Isobaric Vapor−Liquid Equilibria of Binary Mixtures Containing Dimethyl Carbonate under Atmospheric Pressure

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Isobaric vapor−liquid equilibria (VLE) have been determined for the binary systems of dimethyl carbonate (DMC) + ethanol, dimethyl carbonate + diethyl carbonate (DEC), dimethyl carbonate + propylene glycol (PG), and dimethyl carbonate + propylene carbonate (PC) under atmospheric pressure in an Ellis equilibrium still. The data have been checked by employing a global statistic thermodynamic consistency test and also have been correlated by means of both the Wilson equation and the NRTL equation. The experimental results demonstrated that the systems of DMC + ethanol and DMC + PG show strong positive deviations from ideality and that the systems of DMC + DEC and DMC + PC are close to ideality.

Introduction

Dimethyl carbonate (DMC), a low-level toxic and nicely biodegradable chemical, has been given increased consideration in recent years. As "an environmentally benign building block"[1] for chemical synthesis, it was widely used to replace phosgene as carbonylation agent and dimethyl sulfate as alkylation agent. Moreover, DMC was found to be an excellent gasoline additive and painting solvent,[2] which greatly motivated the research on DMC. For the research of its synthesis and application, the vapor−liquid equilibrium data of mixtures containing DMC are prerequisites. Unfortunately, the data are scarce.

Though the vapor−liquid equilibrium of binary mixtures containing DMC as well as diethyl carbonate (DEC) has been reported by Cocero[3,4] and Kehiaian,[5] they focus on the mixture of linear carbonates with alkane or benzene or tetrachloromethane, which is not our interest. The isobaric vapor−liquid equilibria (VLE) data under atmospheric pressure are reported in this contribution for the following binary systems: ethanol + DMC, DMC + DEC, DMC + propylene glycol (PG), and DMC + propylene carbonate (PC). These VLE data are not found in the literature except for Comeli and Franceseconi, who presented similar data (isothermal VLE data) for the ethanol + DMC [6] and DMC + DEC systems.[7]

Experimental Section

Chemicals. All the components used were purchased from commercial sources and are analytical grade chemicals. The purity of all the chemicals was estimated to be greater than 99.5 wt %. Dimethyl carbonate and diethyl carbonate were fractionally distilled in an atmospheric distillation column, and propylene carbonate and propylene glycol were fractionally distilled in advance in a vacuum distillation column as well. Ethanol was not purified beforehand due to its high grade. The above further purification was to reduce the experimental errors as much as possible. The final purity of all the chemicals was higher than 99.9% (by weight), and the gas chromatographic analysis failed to show any significant impurities.

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Table 1. Antoine Coefficients^a of the Pure Components

component	A	B	C
ethanol[16]	7.33827	1650.5	−41.67
dimethyl carbonate[17]	6.4338	1413.0	−44.25
diethyl carbonate[16]	5.8830	1223.77	−84.304
propylene glycol[16]	8.0420	2645.73	−22.46
propylene carbonate[18]	6.6260	2083.26	−63.99

$^a \log_{10} P_i^S$ (kPa) $= A - B/(T \text{ (K)} + C)$.

Apparatus and Procedure. The vapor−liquid equilibrium measurements were carried out in an Ellis equilibrium still, described by Walas.[8] In this still, both liquid and condensed vapor phases are continuously recirculated to provide intimate contact between the phases and to ensure that equilibrium is rapidly established. The temperature in the still was measured to within ±0.1 K by means of a mercury thermometer, and the pressure was maintained at atmospheric pressure and measured to within ±0.01 kPa by a mercury barometer. In each experiment, equilibrium conditions were assumed when constant vapor and liquid temperatures were obtained for at least 30 min. The experiments in Ellis equilibrium still show good reproducibility after the test, and all the experiments were done once more.

The analyses of the vapor and liquid compositions were performed on a Hewlett-Packard GC model 6890 after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with an HP capillary column. The column is 200 cm long and 4 mm in diameter. The carrier gas is H_2, and the column temperature ranges from 100 to 200 °C. The GC response peaks were integrated using an HP 3295 integrator. At least two analyses were done for each vapor and liquid sample. The accuracy of the measured mole fraction is ±0.001.

