



# Ternary liquid–liquid equilibria and binary excess and deviation properties at constant temperature for mixtures of dimethyl carbonate, anisole, methanol, phenol and water

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## ABSTRACT

This study aims to determine the phase equilibria and mixture properties for the separation of reaction intermediates generated during the synthesis of non-phosgene diphenylcarbonate (DPC). The intermediates are based on dimethyl carbonate (DMC), phenol, methanol and anisole, etc. We analytically determined ternary liquid–liquid equilibria (LLE) for the following mixtures at atmospheric pressure and constant temperature: {water + DMC + anisole} at 313.15 K, {water + methanol + anisole} at 308.15 K and {water + methanol + phenol} at 328.15 K. In addition, density, refractive indices, excess molar volumes ( $V^E$ ) and deviations in the molar refractivity ( $\Delta R$ ) of constituent binary systems at 298.15 K were determined. The experimental LLE data correlated well with two excess Gibbs free energy models: Non-Random Two-Liquid (NRTL) and Universal QUAsiChemical (UNIQUAC).  $V^E$  and  $\Delta R$  data were correlated well with Redlich–Kister polynomial.

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## 1. Introduction

Polycarbonate (PC), particularly valued for its light weight, optical clarity and impact resistance, is used in a wide variety of common products including digital media (e.g., CDs, DVDs), electronic equipment, automobiles, construction glazing, sports safety equipment and medical devices [1]. Historically, PC production has involved highly toxic phosgene process. A new route for PC production starting from carbon dioxide or diphenyl carbonate (DPC) with bisphenol A has been developed and has attracted much attention, as this process involves greener and much more sustainable chemistry [2]. Among them, the main focus has been a route from DPC, which produced via dimethyl carbonate (DMC). In this process, DMC reacts with phenol to produce methyl phenyl carbonate (MPC), anisole and methanol first. And then, MPC reacts with phenol to produce DPC and DMC [3]. The purity of the DPC feedstock directly influences downstream PC quality, and highly pure DPC is critical for PC optical media applications [4]. Because of this reason, the phase equilibrium data of related intermediates of the non-phosgene DPC synthetic process is essential for the high purity of DPC. So, we have systematically studied the phase equilibrium data for intermediates of the non-phosgene DPC synthetic

process, which are based on DMC, MPC, phenol, methanol and anisole, etc. By the way, DMC is obtained as a mixture of methanol and water. Water is typical polar solvent and has very high affinity with methanol and phenol because of stronger hydrogen bonds. And anisole is insoluble and DMC is partially soluble in water. Therefore, in this work, we analytically measured ternary liquid–liquid equilibria (LLE) for the following systems of intermediates in the DPC synthetic process with water at atmospheric pressure and constant temperature in stirred, thermo-regulated cells: {water + DMC + anisole} at 313.15 K, {water + methanol + anisole} at 308.15 K and {water + methanol + phenol} at 328.15 K. Anisole contained systems were emulsified at 298.15 K, they are separated into two phase distinctly at least 308.15 K and the melting point of phenol is about 314 K. Therefore we have determined LLE as above mentioned different system temperatures.

Experimental LLE data were well correlated by the Non-Random Two-Liquid (NRTL) and Universal QUAsiChemical (UNIQUAC) activity coefficient models. In addition, density, refractive indices, excess molar volumes ( $V^E$ ) and deviations in the molar refractivity ( $\Delta R$ ) of the constituent binary systems at 298.15 K were determined. Experimentally measured densities were compared with values predicted by Nakata and Sakurai equation, and measured refractive indices were compared with values predicted using the mixing rules of Lorentz–Lorenz [5] and Gladstone–Dale [6]. The determined  $V^E$  and  $\Delta R$  data were satisfactorily correlated using the Redlich–Kister equation.

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## Nomenclature

### List of symbols

$r$	UNIQUAC parameter
$q$	UNIQUAC parameter
OF	objective function
RMSD	root mean square deviation
AAD	absolute average deviation
$x$	mole fraction
$N$	number of experimental data points
$n$	number of fitted parameter
$V^E$	excess molar volume ( $\text{cm}^3 \text{mol}^{-1}$ )
$\Delta R$	deviation of refractive indices
$M$	molecular mass
$R_m$	molar refractivity of mixture
$R_i$	molar refractivity of the component $i$
$A_i$	adjustable parameter for the Redlich–Kister equation

### Greek letters

$\rho$	density ( $\text{g cm}^{-3}$ )
$n_D$	refractive indices
$\alpha$	NRTL parameter
$\rho_i$	density of the component $i$ ( $\text{g cm}^{-3}$ )
$\rho_m$	density of the mixture ( $\text{g cm}^{-3}$ )
$n_{D,i}$	refractive indices of the pure component $i$
$V$	volume
$\phi$	volume fraction of the pure component in the mixture
$\sigma_{st}$	standard deviation
$D$	distribution coefficient
$S$	selectivity

