Methanol and Decane + Dimethyl Carbonate + Methanol at 298.15 K

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Liquid−liquid equilibria for nonane + dimethyl carbonate + methanol and decane + dimethyl carbonate + methanol were determined at 298.15 K. The NRTL and UNIQUAC models were used to correlate both ternary systems. The interaction parameters obtained from both models successfully correlated the equilibrium compositions.

Introduction

The manufacturing of chemical products that take into account environmental considerations in the selection of reactants and reaction conditions or in the elimination of waste and hazardous substances is growing in importance. Changes in manufacturing processes using alternative reagents can be one of the basic solutions. Dimethyl carbonate can be used in many cleaner synthesis reactions as an alternative reagent. For example, it can be substituted for phosgene in a carbonylation reaction[1,2] or for methyl sulfate in a methylation reaction[3] because the methyl carbonate molecule has a carbonyl group and two methoxy groups. The transesterification of dimethyl carbonate and a hydroxy compound is another example; however, it makes methanol as a byproduct. The thermodynamic data for dimethyl carbonate with methanol are required for the design of a separation process. Physical properties of the ternary mixtures such as dimethyl carbonate + methanol + benzene,[4] dimethyl carbonate + methanol + hexane,[5] dimethyl carbonate + methanol + cyclohexane,[6] and dimethyl carbonate + methanol + toluene[7] have been studied by Tojo and co-workers. Liquid−liquid equilibrium data of binary mixtures, containing dimethyl carbonate with decane, dodecane, tetradecane, or hexadecane, were reported by Gonzalez and co-workers.[8] Physical properties of dimethyl carbonate with methanol have been published by several authors.[9−12] In this work, the ternary phase equilibrium data for the nonane + dimethyl carbonate + methanol and decane + dimethyl carbonate + methanol systems have been studied. Tie lines were obtained, and the results of the measurement were correlated by means of the UNIQUAC model[13] and the NRTL model.[14]

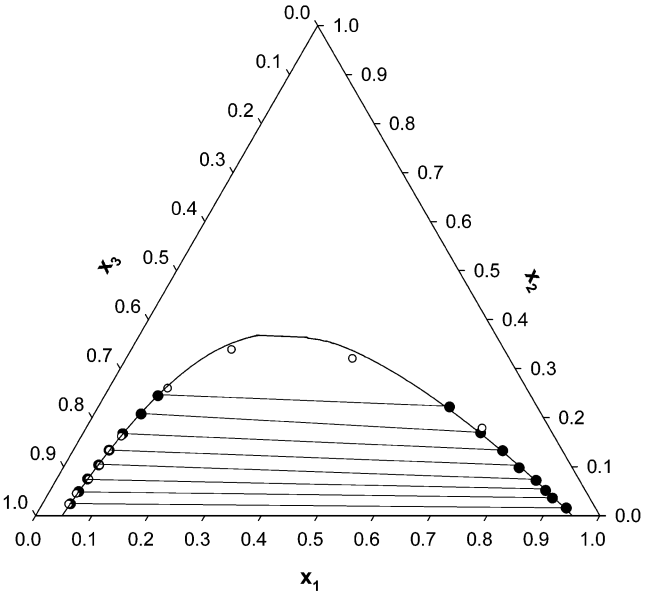

Figure 1. LLE of nonane (1) + dimethyl carbonate (2) + methanol (3) at 298.15 K: ●, experimental tie-line data; ○, experimental solubility data; −, calculated curve by UNIQUAC.

Experimental Section

Dimethyl carbonate (Aldrich, 99+% anhydrous), nonane (Aldrich, 99+% anhydrous), decane (Aldrich, 99+% anhydrous), and methanol (Aldrich, 99.93%) were used without further purification. The experimental solubility data for both ternary systems were determined by the cloud-point method. A binary mixture of known composition of dimethyl carbonate and methanol was prepared by mass with a precision of 0.0001 g on a Mettler AG204 balance and was stirred in a cell (50 mL) equipped with a jacket for circulating water from a constant temperature water bath (298.15 ± 0.1 K). The other component, nonane or decane, was then added by mass until a cloud point was reached.[15] The reproducibility in the composition for all the components was found to be ±0.1% to ±0.3%.

To determine the tie lines, ternary mixtures were prepared by mass with an estimated uncertainty in mole fraction less than 10^{-4}. The experimental apparatus is the same as those already described.[16] The mixtures in the cell were stirred in a temperature-controlled water bath (298.15 ± 0.1 K) for 30 min, and the cells were placed in a temperature-controlled oven (298.15 ± 0.1 K) for 1 day at atmospheric pressure. After equilibrium was reached, each of the liquid phases was sampled by a syringe through the lateral and top orifice. The analysis of dimethyl carbonate, nonane, decane, and methanol was performed using a Hewlett-Packard gas chromatograph equipped with a flame ionization detector and a HP-1 column (25 m × 0.32 mm

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Table 1. Mole Fraction x of the Experimental Solubility Curve

