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# Vapor−Liquid Equilibria, Excess Molar Enthalpies, and Excess Molar Volumes of Dimethyl Carbonate + 1,2-Epoxybutane at 288.15, 298.15, or 313.15 K

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Vapor−liquid equilibria, (VLE), excess molar enthalpies, $H_m^E$, and excess molar volumes, $V_m^E$, of dimethyl carbonate + 1,2-epoxybutane have been determined at 288.15, 298.15, and 313.15 K. The VLE data, obtained by using an all-glass dynamic recirculating still, were tested for thermodynamic consistency and correlated by the Wilson equation. $H_m^E$ and $V_m^E$ values were determined by means of an LKB flow microcalorimeter and an Anton Paar vibrating tube density meter, respectively. All excess properties are positive, with a negligible temperature dependence (maxima values of $H_m^E$ or $V_m^E$ are 295 J·mol$^{-1}$ and 0.17 cm$^3$·mol$^{-1}$). $H_m^E$ and $V_m^E$ values have been correlated by the Redlich−Kister equation, and smooth representations are presented.

## Introduction

The study of carbonic acid esters is arousing an increasing interest because of their good properties as solvents for a variety of extractions of industrial importance, in the synthesis of pharmaceuticals, and in agricultural chemis-

As a part of a long-term study on the temperature dependence of the thermodynamic properties of binary mixtures containing esters of carbonic acid (Comelli and Francesconi, 1994; Francesconi and Comelli, 1995a, 1995b), we now report the vapor−liquid equilibria (VLE), the excess enthalpies, $H_m^E$, and the excess volumes, $V_m^E$, of the dimethyl carbonate + 1,2-epoxybutane binary mixture at 288.15, 298.15, and 313.15 K.

No isothermal VLE or enthalpic or volumetric data have been found in literature for this system.

## Experimental Section

***Materials.*** The liquids used in this paper were purchased from Aldrich. Both dimethyl carbonate (99 mol %) and 1,2-epoxybutane (+99 mol %) were fractionally distilled over sodium in a Vigreux 20-plate column, and only the middle fractions distilling at constant temperature were collected. The purities tested by GLC after purification were 99.9 and 99.8 mol %, respectively. Pure liquids were dried over molecular sieves (Union Carbide, type 4A, $^1/_{16}$-in. pellets) and kept in dark bottles. The purity of the chemicals was verified also by measurements of densities, $\rho$, refracive indices, $n$(D), and boiling points, $T_b/K$, which are reported in Table 1 and compared with literature data.

***Apparatus and Procedure.*** The isothermal VLE measurements were carried out by means of an all-glass dynamic recirculating still (Fritz Gmbh, Normag, Hofheim, Germany) described by Gmehling et al. (1980) and previously used in this laboratory to give accurate VLE data (Comelli and Francesconi, 1994, 1995; Francesconi et al., 1993). Temperature, $T$/K, and pressure, $P$/kPa, were determined by digital instruments (Fritz Gmbh, Normag, Hofheim, Germany) with an accuracy of ±0.05 K and ±0.05 kPa, respectively. Repeated measurements of pressure on at least five samples resulted in a standard deviation in the range 0.1−0.2, the larger limit being typical of the mixtures rich in the more volatile component. The attainment of a constant temperature for at least 20 min was the sign that the steady state had been reached: in these conditions, samples of the liquid and of the vapor phases were withdrawn and analyzed. The compositions of the liquid and condensed phases were determined by density measurements using a vibrating tube density meter (Anton Paar, model DMA 60/602, Graz, Austria) and a $\rho$ vs $x_1$ curve previously obtained.

The apparatus was connected to a Hetotherm bath circulator (Heto, type 01 DBT 623, Birkerød, Denmark) with an accuracy in the temperature control of ±0.005 K.

A flow microcalorimeter (LKB, AB-Produkter, model 2107, Bromma, Sweden) was used to determine the excess molar enthalpies, $H_m^E$. Two identical automatic burets (ABU-Radiometer, Copenhagen, Denmark) were used to pump the liquids. Details of the equipment and operating procedure have been described previously (Monk and Wadso, 1968; Francesconi and Comelli, 1986). The temperature was kept constant to ±0.01 K by means of an electronic thermometer enclosed within the apparatus. The performance of the calorimeter was checked by measuring $H_m^E$ of the test mixture hexane + cyclohexane at 298.15 K, for which literature values (Benson, 1974) are known. Our results agree with literature values within 0.5% in the middle composition.