Since the atmospheric pressure changed slightly during the experiments, the temperatures were corrected to 101.3 kPa with the following equation:[9]

$$T = T_{\text{exp}} + \frac{1}{\displaystyle\sum_{i=1}^{2} \frac{B_i x_i}{(T_{\text{exp}} + C_i)^2}} \frac{101.3 - P_{\text{exp}}}{P_{\text{exp}}} \quad (1)$$

Table 2. Experimental VLE Data of T, x_1, and y_1 and Experimental Activity Coefficients, γ_i, Together with Wilson Parameters, $\alpha_{i,j}$, NRTL Parameters, $\tau_{i,j}$ and $\alpha_{i,j}$, and Mean Deviations, σ,[a] for the Binary Systems at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
				Ethanol (1) + Dimethyl Carbonate (2)					
349.20	0.9105	0.8503	1.009	2.650	349.15	0.3480	0.5320	1.656	1.138
348.44	0.8089	0.7562	1.041	2.074	351.19	0.2170	0.4350	2.006	1.068
348.05	0.7060	0.6780	1.086	1.805	354.14	0.1169	0.3100	2.369	1.048
348.18	0.6203	0.6397	1.160	1.556	357.56	0.0520	0.1760	2.561	1.043
348.32	0.5312	0.6234	1.313	1.311	361.13	0.0114	0.0650	2.734	1.013

Wilson parameter: $\alpha_{1,2} = 605.69$, $\alpha_{2,1} = 360.84$, $\sigma = 0.007$
NRTL parameter: $\tau_{1,2} = 353.22$, $\tau_{2,1} = 594.25$, $\alpha_{1,2} = \alpha_{2,1} = 0.40$; $\sigma = 0.007$

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
				Dimethyl Carbonate (1) + Diethyl Carbonate (2)					
364.41	0.8928	0.9646	1.044	1.026	381.80	0.3406	0.6411	1.0779	0.978
367.46	0.7683	0.9147	1.046	1.025	385.95	0.2356	0.5190	1.0822	0.962
371.31	0.6215	0.8508	1.068	0.990	390.50	0.1499	0.3626	1.0873	0.987
375.92	0.5001	0.7808	1.061	0.985	394.44	0.0680	0.1920	1.1016	1.015

Wilson parameter: $\alpha_{1,2} = -357.61$, $\alpha_{2,1} = 2537.56$, $\sigma = 0.005$
NRTL parameter: $\tau_{1,2} = 2684.32$, $(g_{2,1} - g_{1,1}) = -2095.07$, $\alpha_{j,i} = \alpha_{i,j} = 0.067$; $\sigma = 0.008$

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
				Dimethyl Carbonate (1) + Propylene Glycol (2)					
366.35	0.8222	0.9907	1.099	2.750	377.15	0.3973	0.9753	1.6318	1.0367
366.75	0.8110	0.9849	1.094	2.610	379.35	0.3023	0.9686	2.0025	1.0253
368.45	0.7085	0.9856	1.191	1.915	394.85	0.1472	0.9228	2.6005	1.0214
370.65	0.5823	0.9828	1.354	1.430	403.65	0.1088	0.8763	2.6953	1.0780

Wilson parameter: $\alpha_{1,2} = 202.04$, $\alpha_{2,1} = 1359.94$, $\sigma = 0.002$
NRTL parameter: $\tau_{1,2} = 3266.38$, $(g_{2,1} - g_{1,1}) = -1707.44$, $\alpha_{j,i} = \alpha_{i,j} = 0.057$; $\sigma = 0.002$

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
				Dimethyl Carbonate (1) + Propylene Carbonate (2)					
425.55	0.1098	0.9178	1.723	1.012	369.85	0.7424	0.9941	1.0995	1.3730
412.85	0.1919	0.9570	1.350	1.034	369.65	0.7478	0.9937	1.0976	1.3771
393.65	0.3368	0.9838	1.249	1.098	367.75	0.8594	0.9940	1.0112	1.4611
376.45	0.6051	0.9960	1.116	1.270					

Wilson parameter: $\alpha_{1,2} = 718.505$, $\alpha_{2,1} = -122.367$, $\sigma = 0.003$
NRTL parameter: $\tau_{1,2} = -202.569$, $\tau_{2,1} = 797.435$, $\alpha_{j,i} = \alpha_{i,j} = 0.372$; $\sigma = 0.003$

[a] $\sigma = (\sum |y_i(\text{exp}) - y_i(\text{cal})|)/N$; N = number of data points.

where T_{exp}/K is the experimental temperature at the actual pressure P_{exp}/kPa, B_i and C_i are the Antoine constants of component i, shown in Table 1, and x_i is the mole fraction in the liquid phase.