Nonane (1) + Dimethyl Carbonate (2) + Methanol (3) System		Decane (1) + Dimethyl Carbonate (2) + Methanol (3) System	
x_1	x_2	x_1	x_2
0.0470	0.0234	0.0503	0.2234
0.0493	0.0451	0.0651	0.2824
0.0574	0.0744	0.0837	0.3518
0.0623	0.1030	0.1201	0.4425
0.0637	0.1333	0.1474	0.4809
0.0710	0.1617	0.2054	0.5070
0.1040	0.2599	0.2469	0.5040
0.1776	0.3389	0.3144	0.4827
0.4011	0.3206	0.4258	0.4192
0.7018	0.1786	0.7866	0.1248

Table 2. Parameters of the UNIQUAC and NRTL Models and Their RMSD Values

model	b_{ij}/K			RMSD
	Nonane (1) + Dimethyl Carbonate (2) + Methanol (3) at 298.15 K			
UNIQUAC	$b_{12} = 51.62348$	$b_{13} = -867.524$	$b_{23} = -133.15$	
	$b_{21} = -124.116$	$b_{31} = 4.34745$	$b_{32} = 116.7577$	0.000 03
NRTL	$b_{12} = 643.8176$	$b_{13} = 469.0719$	$b_{23} = 215.3456$	
	$b_{21} = 42.1084$	$b_{31} = 702.5961$	$b_{32} = 361.7841$	0.000 08
		α_{ij}		
	$\alpha_{12} = 0.3$	$\alpha_{13} = 0.2$	$\alpha_{23} = 0.3$	
	Decane (1) + Dimethyl Carbonate (2) + Methanol (3) at 298.15 K			
UNIQUAC	$b_{12} = -139.623$	$b_{13} = -822.000$	$b_{23} = -332.951$	
	$b_{21} = -18.254$	$b_{31} = -9.307$	$b_{32} = 7.016$	0.000 03
NRTL	$b_{12} = -35.707$	$b_{13} = 445.571$	$b_{23} = 57.467$	
	$b_{21} = 633.218$	$b_{31} = 814.875$	$b_{32} = 332.859$	0.000 03
		α_{ij}		
	$\alpha_{12} = 0.3$	$\alpha_{13} = 0.2$	$\alpha_{23} = 0.3$	

Table 3. UNIQUAC r and q Values

compound	van der Waals volume, r	van der Waals area, q
dimethyl carbonate	3.0481	2.816
methanol	1.4311	1.432
nonane	6.5227	5.476
decane	7.1984	6.016

× 1.05 μm film thickness, Hewlett-Packard). After 2 min of operation at 60 °C, the oven temperature was programmed to reach 240 °C at the rate of 20 °C/min. The injection port temperature and the detector temperature were held at 250 °C and 275 °C, respectively. Helium was the carrier gas with the column flow rate of 1.25 mL/min. It was operated in the split mode with a split ratio of 100.

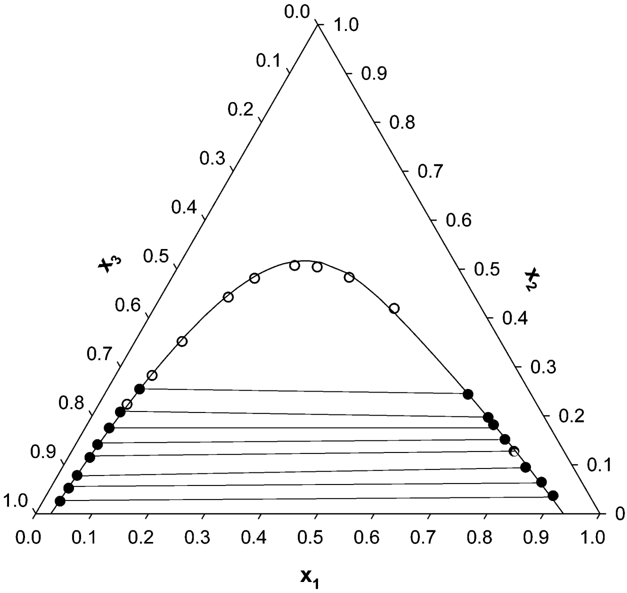

Figure 2. LLE of decane (1) + dimethyl carbonate (2) + methanol (3) at 298.15 K: ●, experimental tie-line data; ○, experimental solubility data; —, calculated curve by UNIQUAC.

The response factors for all components were measured at the same conditions as those used in the gas chromatography measurement for each phase equilibrium data point.

Results and Discussion

The tie-line data for the nonane + dimethyl carbonate + methanol system and the decane + dimethyl carbonate + methanol system are presented in Figures 1 and 2, respectively. The solubility data for both systems are also presented in Figures 1 and 2 and Table 1. The immiscibility region of the decane + dimethyl carbonate + methanol system is larger than that of nonane + dimethyl carbonate + methanol. The hexane + dimethyl carbonate + methanol system[5] has a much smaller immiscibility region compared with that of the nonane + dimethyl carbonate + methanol system. This implies that the longer chain length of the alkane gives a larger immiscibility region for the dimethyl carbonate extraction process.