Mole fractions were determined from the flow rates and the fluid density. The accuracies in $H_m^E$ and in the mole fraction $x_1$ are estimated to be better than 1% and $5 \times 10^{-4}$, respectively.

Excess molar volumes, $V_m^E$, were obtained using a vibrating tube density meter (Anton Paar, model DMA 60/602), from density determinations. The apparatus, described elsewere (Fermeglia and Lapasin, 1988), operates on the basis of the following relationship between the

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**Table 1. Densities, $\rho$, Refractive Indices, $n$(D), and Boiling Points, $T_b$, of Pure Components**

| | $\rho$(298.15 K)/(g·cm$^{-3}$) | | $n$ (D, 298.15 K) | | $T_b$ (101.3 kPa)/K | |
|---|---|---|---|---|---|---|
| component | exptl | lit. | exptl | lit. | exptl | lit. |
| dimethyl carbonate | 1.063 28 | 1.063 50[a] | 1.3667 | 1.3667[a] | 363.60 | 363−4[b] |
| 1,2-epoxybutane | 0.824 63 | 0.824[c] | 1.3815 | 1.381[c] | 336.65 | 336.574[c] |

[a] Garcia de la Fuente et al., 1992. [b] *CRC Handbook*, 1979. [c] Riddick et al., 1986.

**Table 2. Clausius−Clapeyron Coefficients, A and B, Correlation Coefficients, $R$, and Standard Deviations, $\sigma(P°_i)$, for the Vapor Pressure $P°_i$ of Pure Components, eq 2**

| component | temp range/K | $A$ | $B$ | $R$ | $\sigma(P°_i/\text{kPa})$ |
|---|---|---|---|---|---|
| dimethyl carbonate | 288−352 | 7.2973 | −1915.94 | −0.99993 | 0.18 |
| 1,2-epoxybutane | 288−323 | 7.0486 | −1693.34 | −0.99998 | 0.11 |

density, $\rho$, and the period of oscillation, $\tau$, at the temperature $T$/K:

$$\rho(T/\text{K}) = (\tau^2 - B)/A \qquad (1)$$

where A and B are constants which are determined by calibration with fluids of known densities such as dried air and twice distilled water at 288.15, 298.15, and 318.15 K.

We have selected, for each measurement, the period $\tau$ of 5000 oscillation cycles, and the temperature equilibration was conventionally followed until the $\tau$ value became constant to ±1. The precision on $\tau$ is $1 \times 10^{-6}$ s, which leads to a precision in density measurements of the order $\times 10^{-5}$ g·cm$^{-3}$ corresponding to a mean uncertainty in the excess volume of $2 \times 10^{-3}$ cm$^3$·mol$^{-1}$. Mixtures were prepared by mass in air stoppered bottles (capacity ≈ 20 ) using an analytical balance (Mettler, model AE 160), with a precision of $\pm 1 \times 10^{-4}$ g and following the procedure used by other authors (Fermeglia and Lapasin, 1988). All measurements were corrected for buoyancy and for evaporation of the components. The thermal control was checked by digital thermometers (Anton Paar DT-15, DT-25, DT-40) with an accuracy of ±0.01 K.

Before measurements, the density meter was calibrated with the benzene + cyclohexane test mixture (Wilhelm and Grolier, 1985): our data show a discrepancy from literature data less than 0.5% over the central range of mole fraction of benzene.

## Results and Discussion

Values of vapor pressure $P°_i$ of pure components are necessary for the thermodynamic treatment of the VLE data. Parameters $A$ and $B$ of the Clausius−Clapeyron vapor pressure equation

$$\log_{10}(P°_i/\text{kPa}) = A + B/T(\text{K}) \qquad (2)$$

have been determined by least-squares method and are shown in Table 2, together with the correlation coefficients $R$ and standard deviations $\sigma(P°_i/\text{kPa})$.

