Isothermal Vapor−Liquid Equilibria of Dimethyl Carbonate + Diethyl Carbonate in the Range (313.15 to 353.15) K

Fabio Comelli,[†] **Romolo Francesconi,***[,‡] **and Stefano Ottani**[†]

Centro di Studio per la Fisica delle Macromolecole del CNR, and Dipartimento di Chimica "G. Ciamician", Universitá degli Studi, via Selmi 2, I-40126 Bologna, Italy

Isothermal vapor−liquid equilibria (VLE) have been determined for the dimethyl carbonate + diethyl carbonate mixture at five temperatures in the range (313.15 to 353.15) K in an equilibrium still with circulation of both the vapor and liquid phases. The data have been correlated by means of the Wilson equation. The system shows small positive deviations from ideality with liquid-phase activity coefficients not exceeding 1.26.

Introduction

As a continuation of our studies on the thermodynamic properties of binary mixtures containing esters of carbonic acid (Comelli and Francesconi, 1994, 1995; Francesconi and Comelli, 1994, 1995), used in the synthesis of pharmaceuticals (Martindale, 1989), in agricultural chemicals, and as solvents, for many synthetic and natural resins and polymers (Annesini et al., 1984; Merck Index, 1989), we report in this paper the vapor−liquid equilibrium data (VLE) of the mixture containing dimethyl carbonate + diethyl carbonate at (313.15, 323.15, 333.15, 343.15, and 353.15) K.

In a previous work (Francesconi and Comelli, 1995) we have determined the excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, of the same mixtures at lower temperatures than those studied in this paper, with the exception of $T = 313.15$ K. In the present study, investigations have been extended to VLE measurements with the aim of correlating all the experimental data. A survey of the literature showed that no such measurements have been previously reported.

Experimental Section

Chemicals. Both components were supplied by Aldrich Chemical Co.: dimethyl carbonate (purity 99 mass %) and diethyl carbonate (purity +99 mass %), the same used in a previous paper (Francesconi and Comelli, 1995), were used as received and stored in dark stoppered bottles over molecular sieves (Acros Chimica type 4A, 8−12 mesh, $^1/_{16}$ in. beads) before measurements. GLC analysis did not show any significant impurities. The properties of the pure components in comparison with the literature data are reported in Table 1.

Apparatus and Procedure. The refractive indices n(D), shown in Table 1, have been determined using an Abbe refractometer (Carl-Zeiss-Jena, precision ±0.0001) at 298.15 K after calibration with standard liquids, supplied with the instrument.

Isothermal VLE measurements were determined using an equilibrium still (Fritz Gmbh, Normag, Hofheim, Germany) described in detail by Gmehling et al. (1980). In this apparatus, both liquid and vapor phases are continuously recirculated to provide mixing of the phases and to ensure that equilibrium is rapidly established. The pressure P/kPa in the still was measured to ±0.05 kPa using a digital manometer, and the temperature was kept constant to ±0.05 K by means of a digital thermometer (both purchased from Fritz Gmbh, Normag, Hofheim, Germany). The liquid and vapor mole fractions, x_1 and y_1, in the liquid and in the vapor phases were determined by density analysis using a density meter (Anton Paar, model 60/602, Graz, Austria) based on measuring the period of oscillation τ of the vibrating U-shaped tube filled with the sample. The precision on τ is $\pm 1 \times 10^{-6}$ s, which leads to a precision in density measurements of the order $\pm 1 \times 10^{-5}$g·cm^{-3}. Densities, ρ, of known mole fractions, prepared by mass in air stoppered bottles (capacity ≈ 15 cm^3) using a Mettler balance (model AE 160, precision ±0.0001), were determined at 298.15 K and are reported in Table 2. The characteristics of the apparatus and the procedure used to prepare mole fractions are the same described by Fermeglia and Lapasin (1988). A Hetotherm bath circulator (Heto type 01 DBT 623, Birkeród, Denmark) maintained the temperature constant to within ±0.005 K.

We estimate the molar fraction composition derived from VLE measurements to be precise to within ±0.002.

Before measurements, the density meter was checked with the benzene + cyclohexane test mixture (Wilhelm, 1981) and the discrepancy with literature values of excess volume was found to be less than 0.5% over the central range of composition.