The UNIQUAC model was used to correlate the experimental results. The interaction parameters, b_{ij}, are shown in Table 2 for nonane + dimethyl carbonate + methanol and decane + dimethyl carbonate + methanol with root-

Table 4. Experimental and Predicted LLE Data at 298.15 K

methanol-rich phase (mole fraction)						alkane-rich phase (mole fraction)					
x_1^{exp}	x_1^{UNIQ}	x_1^{NRTL}	x_2^{exp}	x_2^{UNIQ}	x_2^{NRTL}	x_1^{exp}	x_1^{UNIQ}	x_1^{NRTL}	x_2^{exp}	x_2^{UNIQ}	x_2^{NRTL}
Nonane (1) + Dimethyl Carbonate (2) + Methanol (3)											
0.0497	0.0495	0.0426	0.0239	0.0237	0.0235	0.9327	0.9297	0.9195	0.0154	0.0155	0.0157
0.0520	0.0525	0.0482	0.0489	0.0510	0.0508	0.8978	0.9026	0.8962	0.0358	0.0348	0.0349
0.0546	0.0553	0.0533	0.0748	0.0738	0.0737	0.8782	0.8784	0.8753	0.0512	0.0519	0.0520
0.0604	0.0591	0.0601	0.1031	0.1005	0.1004	0.8508	0.8478	0.8486	0.0718	0.0731	0.0734
0.0637	0.0644	0.0686	0.1333	0.1318	0.1295	0.8082	0.8089	0.8154	0.0973	0.0996	0.0995
0.0711	0.0714	0.0794	0.1668	0.1669	0.1617	0.7613	0.7614	0.7704	0.1323	0.1311	0.1339
0.0836	0.0816	0.0921	0.2072	0.2070	0.1932	0.7042	0.7016	0.7072	0.1686	0.1695	0.1799
0.0946	0.0960	0.1031	0.2444	0.2502	0.2171	0.6227	0.6299	0.6159	0.2216	0.2135	0.2414
Decane (1) + Dimethyl Carbonate (2) + Methanol (3)											
0.0306	0.0300	0.0292	0.0253	0.0267	0.0262	0.8987	0.8986	0.8951	0.0364	0.0344	0.0350
0.0326	0.0319	0.0313	0.0518	0.0517	0.0510	0.8644	0.8632	0.8602	0.0640	0.0642	0.0651
0.0345	0.0343	0.0339	0.0779	0.0792	0.0784	0.8208	0.8266	0.8247	0.0945	0.0945	0.0953
0.0385	0.0376	0.0376	0.1146	0.1144	0.1140	0.7838	0.7836	0.7831	0.1274	0.1300	0.1305
0.0393	0.0402	0.0404	0.1409	0.1392	0.1390	0.7558	0.7556	0.7562	0.1516	0.1529	0.1530
0.0428	0.0442	0.0447	0.1750	0.1723	0.1725	0.7206	0.7205	0.7229	0.1815	0.1812	0.1806
0.0462	0.0475	0.0483	0.2076	0.1979	0.1984	0.7036	0.6954	0.6989	0.1967	0.2013	0.2002
0.0569	0.0565	0.0579	0.2544	0.2551	0.2554	0.6443	0.6436	0.6501	0.2437	0.2421	0.2397

mean-square deviation (RMSD) values. The van der Waals volumes and surface areas used in the UNIQUAC model were calculated using the software package Aspen Plus 10.2 and are listed in Table 3. The RMSD value is defined as follows.[17]

$$\mathrm{RMSD} = \left(\sum_{k}^{M} \sum_{j}^{2} \sum_{i}^{3} (x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{cal}})^2 / 6M \right)^{1/2} \qquad (1)$$

where M is the number of tie lines, x^{exp} is the experimental mole fraction, x^{calc} indicates the calculated mole fraction, and the subscript i indexes the components, j the phase, and k the tie lines.

The NRTL model was also applied to correlate each tie-line data point from experimental results. The randomness parameters α_{ij} for the NRTL model[18] are shown in Table 2 for the nonane + dimethyl carbonate + methanol system and the decane + dimethyl carbonate + methanol system. The NRTL binary parameters of both ternary systems correlated at 298.15 K are listed in Table 2 with the RMSD values. The results of both the NRTL and UNIQUAC models are shown in Table 4 with the experimental data. The phase behavior of the decane + dimethyl carbonate + methanol system was well described by both the NRTL and UNIQUAC models. In the case of the nonane + dimethyl carbonate + methanol system, the correlated results obtained with UNIQUAC are better than those with NRTL, as shown in Tables 2 and 4.

Conclusion

Tie-line data for the nonane + dimethyl carbonate + methanol and decane + dimethyl carbonate + methanol systems were measured at 298.15 K with their solubility curves. The separation of dimethyl carbonate from methanol can be achieved by using nonane or decane as a solvent. The tie-line correlation was made using the UNIQUAC and NRTL models, and the parameters for both models were calculated.

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