Our values agree with those of the literature (Cocero et al., 1989; Jónasson et al., 1994), within the limits of experimental errors. The VLE data are reported in Table 3 while the $P-x_1-y_1$ plots are graphically represented in Figure 1. The experimental liquid-phase activity coefficients, $\gamma_i$, were evaluated from the equation

$$\gamma_i = Py_i/x_iP_i \qquad (3)$$

**Table 3. Pressures, $P$/kPa, Mole Fractions, $x_1$ and $y_1$, Experimental Activity Coefficients, $\gamma_i$, Wilson Parameters, $a_{12}$ and $a_{21}$(J·mol$^{-1}$) and Standard Deviation $\sigma$ from Least-Squares Analysis of Dimethyl Carbonate (1) + 1,2-Epoxybutane (2) at 288.15, 298.15, and 313.15 K**

| $P$/kPa | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|
| | | $T$ = 288.15 K | | |
| 14.05 | 0.089 | 0.035 | 1.23 | 1.00 |
| 13.75 | 0.130 | 0.058 | 1.37 | 1.00 |
| 13.30 | 0.174 | 0.078 | 1.33 | 1.00 |
| 12.80 | 0.230 | 0.101 | 1.26 | 1.01 |
| 12.20 | 0.295 | 0.131 | 1.21 | 1.01 |
| 11.50 | 0.367 | 0.159 | 1.11 | 1.03 |
| 10.90 | 0.425 | 0.193 | 1.11 | 1.03 |
| 10.65 | 0.468 | 0.212 | 1.08 | 1.06 |
| 9.95 | 0.533 | 0.250 | 1.04 | 1.08 |
| 9.45 | 0.580 | 0.290 | 1.06 | 1.08 |
| 8.55 | 0.668 | 0.353 | 1.01 | 1.13 |
| 7.70 | 0.750 | 0.438 | 1.01 | 1.17 |
| 7.20 | 0.790 | 0.525 | 1.07 | 1.10 |
| 6.65 | 0.829 | 0.632 | 1.14 | 0.97 |
| 6.05 | 0.880 | 0.731 | 1.13 | 0.92 |
| 5.65 | 0.915 | 0.798 | 1.11 | 0.91 |
| 5.10 | 0.956 | 0.901 | 1.08 | 0.77 |
| 4.80 | 0.980 | 0.951 | 1.05 | 0.80 |
| $a_{12}$ = 3306.0; $a_{21}$ = −1873.2; $\sigma$ = 0.19; $I$ = 0.120 (2.6 × 10$^{-6}$); $\delta I$ = 0.008 | | | | |
| | | $T$ = 298.15 K | | |
| 23.00 | 0.045 | 0.019 | 1.29 | 1.01 |
| 22.40 | 0.088 | 0.042 | 1.42 | 1.01 |
| 22.05 | 0.118 | 0.055 | 1.37 | 1.01 |
| 21.60 | 0.153 | 0.068 | 1.28 | 1.02 |
| 20.90 | 0.194 | 0.090 | 1.29 | 1.01 |
| 19.90 | 0.258 | 0.122 | 1.26 | 1.01 |
| 19.00 | 0.323 | 0.146 | 1.15 | 1.03 |
| 18.20 | 0.384 | 0.179 | 1.13 | 1.04 |
| 17.55 | 0.432 | 0.204 | 1.11 | 1.05 |
| 16.00 | 0.529 | 0.263 | 1.06 | 1.07 |
| 14.85 | 0.608 | 0.318 | 1.04 | 1.11 |
| 13.45 | 0.693 | 0.398 | 1.04 | 1.13 |
| 11.90 | 0.775 | 0.484 | 1.00 | 1.17 |
| 10.70 | 0.841 | 0.579 | 0.99 | 1.22 |
| 9.70 | 0.888 | 0.670 | 0.98 | 1.23 |
| 9.15 | 0.923 | 0.745 | 0.99 | 1.30 |
| 8.15 | 0.965 | 0.859 | 0.98 | 1.41 |
| $a_{12}$ = 340.9; $a_{21}$ = 563.2; $\sigma$ = 0.04; $I$ = 0.007; $\delta I$ = 0.008 | | | | |
| | | $T$ = 313.15 K | | |
| 42.60 | 0.065 | 0.030 | 1.28 | 1.01 |
| 41.35 | 0.118 | 0.059 | 1.35 | 1.01 |
| 40.25 | 0.170 | 0.082 | 1.27 | 1.02 |
| 38.85 | 0.223 | 0.108 | 1.23 | 1.02 |
| 37.20 | 0.288 | 0.140 | 1.18 | 1.03 |
| 35.30 | 0.363 | 0.181 | 1.15 | 1.04 |
| 32.75 | 0.457 | 0.237 | 1.11 | 1.06 |
| 31.20 | 0.513 | 0.275 | 1.10 | 1.07 |
| 29.70 | 0.566 | 0.313 | 1.08 | 1.08 |
| 28.35 | 0.613 | 0.351 | 1.07 | 1.09 |
| 26.95 | 0.663 | 0.389 | 1.04 | 1.12 |
| 25.10 | 0.724 | 0.454 | 1.04 | 1.14 |
| 22.60 | 0.804 | 0.554 | 1.03 | 1.19 |
| 21.70 | 0.827 | 0.590 | 1.02 | 1.19 |
| 20.20 | 0.874 | 0.665 | 1.01 | 1.24 |
| 17.90 | 0.938 | 0.802 | 1.01 | 1.32 |
| 16.60 | 0.972 | 0.889 | 1.00 | 1.52 |
| $a_{12}$ = −391.5; $a_{21}$ = 1420.4; $\sigma$ = 0.04; $I$ = 0.008; $\delta I$ = 0.007 | | | | |