The experimental temperature T and the mole fractions x_1 and y_1 of the liquid and vapor phases are listed in Table 2, together with the experimental activity coefficients γ_i. The activity coefficients were calculated with the following equation[10] relating the experimental values P, T, x_i, and y_i:

$$\gamma_i = \frac{P y_i \hat{\varphi}_i^{V}}{x_i P_i^{S} \varphi_i^{S} \exp\left[\dfrac{V_i^{L}(P - P_i^{S})}{RT}\right]} \quad (2)$$

where P_i^{S} is the vapor pressure of pure component i, estimated with the Antoine equation, V_i^{L} is the mole volume of pure component i, and φ_i^{V} and φ_i^{S} are the fugacity coefficients of component i in the pure and mixture vapor phases, respectively, estimated by using the modified Peng−Robinson equation:[11]

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \quad (3)$$

$$a = 0.45724(RT_c)^2/P_c\alpha(T_r); \quad b = 0.778RT_c/P_c$$

$$\alpha(T_r) = 1 + (1 - T_r)(m + n/T_r^2)$$

where P, T, and v are the system pressure (Pa), temperature (K), and volume (m³·mol⁻¹), respectively, m and n are the empirical parameters fit to the saturated vapor pressure data of the pure components, and R is the gas constant.
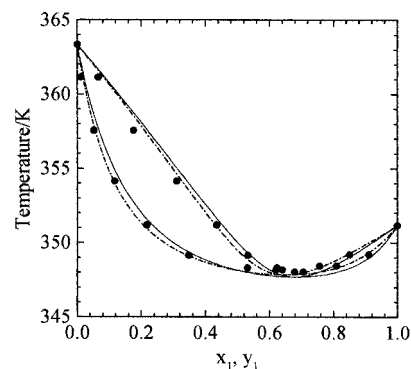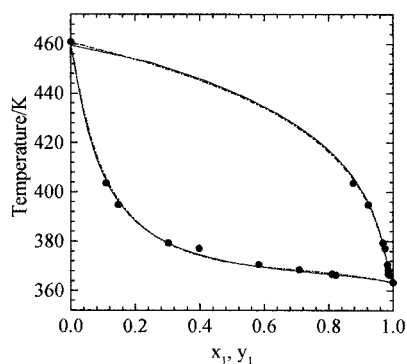

Figure 1. $T-x_1-y_1$ plots for the mixture ethanol (1) + dimethyl carbonate (2) at 101.3 kPa: (●) experimental points; (—) calculated points from the Wilson equation; (− · −) calculated points from the NRTL equation.

Graphical representations of the VLE data are shown in Figures 1−4. The vapor pressures of all the pure components are calculated with the Antoine equation.

In the experiments on the system of DMC + PG, at $T > 413.15$ K, water was found, especially in the vapor phase, as a result of the condensation of PG producing water and dipropylene glycol, whose existence was proven by the mass spectrum. For the system of DMC + PC, at $T > 453.15$ K, several compounds were found in the mixture by a mass spectrum determination, including CO_2, propylene oxide, and so forth, as a result of both the thermolysis of PC and the transesterification between DMC and PC. All these phenomena have been verified by repeated experiments, and as a consequence, precise VLE data at higher temperature are unavailable for the systems at atmospheric pressure. Therefore, only the VLE data at lower temperatures are reported here and further research under vacuum is needed.
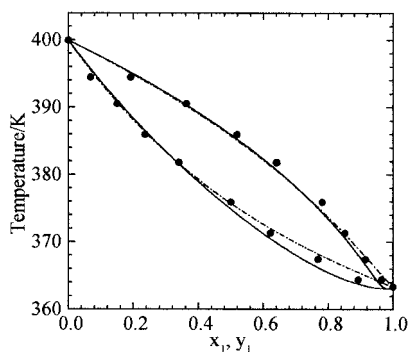
Figure 2. $T-x_1-y_1$ plots for the mixture dimethyl carbonate (1) + diethyl carbonate (2) at 101.3 kPa: (●) experimental points; (—) calculated points from the Wilson equation; (− · −) calculated points from the NRTL equation.