The vapor pressures of pure components, $P°_i$, were determined with the same still used for the other VLE data. The constants A and B of the Clausius−Clapeyron equation, correlation cofficients R, and standard deviations σ($P°_i$) are reported in Table 3. The pressures P and mole fractions x_1 and y_1 of the liquid and vapor phases are reported in Table 4 together with the "experimental" activity coefficients γ_i. These coefficients were evaluated by the equation relating the experimental values P, T, x_i, y_i

$$\gamma_i = Py_i/P_ix_i \qquad (1)$$

where P_i is the corrected vapor pressure of component i (Prausnitz, 1969), obtained from the virial coefficients, calculated from the Whol formula (Hala et al., 1967).

---

* Corresponding author.

[†] Centro di Studio per la Fisica delle Macromolecole del CNR.

[‡] Universitá degli Studi.

0021-9568/96/1741-0534$12.00/0

Table 1. Experimental Boiling Points, T_b, Densities, ρ, and Refractive Indices, n(D), and Comparison with Literature Values

	T_b(101.3 kPa)/K		ρ(298.15 K)/g·cm^{-3}		n(D, 298.15 K)	
component	exptl	lit.	exptl	lit.	exptl	lit.
dimethyl carbonate	363.35	363.65[a]	1.063 30	1.063 50[b]	1.3666	1.36 67[c]
diethyl carbonate	399.95	400.0[d]	0.969 27	0.969 26[d]	1.3827	1.382 77[d]

[a] *CRC Handbook* (1967). [b] Garcia et al. (1992). [c] Garcia et al. (1988). [d] Riddick et al. (1986).

Table 2. Experimental Density Values, ρ, for the Mixture Dimethyl Carbonate (1) + Diethyl Carbonate (2) as a Function of the Mole Fraction x_1 at 298.15 K

x_1	ρ/g·cm^{-3}	x_1	ρ/g·cm^{-3}
0.0207	0.970 53	0.6318	1.019 43
0.0654	0.973 41	0.6714	1.023 49
0.1980	0.982 49	0.7108	1.027 67
0.3150	0.991 28	0.7768	1.034 99
0.3852	0.996 92	0.8269	1.040 83
0.4467	1.002 13	0.9121	1.051 43
0.5093	1.007 70	0.9484	1.056 22
0.5617	1.012 56	0.9877	1.061 57
0.5856	1.014 87		

Table 3. Clausius−Clapeyron Coefficients A and B, Correlation Coefficients, $|R|$, and Standard Deviations, $\sigma(P°_i)$, for Pure Components Vapor Pressure $P°_i$[a]

component	temp range/K	A	B	$\lvert R\rvert$	$\sigma(P°_i)$/kPa
dimethyl carbonate	298.15−362.45	7.2973	−1915.9	0.9999	0.004
diethyl carbonate	308.85−369.75	7.4230	−2150.8	0.9999	0.004

[a] $\log_{10} P°_i/\text{kPa} = A + B/T$ (K).

Table 4. Pressures, P, Mole Fractions, x_1 and y_1, Experimental Activity Coefficients, γ_i, Wilson Parameters a_{12} and a_{21} and Standard Deviation, σ, from Least-Squares Analysis for Dimethyl Carbonate (1) + Diethyl Carbonate (2) in the Range (313.15 to 353.15) K