where $P_i$ is the "corrected vapor pressure" (Prausnitz, 1969, p 204) obtained from the virial coefficients by following the procedure described in a previous paper (Francesconi and Cojutti, 1971). Critical values of temperature and pressure, necessary to evaluate virial coefficients, were calculated

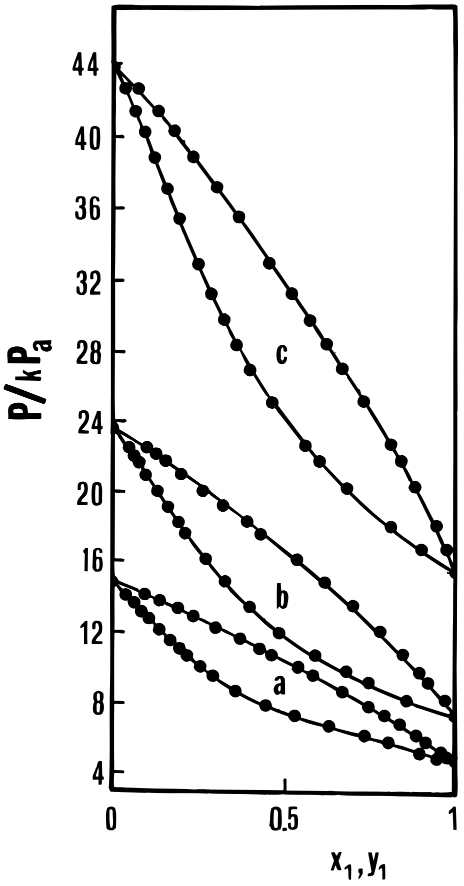

**Figure 1.** $P-x_1-y_1$ plots of dimethyl carbonate + 1,2-epoxybutane: (a−c) $T$ = 288.15, 298.15, 313.15 K; (●) experimental points; (solid lines) eq 5.

by the method of Klincewicz and Reid (1984).

The system dimethyl carbonate + 1,2-epoxybutane shows moderate deviations from ideal behavior (the activity coefficients $\gamma$ range from 0.77 to 1.52).

The thermodynamic consistency of the VLE experimental data was checked by the area test (Prausnitz, 1969, p 215) according to which the following integral

$$I = \int_0^1 [\ln(\gamma_1/\gamma_2) + (V_m^E/RT)\, dP/dx_1]\, dx_1 \qquad (4)$$

is compared with its uncertainty $\delta I$, evaluated by variance analysis from knowledge of errors on all experimental values occurring in $I$.

The thermodynamic consistency of VLE data is established when $|I|$ and the uncertainty $\delta I$ are of the same magnitude or $\delta I \geq |I|$.

This criterion is satisfied for the mixtures at $T$ = 298.15 or 313.15 K, whereas at the lower temperature, 288.15 K, $|I|$ and $\delta I$ show a marked difference, which will be discussed below.

Table 3 reports values of $I$ and $\delta I$ for the three temperatures.

The activity coefficients of the binary mixtures, $\gamma_i$, were correlated by the Wilson equation (Van Ness and Abbot, 1982)

$$\ln \gamma_k = -\ln(x_k + \Lambda_{kj}x_j) + x_j[(\Lambda_{kj}/(x_k + \Lambda_{kj}x_j) - \Lambda_{jk}/(x_j + \Lambda_{jk}x_k)] \quad (5)$$

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

through the least-squares procedure used in a previous paper (Francesconi et al., 1993), reporting the minimized objective function.

