Liquid–liquid equilibria of ternary mixtures of dimethyl carbonate, diphenyl carbonate, phenol and water at 358.15 K

In-Chan Hwang, So-Jin Park*

Department of Chemical Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea

ARTICLE INFO

ABSTRACT

The ternary liquid–liquid equilibria (LLE) of the following systems were analytically determined at 358.15 K at atmospheric pressure using stirred and thermo-regulated cells: {dimethyl carbonate (DMC) + diphenyl carbonate (DPC) + water}, {DMC + phenol + water} and {DPC + phenol + water}. The experimental ternary LLE data were correlated with the NRTL and UNIQUAC activity coefficient models. Additionally, the Bachman–Brown correlation was used to ascertain the reliability of the experimental data for each system.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The viscosity of suitable polymers is preferably from 3 to 120 centipoises measured according to DIN 53,015.

Alkyl carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylene carbonate (EC), and diphenyl carbonate (DPC) are excellent solvents for cellulose ethers, esters and salts, and also in the industry of pharmaceutical and cosmetics, natural and synthetic resins and polymers [1]. DMC is a carbonate ester and is used as a methylating agent and a benign fuel additive in unleaded gasoline. DPC is a very useful chemical intermediate in the synthesis of aromatic and aliphatic polycarbonates and industrially significant polymers. DPC has several desirable properties, such as good electrical insulation, a high heat of distortion, transparency, and impact resistance. DMC is usually synthesized from CO, methanol, and O_2. High-purity DMC, CO_2, and water are the reaction products. In this process, when DMC reacts with phenol and bisphenol A by trans-esterification, DPC and methanol to be produced. This newly developed DPC synthesis process is considered to be a "green process" because it does not use phosgene, a highly toxic environmental pollutant. However, to date, relatively very few investigations of the phase equilibria and mixture properties of systems containing DPC have been reported [2].

In the present work, we analytically determined the ternary liquid–liquid equilibria (LLE) at 358.15 K and at atmospheric pressure using stirred and thermo-regulated cells of the following systems: {DMC + DPC + water}, {DPC + phenol + water} and {DMC + phenol + water}. We chose these systems because they may be encountered in the environmentally friendly DPC synthesis process. The experimental LLE data for the above ternary systems were correlated using two activity coefficient models: the NRTL and the UNIQUAC models. Additionally, Bachman–Brown [3] correlations were used to examine the reliability of the experimental data for each system.

2. Experimental

2.1. Chemicals

Commercial-grade analytical chemicals were used in this investigation. Water (H_2O, $M = 18.02\,g\,mol^{-1}$, CAS-RN 7732-18-5, 99.9%) was provided by J.T Baker Chemical Co. DMC ($C_3H_6O_3$, $M = 90.08\,g\,mol^{-1}$, CAS-RN 616-38-6, 99.9%), DPC ($C_{13}H_{10}O_3$, $M = 214.22\,g\,mol^{-1}$, CAS-RN 102-09-0. 99.0%) and phenol (C_6H_6O, $M = 94.11\,g\,mol^{-1}$, CAS-RN 108-95-2, 99.9%) were obtained from Aldrich Co. All chemicals were dried using molecular sieves with a pore diameter of 0.4 nm. The water content of the chemicals, determined using a Karl–Fischer titrator (Metrohm 684 KF-Coulometer), was less than $7 \times 10^{-5}\,g/g$. The purity of the chemicals was checked by gas chromatography and by comparing the densities with values reported in the literature [2,4–6]. The purities, densities and UNIQUAC parameters of the chemicals are listed in Table 1 along with the reported values.

* Corresponding author. Tel.: +82 42 821 5684; fax: +82 42 823 6414.
  E-mail address: sjpark@cnu.ac.kr (S.-J. Park).

Table 1
The purities, densities and UNIQUAC parameters of chemicals used in this work.

Chemical	GC analysis (wt %)	ρ/g cm³ at 298.15 K		UNIQUAC[a]	
		This work	Lit. value	r-Value	q-Value
DMC	>99.9	1.06322	1.06328[a]	3.0613	2.8160
DPC	>99.7	1.11312[b]	1.07400[c]	7.6260	5.6340
Phenol	>99.9	1.05845[d]	1.05830[e]	3.5517	2.6800
Water	>99.9	0.99704	0.99704[f]	0.9200	1.4000

[a] Ref. [4].
[b] At 358.15 K.
[c] Ref. [2] at 393.15 K.
[d] At 313.15 K.
[e] Ref. [5].
[f] Ref. [6].

2.2. Procedure

Densities were measured by a digital vibrating glass tube densimeter (Anton Paar, model DMA 5000, Graz, Austria). The densimeter was automatically calibrated by itself with distilled water and dry air. The uncertainty of the density meter is stated by manufacturer as 5×10^{-6} g cm⁻³ in the density range of 0–3 g cm⁻³. Temperature was controlled within ±0.01 K. The details of operating procedures have been described elsewhere [7,8].