P/kPa	x_1	y_1	γ_1	γ_2	P/kPa	x_1	y_1	γ_1	γ_2
$T = 313.15$ K									
3.90	0.025	0.121	1.26	0.98	8.90	0.428	0.770	1.06	1.03
4.80	0.090	0.336	1.19	0.98	9.95	0.504	0.824	1.08	1.05
5.15	0.116	0.398	1.18	0.98	10.75	0.583	0.862	1.06	1.06
5.75	0.157	0.485	1.18	0.98	11.70	0.658	0.895	1.02	1.08
6.40	0.216	0.576	1.13	0.96	12.35	0.727	0.920	1.04	1.10
7.15	0.277	0.651	1.12	0.96	13.35	0.803	0.944	1.04	1.12
8.05	0.349	0.711	1.09	1.02	14.70	0.935	0.983	1.02	1.18
$a_{12} = 1143.4$; $a_{21} = -651.7$; $\sigma = 0.09$									
$T = 323.15$ K									
6.50	0.027	0.115	1.20	1.01	16.00	0.543	0.832	1.05	1.00
8.10	0.104	0.346	1.16	1.01	16.90	0.594	0.860	1.05	1.00
8.85	0.151	0.445	1.12	0.99	18.20	0.660	0.891	1.05	1.00
9.75	0.201	0.532	1.11	0.97	19.40	0.733	0.916	1.04	1.03
11.30	0.280	0.643	1.11	0.96	20.60	0.809	0.944	1.03	1.02
12.10	0.325	0.680	1.09	0.98	21.90	0.888	0.968	1.02	1.06
12.90	0.371	0.719	1.08	0.98	23.05	0.973	0.992	1.01	1.16
14.50	0.462	0.785	1.06	0.99					
$a_{12} = -89.2$; $a_{21} = 876.4$; $\sigma = 0.07$									
$T = 333.15$ K									
11.00	0.063	0.206	1.04	1.00	23.60	0.515	0.812	1.06	0.98
11.80	0.093	0.286	1.04	0.99	25.15	0.571	0.844	1.06	0.98
14.43	0.183	0.475	1.06	0.98	27.05	0.646	0.880	1.05	0.98
16.50	0.255	0.581	1.08	0.99	28.80	0.711	0.908	1.05	0.98
18.95	0.344	0.684	1.08	0.98	30.40	0.784	0.930	1.04	1.05
20.05	0.386	0.722	1.07	0.97	31.40	0.826	0.946	1.02	1.04
21.75	0.449	0.767	1.06	0.99	33.60	0.927	0.976	1.01	1.18
$a_{12} = -1224.8$; $a_{21} = 3724.7$; $\sigma = 0.03$									
$T = 343.15$ K									
15.60	0.030	0.100	1.02	1.01	37.75	0.574	0.832	1.06	1.01
17.40	0.067	0.215	1.09	1.02	40.05	0.630	0.860	1.06	1.05
18.80	0.100	0.301	1.11	1.02	41.80	0.672	0.884	1.07	1.02
21.40	0.162	0.425	1.10	1.02	44.20	0.742	0.910	1.05	1.06
23.90	0.230	0.543	1.10	0.99	47.30	0.828	0.944	1.04	1.06
26.00	0.280	0.605	1.10	0.99	48.25	0.862	0.956	1.04	1.06
27.60	0.327	0.647	1.07	1.01	49.60	0.908	0.972	1.03	1.04
30.70	0.404	0.721	1.07	1.01	50.35	0.935	0.980	1.02	1.07
$a_{12} = -121.8$; $a_{21} = 665.8$; $\sigma = 0.04$									
$T = 353.15$ K									
24.00	0.043	0.150	1.14	0.99	48.00	0.475	0.757	1.04	1.02
28.55	0.119	0.338	1.11	0.99	51.85	0.543	0.800	1.03	1.04
31.20	0.170	0.425	1.06	1.00	57.65	0.667	0.866	1.01	1.06
35.20	0.241	0.538	1.07	0.99	61.00	0.727	0.897	1.01	1.05
37.05	0.275	0.580	1.06	0.99	63.80	0.783	0.925	1.02	1.01
39.45	0.324	0.622	1.03	1.02	67.30	0.850	0.950	1.01	1.02
45.25	0.420	0.719	1.05	1.01	70.00	0.904	0.968	1.01	1.06
$a_{12} = 2852.2$; $a_{21} = -2200.0$; $\sigma = 0.03$									

Critical values of pressure and temperature needed in the least-squares procedure were calculated by following the procedure used by Klincewicz and Reid (1984).

Graphical representations of the VLE data are shown in Figures 1 to 3.

Results and Discussion

The thermodynamic consistency of the VLE data has been checked by means of the area test (Comelli and Francesconi, 1994)

$$I = \int_0^1 [\ln(\gamma_1/\gamma_2) + (V^E/RT)\, dP/dx_1]\, dx_1 \tag{3}$$

with γ_i obtained by eq 1. Integral I and its uncertainty δI, evaluated by variance analysis (Green and Margerison, 1977), are of the same order; thus, in the limit of the experimental errors, the test area is verified.