**Table 4. Mole Fractions, $x_1$, Experimental Excess Molar Enthalpies, $H_m^E$, Adjustable Parameters, $a_k$, eq 7, and Standard Deviation, $\sigma(H_m^E)$, from Least-Squares Analysis of Dimethyl Carbonate (1) + 1,2-Epoxybutane (2) at 288.15, 298.15, or 313.15 K**

| $x_1$ | $H_m^E$/J·mol$^{-1}$ | $x_1$ | $H_m^E$/J·mol$^{-1}$ |
|---|---|---|---|
| $T$ = 288.15 K | | | |
| 0.0412 | 28.5 | 0.6074 | 277.6 |
| 0.0791 | 58.3 | 0.6735 | 247.7 |
| 0.1156 | 92.6 | 0.7557 | 192.7 |
| 0.1484 | 122.9 | 0.8049 | 154.9 |
| 0.2072 | 175.2 | 0.8610 | 99.8 |
| 0.2584 | 212.5 | 0.8919 | 69.5 |
| 0.3433 | 260.9 | 0.9252 | 40.8 |
| 0.4137 | 283.9 | 0.9612 | 16.2 |
| 0.5111 | 295.0 | | |
| $a_0$ = 1180.0; $a_1$ = 0; $a_2$ = −261.7; $a_3$ = −170.1; $a_4$ = −545.3; $\sigma(H_m^E$/J·mol$^{-1})$ = 1.2 | | | |
| $T$ = 298.15 K | | | |
| 0.0412 | 28.2 | 0.6077 | 266.9 |
| 0.0792 | 57.7 | 0.6737 | 242.8 |
| 0.1143 | 94.6 | 0.7559 | 192.1 |
| 0.1468 | 124.5 | 0.8050 | 152.8 |
| 0.2051 | 182.9 | 0.8610 | 101.7 |
| 0.2560 | 219.2 | 0.8920 | 73.0 |
| 0.3404 | 260.2 | 0.9253 | 43.8 |
| 0.4076 | 277.2 | 0.9612 | 18.2 |
| 0.5079 | 285.7 | | |
| $a_0$ = 1141.3; $a_1$ = −97.6; $a_2$ = 0; a$_3$ = 0; $a_4$ = −787.4; $\sigma(H_m^E$/J·mol$^{-1})$ = 1.7 | | | |
| $T$ = 313.15 K | | | |
| 0.0413 | 33.5 | 0.6080 | 274.4 |
| 0.0793 | 68.1 | 0.6740 | 246.2 |
| 0.1144 | 106.2 | 0.7562 | 197.3 |
| 0.1470 | 130.4 | 0.8053 | 157.5 |
| 0.2054 | 181.8 | 0.8612 | 108.2 |
| 0.2563 | 220.7 | 0.8921 | 76.7 |
| 0.3408 | 266.8 | 0.9254 | 47.4 |
| 0.4080 | 283.9 | 0.9613 | 20.9 |
| 0.5083 | 294.8 | | |
| $a_0$ = 1174.7; $a_1$ = −49.9; $a_2$ = −121.4; $a_3$ = −118.0; $a_4$ = −514.5; $\sigma(H_m^E$/J·mol$^{-1})$ = 1.9 | | | |

Parameters $a_{ij}$ and standard deviations $\sigma$ are reported in Table 3. The standard deviation $\sigma$ is 0.19 at 288.15 K, about 5 times larger than those obtained at the higher temperatures. Also the larger values of the Wilson parameters $a_{12}$ and $a_{21}$ at 288.15 K reflect the different behavior of the mixtures at the lower temperature. These mixtures were therefore submitted to an additional analysis, by applying a method capable of detecting the existence of eventual strong interactions between molecules (Francesconi and Trevissoi, 1971). The resulting value of $I$ for the mixture at 288.15 K is given in Table 3, between brackets, and seems to indicate the existence of molecular interactions between ester and ether.

Validity of this result, however, must be taken prudently since VLE data at the lower temperature are affected by larger uncertainties which can match with least-squares analysis to give unreliable conclusions.

Tables 4 and 5 list the experimental values and Figures 2 and 3 show the graphical representations of excess molar enthalpies, $H_m^E$, and excess molar volumes, $V_m^E$, respectively.