LLE measurements were carried out by determining the end points of the tie-lines for all the ternary systems. The system designed in our laboratory to measure the liquid–liquid equilibrium is similar to that reported by Correa et al. [9]. It consists of three parts: an equilibrium glass vessel jacket, a thermostat (Lauda MD 20 with DLK15 cooler) with a system that precisely measures the temperature (AΣA F250), and a Corning PC-320 magnetic stirrer. The temperature of the liquid sample in the equilibrium vessel was regulated by the thermostat within an accuracy within ± 0.02 K. The sample mixture was stirred rigorously in the equilibrium vessel for about 4 h, and was then allowed to settle for more than 8 h at a constant temperature, allowing the upper and lower phases to reach phase equilibrium. After reaching the equilibrium state between the two liquid phases, sampling was carefully carried out from the top for the upper liquid phase and from the bottom for the lower liquid phase without cross contamination during the sampling procedure. The analysis was done using a gas chromatography system (HP 6890N) equipped with an HP-5 (30 m × 0.32 mm × 0.25 μm) capillary column and a thermal conductivity detector. The

chromatographic method involved an injection volume of 1 μL with a split ratio of 50:1. The injector and detector temperatures were set to 483.15 K and 493.15 K, respectively. The oven temperature was maintained at 323.15 K for 3 min and then increased at a rate of 50 °C min⁻¹ to reach the final temperature of 473.15 K, which was maintained for 5 min. The carrier gas was helium, with a total flow rate of 2.0 mL s⁻¹ throughout the column. The uncertainty of the calculated mole fractions was estimated to be less than $\pm 1 \times 10^{-4}$. The procedure is described in detail elsewhere [10].

3. Results and discussion

The experimental ternary LLE data for the ternary systems {DMC + DPC + water}, {DMC + phenol + water} and {DPC + phenol + water} at 358.15 K are given in Table 2. These ternary LLE data were correlated using the NRTL and UNIQUAC models. The binary parameters of each constituent were regressed by minimizing the differences between the experimental and calculated mole fractions for each component of both liquid phases over all of the measured systems. The objective function (OF) used was

$$OF = \min \sum_i \sum_\alpha \sum_k (x_{ik}^{\alpha(\exp)} - x_{ik}^{\alpha(cal)})^2 \qquad (1)$$

where $x_{ik}^{\alpha(\exp)}$ and $x_{ik}^{\alpha(cal)}$ are the experimental and calculated mole fractions at α phase, respectively. The subscripts i, α and k denote the component, phase and tie-line, respectively. The optimality of the parameters can be evaluated according to the mean deviation in the compositions of the coexisting phases [11]. The root mean square deviation (RMSD) between the experimental and calculated phase compositions according to the model parameters was defined as

$$RMSD = \left[\frac{\sum_i \sum_\alpha \sum_k (x_{ik}^{\alpha(\exp)} - x_{ik}^{\alpha(cal)})^2}{6N} \right]^{1/2} \qquad (2)$$

where N is the number of tie-lines.

The ternary LLE of each system at 358.15 K was plotted in the form of a Gibbs triangles (Figs. 1–3). The dashed lines are the calculated tie-lines using the NRTL model. The experimental and

Table 2
Experimental LLE data for the ternary systems {DMC (1) + DPC (2) + water (3)}, {DMC (1) + phenol (2) + water (3)} and {DPC (1) + phenol (2) + water (3)} at 358.15 K.

	Organic phase		Aqueous phase	
	x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}
{DMC + DPC + water}	0.6231	0.0000	0.0353	0.0000
	0.5928	0.0671	0.0269	0.0001
	0.5595	0.1494	0.0246	0.0001
	0.4921	0.2843	0.0171	0.0002
	0.4019	0.4211	0.0109	0.0002
	0.2765	0.5849	0.0064	0.0002
	0.1515	0.7251	0.0028	0.0002
	0.0000	0.8653	0.0000	0.0001
{DMC + phenol + water}	0.6231	0.0000	0.0353	0.0000
	0.4547	0.1160	0.0247	0.0014
	0.3641	0.1636	0.0207	0.0060
	0.2721	0.2148	0.0180	0.0098
	0.1206	0.2526	0.0100	0.0184
	0.0452	0.2395	0.0023	0.0350
{DPC + phenol + water}	0.8653	0.0000	0.0001	0.0000
	0.7506	0.0757	0.0006	0.0002
	0.5937	0.1770	0.0007	0.0030
	0.4008	0.2664	0.0007	0.0044
	0.2914	0.3155	0.0004	0.0065
	0.1510	0.3607	0.0005	0.0131
	0.0454	0.3674	0.0002	0.0166