The second term between brackets in eq 3 has been calculated with V_m^E values taken from our previous work (Francesconi and Comelli, 1995).

The VLE data were then correlated by using a least-squares procedure (Comelli and Francesconi, 1994) and making use of the Wilson equation (Van Ness and Abbot, 1982) to calculate the activity coefficients γ_i

$$\ln \gamma_k = -\ln(x_k - \Lambda_{kj}x_j) + x_j[\Lambda_{kj}/(x_k + \Lambda_{kj}x_j) - a_{jk}/(x_j + \Lambda_{jk}x_k)] \tag{2}$$

$$\Lambda_{ij} = (V_j/V_i)\exp(-a_{ij}/RT); \qquad k = 1, 2;\ k \neq \text{j}$$

The results of least-squares analysis are reported in Table 4.

Since the system is close to ideality, the maximum value of γ_i never exceeding 1.26, only physical interactions among the molecules will give a sensible contribution to the energy of the mixture (particularly, dipole−dipole interactions related to the C=O groups). This result has been confirmed by the thermodynamic analysis which was applied by us to other binary systems (Castellari et al., 1988). Such a method is able to detect the formation of complexes between the components (by hydrogen bonding or charge transfer).

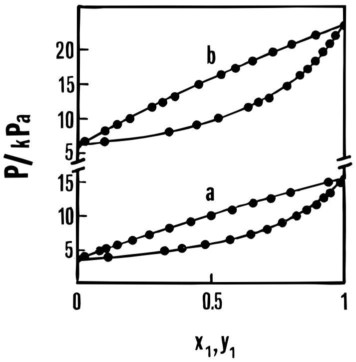

Figure 1. $P-x_1-y_1$ plots for the mixture dimethyl carbonate (1) + diethyl carbonate (2): (a) T = 313.15 K; (b) T = 323.15 K; (●) experimental points; (solid lines) calculated with eq 2.

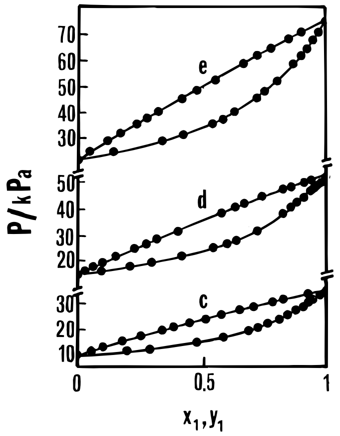

Figure 2. $P-x_1-y_1$ plots for the mixture dimethyl carbonate (1) + diethyl carbonate (2): (c) T = 333.15 K; (d) T = 343.15 K; (e) T = 353.15 K; (●), experimental points; (solid lines) calculated with eq 2.

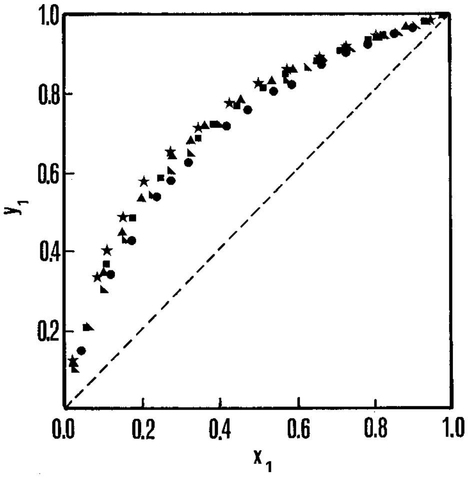

Figure 3. x_1-y_1 plots for dimethyl carbonate (1) + diethyl carbonate (2). (★, ▲, ■, ◪, ●), Experimental points at (313.15, 323.15, 333.15, 343.15, and 353.15) K.

Also, plots of H_m^E and V_m^E, previously obtained (Francesconi and Comelli, 1995) as a function of the mole fraction, show values typical of systems with small deviations from ideality: maximum H_m^E's around 150 J·mol^{-1} and V_m^E's less than 0.1 cm^3·mol^{-1}, with negligible temperature dependence.