### Superscripts

$exp$	experimental
$calc$	calculated

$\alpha$	phase
I	aqueous phase
II	organic phase

### Subscripts

$i$	component $i$
$k$	tie-line $k$

## 2. Experimental

### 2.1. Materials

Analytical grade chemicals were obtained from various chemical suppliers. Anisole was supplied by Junsei Chemical Co. Ltd (Japan). DMC was obtained from Sigma–Aldrich (USA). Phenol, methanol and distilled water were supplied by Samchun Chemical (Korea). Anisole, DMC, and methanol were dried using pellet-type molecular sieves with a 0.3 nm pore diameter. The water content of the chemicals, determined using a Karl–Fischer titrator (Metrohm 684 KF–Coulometer), was less than 65 ppm. The manufacturer states that the uncertainty of this titration is  $5 \times 10^{-6}$  g/g. The purities, CAS number, water content, densities, heats of fusion and UNIQUAC parameters of the chemicals are summarized in Table 1 along with literature values [7,8].

### 2.2. LLE

LLE were measured by determining the tie line end points for each ternary system using a self-designed experimental apparatus, which consisted of a 70 cm<sup>3</sup> thermo-regulated double glass jacket (equilibrium vessel), magnetic stirrer, thermostat (Lauda MD 20 with a DLK 15 cooler, Germany) and temperature monitoring system. The temperature inside the equilibrium vessel was kept constant by circulating thermally controlled water from the thermostat. The thermostat temperature was precisely monitored using a digital thermometer (A $\Sigma$ A F250, UK) connected to an IBM PC. The uncertainty of the equilibrium temperature was regulated within  $\pm 0.02$  K. The sample mixture in the equilibrium vessel was stirred vigorously using a Corning PC-320 magnetic stirrer for 6 h and then allowed to settle for 12 h at constant equilibrium temperature. Samples were taken cautiously from both the upper and lower liquid phases to avoid contamination. Equilibrated samples were analyzed by a gas chromatograph (Agilent 6890N, USA) equipped with a capillary column: HP-FFAP (Nitroterephthalic acid modified polyethylene glycol TPA, 25 m  $\times$  0.20 mm  $\times$  0.30  $\mu$ m) and a thermal conductivity detector (TCD). Before every LLE determination, the response factor of each constituent component was carefully determined using self-made standards. High purity helium gas was used and the temperatures of the injector and detector were set to 503.15 K and 523.15 K, respectively. The oven temperature was maintained at 333.15 K for 4 min and was then increased at a rate of 50 °C min<sup>-1</sup> to a final temperature of 503.15 K, which was maintained for 8 min. Each sample was analyzed three times, and the mean concentration was taken as the equilibrium concentration. For this procedure, the uncertainty of the determined LLE mole fractions was estimated to be less than  $1 \times 10^{-4}$ . This procedure has been described in detail elsewhere [9].

### 2.3. Excess and deviation properties

Density ( $\rho$ ) was measured using a digital vibrating glass U tube densimeter (Anton Paar, model DMA 5000, Austria). We estimated uncertainty of the density measurement was less than  $1 \times 10^{-5}$  g cm<sup>-3</sup>. Temperature oscillations in the densitometer were kept within 0.01 K. The calibration and measurement procedures used here have been described previously in the literature [10].

Refractive indices ( $n_D$ ) of the pure substances and binary mixtures were measured using a digital precision refractometer (KEM, model RA-520N, Japan). The uncertainty of the refractive index measurement was estimated less than  $1 \times 10^{-4}$ . The observed deviation in the densimeter and refractometer measurements coincided with the uncertainties given by the manufacturer. Before each series of measurements, the densimeter and refractometer were calibrated with distilled water and dried air. Samples were prepared by placing approximately 5 cm<sup>3</sup> of total volume into a glass vial, and the mass of each reagent was measured using a microbalance (A&D, HA202, Japan) with a precision of  $1 \times 10^{-5}$  g. The estimated uncertainty in the mole fraction of the sample mixtures was less than  $1 \times 10^{-4}$ .  $V^E$  and  $\Delta R$  were determined from the experimental pure and mixture density and refractive index data.

## 3. Results and discussion

### 3.1. LLE and correlation

The experimental ternary LLE data for the systems {water + DMC + anisole} at 313.15 K, {water + methanol + anisole} at 308.15 K and {water + methanol + phenol} at 328.15 K are given in Table 2. Equilibrium concentrations are expressed

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