Figure 3. $T-x_1-y_1$ plots for the mixture dimethyl carbonate (1) + propylene glycol (2) at 101.3 kPa: (●) experimental points; (—) calculated points from the Wilson equation; (− · −) calculated points from the NRTL equation.
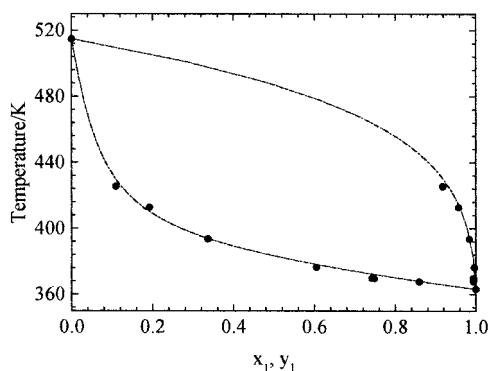

Figure 4. $T-x_1-y_1$ plots for the mixture dimethyl carbonate (1) + propylene carbonate (2) at 101.3 kPa: (●) experimental points; (—) calculated points from the Wilson equation; (− · −) calculated points from the NRTL equation.

Results and Discussion

The thermodynamic consistency of the VLE data has been checked by means of the global statistic test,[12] a reliable test based on statistical theory that can offer a reasonable evaluation and error analysis simultaneously. The corresponding deviation grades are listed in Table 3, and the test results are demonstrated in Table 4. As can be seen, the test is verified under the rule that the experimental mean deviation, δ_x and δ_y, should be less than 0.01.[13]

Using a least-squares procedure developed by Fredenslund et al.,[13] the VLE data were then correlated by
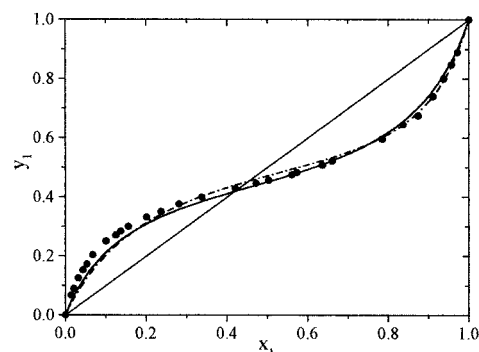
Figure 5. x_1-y_1 plot for the system dimethyl carbonate (1) + ethanol (2) at 313.15 K: (●) experimental data by Comelli et al.;[3] (—) predicted data from the Wilson equation in this work; (− · −) predicted data from the NRTL equation in this work.

Table 3. Deviation Grades of the Global Statistical Test Method[12]

grade	$\delta_x{}^a$	$\delta_y{}^b$	$\delta_T{}^c$ (K)	$\delta_P{}^d$ (kPa)
I	0.0005	0.0005	0.02	0.027
II	0.001	0.001	0.04	0.053
III	0.002	0.002	0.08	0.107
IV	0.004	0.004	0.16	0.213
V	0.008	0.008	0.32	0.427
VI	0.016	0.016	0.64	0.853

$^a \delta_x =$ the absolute deviation of the mole fraction in the liquid phase. $^b \delta_y =$ the absolute deviation of the mole fraction in the vapor phase. $^c \delta_T =$ the absolute deviation of the temperature. $^d \delta_P =$ the absolute deviation of the pressure.

Table 4. Results of the Thermodynamic Consistency Test

system	grade
ethanol + DMC	III
DMC + DEC	IV
DMC + PG	IV
DMC + PC	IV

minimizing the following objective function (OF):

$$OF = \sum_{}^{i}\sum_{}^{j}[\ln \gamma_i(\exp) - \ln \gamma_i(\text{cal})]_j^2 \qquad (4)$$

where $\gamma_i(\exp)$ is the experimental activity coefficient calculated with eq 2 and $\gamma_i(\text{cal})$ is the activity coefficient calculated with the Wilson equation[14] or by using the NRTL equation.[15]

The fitted parameters in both the Wilson and the NRTL equations are reported in Table 2, together with the mean deviation, σ, from the least-squares analysis. The comparisons between the VLE data predicted with the Wilson and NRTL equations and the experimental data are shown in Figures 1–4. As verification of the parameters as well as the VLE data, the parameters of the Wilson and the NRTL equations for the DMC−ethanol system were used to predict the isothermal VLE data at 313.15 K, whose experimental data were reported by Comelli et al.[6] The comparison is presented in Figure 5. As can be seen, they agree very well. Similar results have been obtained for the DMC + DEC system.

Obviously, the systems of DMC + PC and DMC + DEC are close to ideal, with the value of γ_i never exceeding 1.73. This ideality of the system of DMC + DEC has already been demonstrated by Comelli et al.[6] However, the system of DMC + PG shows strong deviation from ideality, as the maximum value of γ_i exceeds 2.75. The system of DMC + ethanol displays similar behavior. Its maximum value of γ_i exceeds 2.65, and an azeotrope is formed at 347.85 K

with a DMC mole concentration of 35.0%. This phenomenon for the system of DMC + ethanol has been studied by Comelli et al.,[7] and they obtained a similar conclusion as well. The strong positive deviation from ideality may be due to the formation of hydrogen bonds between the C==O group of DMC and the OH group of ethanol or propylene glycol.