Literature Cited

Annesini, M. C.; De Sanctis, R.; Kikic, I.; Marrelli, R. Excess Enthalpy and $T-x$ Data of Aromatic−Propylene Carbonate Mixtures. *J. Chem. Eng. Data* **1984**, *29*, 39−41.

Castellari, C.; Francesconi, R.; Comelli, F. Vapor-Liquid Equilibrium, Excess Gibbs Energy and Excess Enthalpy of 1,3-Dioxolane-Methylcyclohexane at T = 313.15 K. *Can. J. Chem. Eng.* **1988**, *66*, 131−135.

Comelli, F.; Francesconi, R. Isothermal Vapor−Liquid Equilibria, Densities, Refractive Indices, Excess Molar Volumes, and Excess Molar Enthalpies of Dimethyl Carbonate + 1,2-Dichloroethane and + 1,1,1-Trichloroethane. *J. Chem. Eng. Data* **1994**, *39*, 560−564.

Comelli, F.; Francesconi, R. Excess Molar Enthalpy of Binary Mixtures of Diethyl Carbonate + Nine Chloroalkanes at 298.15 K and Atmospheric Pressure. *J. Chem. Eng. Data* **1995**, *40*, 509−511.

CRC, Handbook of Tables for Organic Compound Identification; 3rd ed.; Chemical Rubber Co.: Cleveland, OH, 1967.

Fermeglia, M.; Lapasin, J. Excess Volumes and Viscosities of Binary Mixtures of Organics. *J. Chem. Eng. Data* **1988**, *33*, 415−417.

Francesconi, R.; Comelli, F. Excess Molar Volumes of Binary Mixtures Containing Dimethyl Carbonate + Linear and Cyclic Ethers. *J. Chem. Eng. Data* **1994**, *39*, 106−107.

Francesconi, R.; Comelli, F. Excess Molar Enthalpies, Densities and Excess Molar Volumes of Binary Mixtures Containing Esters of Carbonic Acid at 298.15 and 313.15 K. *J. Chem. Eng. Data* **1995**, *40*, 811−814.

Garcia, I.; Cobos, J. C.; Gonzales, J. A.; Casanova, G. Thermodynamics of Binary Mixtures Containing Organic Carbonates. 1. Excess Enthalpies of Dimethyl Carbonate + Hydrocarbons or + Tetrachloromethane. *J. Chem. Eng. Data* **1988**, *33*, 423−426.

Garcia, I.; Gonzales, J. A.; Cobos, C.; Casanova, C. Excess Molar Volumes for Dimethyl Carbonate−Heptane, Decane, 2,2,4-Trimethylpentane, Cyclohexane, Benzene, Toluene, or Tetrachloroethane. *J. Chem. Eng. Data* **1992**, *37*, 535−537.

Gmehling, J.; Onken, V.; Shulte, H. N. Vapor−Liquid Equilibria for the Binary System Diethyl Ether−Halothane (1,1,1-Trifluoro-2-bromo-2-chloroethane), Halothane−Methanol, and Diethyl Ether−Methanol. *J. Chem. Eng. Data* **1980**, *25*, 29−32.

Green, J. R.; Margerison, D. *Statistical Treatment of Experimental Data*; Elsevier North-Holland Inc.: Amsterdam, 1977.

Hala, E.; Pick, J.; Fried, O.; Vilim, O. *Vapour-Liquid Equilibrium*, 2nd ed.; Pergamon Press: Oxford, U.K., 1967.

Klincewicz, K. M.; Reid, R. C. Estimation of Critical Properties with Group Contribution Methods. *AIChE J.* **1984**, *30*, 137−142.

Martindale, W. *The Extra Pharmacopoeia*; Pharmaceutical Press: London, 1989.

The Merck Index; Merck Co. Inc.: Rahway, NJ, 1989.

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

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986.

Van Ness, H. C.; Abbot, M. M. *Classical Thermodynamics of Nonelectrolyte Solutions*; Mc Graw-Hill Book Co.: New York, 1982.

Wilhelm, E. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1981**, *9* (1), 164.

Received for review November 13, 1995. Accepted February 2, 1996.⊗

JE950287T

⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1996.