Literature Cited

(1) Ono, Y. Catalysis in the Production and Reaction of Dimethyl Carbonate, an Environmentally Benign Building Block. *Appl. Catal. A* **1997**, *155*, 133−166.

(2) Pacheco, M. A.; Marshall, C. L. Review of Dimethyl Carbonate (DMC) Manufacture and Its Characteristics as a Fuel Additive. *Energy Fuels* **1997**, *11*, 2−29.

(3) Cocero, M. J.; Garcia, I.; Gonzalez, J. A.; et al. Thermodynamics of Binary Mixtures Containing Organic Carbonates VI Isothermal Vapor-liquid Equilibria for Dimethyl Carbonate + Normal Alkanes. *Fluid Phase Equilib.* **1991**, *68*, 151−161.

(4) Cocero, M. J.; Mato, F.; Garcia, I.; et al. Thermodynamics of Binary Mixtures Containing Organic Carbonates. 3. Isothermal Vapor−Liquid Equilibria for Diethyl Carbonate + Cyclohexane, + Benzene, or + Tetrachloromethane. *J. Chem. Eng. Data* **1989**, *34*, 443−445.

(5) Kehiaian, H. V.; Gonzalez, J. A.; Garcia, I.; et al. Priction of Vapour-liquid and Liquid−liquid Equilibria and of Enthalpies of Mixing in Linear Carbonates + *n*-alkane or + Cyclohexane Mixture Using DISQUAC. *Fluid Phase Equilib.* **1991**, *64*, 1−121.

(6) Comelli, F.; Francesconi, R. Isothermal Vapor−Liquid Equilibria Measurements, Excess Molar Enthalpies, and Excess Molar Volumes of Dimethyl Carbonate + Methanol, + Ethanol, and + Propanol at 313.15 K. *J. Chem. Eng. Data* **1997**, *42*, 705−709.

(7) Comelli, P.; Francesconi, R.; Ottani, S. Isothermal Vapor−Liquid Equilibrium of Dimethyl Carbonate + Diethyl Carbonate in the Range (313.15 to 353.15) K. *J. Chem. Eng. Data* **1996**, *41*, 534−536.

(8) Walas, S. M. *Phase Equilibria in Chemical Engineering*; Butterworth: London, 1985.

(9) Hiaki, T.; Kawai, A. Vapor-liquid Equilibria Determination for a Hydrofluoroether with Several Alcohols. *Fluid Phase Equilib.* **1999**, *158−160*, 979−989.

(10) Pransnitz, J. M. *Molecular Thermodynamics of Fluid-Phase Equilibria;* Prentice Hall: Englewood Cliffs, NJ, 1969.

(11) Liu, H.; Feng, G.; Hu, Y. A Modified PR Equation. *Tianranqi Huagong (Nat. Gas Chem. Ind.)* **1987**, *1*, 47−5 (in Chinese).

(12) Hu, Y.; Ying, X. G.; Tang, X. H. Application of Statistical Theory in Studying Vapor−Liquid Equilibria, (1) Thermodynamic Consistency Test. *Huadong Huagong Xueyuan Xuebao (J. East China Inst. Chem. Technol.)* **1984**, *2*, 205−213 (in Chinese).

(13) Frendenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor−Liquid Equilibria Using UNIFAC, a Group-Contribution Method*; Elsevier: Amsterdam, 1977.

(14) Wilson, G. M. Vapor−Liquid Equilibrium. XI A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−135.

(15) Renon, H.; Pransnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−141.

(16) AIChE. *Physical & Thermodynamic Property of Pure Chemicals Data Compilation*; McGraw-Hill: New York, 1992.

(17) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Smith, N. K. Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for Dicyclohexyl Sulfide, Diethylenetriamine, Di-*n*-octyl Sulfide, Dimethyl Carbonate, Piperazine, Hexachloroprop-1-ene, Tetrakis(dimethylamino)ethylene, N,N′-Bis-(2-hydroxyethyl)-ethylenediamine, and 1,2,4-Triazolo[1,5-*a*]pyrimidine. *J. Chem. Eng. Data* **1997**, *42*, 1037−1052.

(18) Luo, H. P. Study on the Transesterification between Ethanol and DMC. M.Sc. Thesis, East China University of Science and Technology, Shanghai, 1999 (in Chinese).