The excess molar volumes, $V_m^E$, were calculated from the equation

$$V_m^E = (x_1M_1 + x_2M_2)/\rho - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \qquad (6)$$

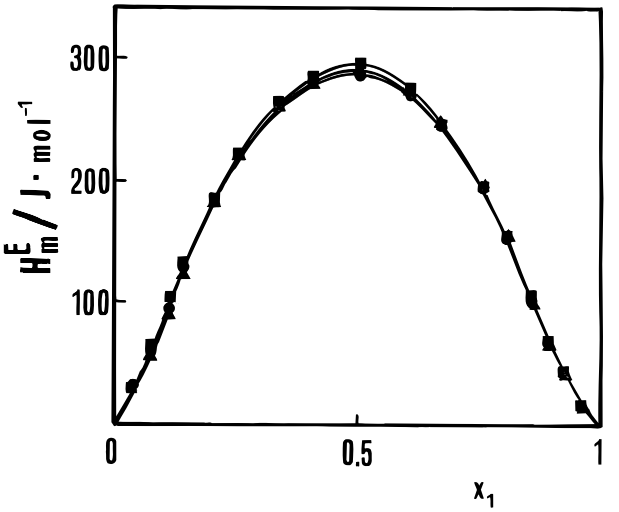

**Figure 2.** Excess molar enthalpies, $H_m^E$, of dimethyl carbonate (1) + 1,2-epoxybutane (2): (▲, ●, ■) experimental points at 288.15, 298.15, 313.15 K; (solid lines) eq 7.

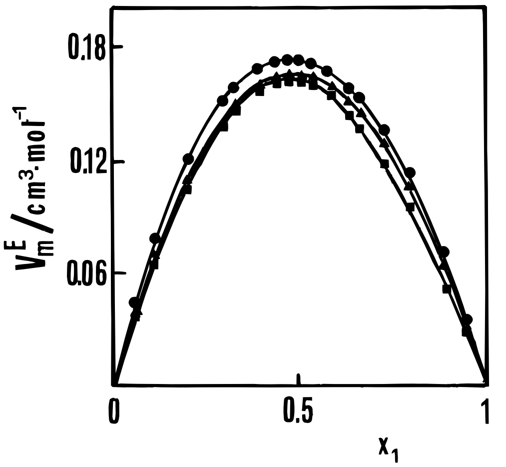

**Figure 3.** Excess molar volumes, $V_m^E$, of dimethyl carbonate (1) + 1,2-epoxybutane (2): (▲, ●, ■) experimental points at 288.15,298.15, and 313.15 K; (solid lines) eq 7.

**Table 5. Mole Fractions, $x_1$, Experimental Densities, $\rho$, Excess Molar Volumes, $V_m^E$, Adjustable Parameters, $a_k$, Eq 7, and Standard Deviation, $\sigma(V_m^E)$, from Least-Squares Analysis of Dimethyl Carbonate (1) + 1,2-Epoxybutane (2) at 288.15, 298.15, or 313.15 K**

| | $\rho$/g·cm$^{-3}$ | $V_m^E$/cm$^3$·mol$^{-1}$ | $x_1$ | $\rho$/g·cm$^{-3}$ | $V_m^E$/cm$^3$·mol$^{-1}$ |
|---|---|---|---|---|---|
| | | | $T = 288.15$ K | | |
| 0.0000 | 0.83544 | 0.000 | 0.5399 | 0.96182 | 0.163 |
| 0.0667 | 0.85066 | 0.039 | 0.5819 | 0.97199 | 0.159 |
| 0.1219 | 0.86335 | 0.068 | 0.6306 | 0.98385 | 0.151 |
| 0.2083 | 0.88332 | 0.106 | 0.6668 | 0.99269 | 0.146 |
| 0.3347 | 0.91286 | 0.147 | 0.7299 | 1.00824 | 0.130 |
| 0.4006 | 0.92846 | 0.157 | 0.7944 | 1.02428 | 0.107 |
| 0.4404 | 0.93790 | 0.163 | 0.8899 | 1.04828 | 0.064 |
| 0.4709 | 0.94522 | 0.164 | 0.9473 | 1.06278 | 0.037 |
| 0.5079 | 0.95407 | 0.165 | 1.0000 | 1.07634 | 0.000 |
| $a_0 = 0.6557$; $a_1 = 0.0069$; $\sigma(V_m^E/\text{cm}^3\cdot\text{mol}^{-1}) = 0.0016$ | | | | | |
| | | | $T = 298.15$ K | | |
| 0.0000 | 0.82463 | 0.000 | 0.5079 | 0.94205 | 0.171 |
| 0.0666 | 0.83963 | 0.044 | 0.5399 | 0.94970 | 0.171 |
| 0.1219 | 0.85215 | 0.078 | 0.5819 | 0.95980 | 0.165 |
| 0.2083 | 0.87188 | 0.120 | 0.6306 | 0.97156 | 0.157 |
| 0.3057 | 0.89442 | 0.151 | 0.6668 | 0.98034 | 0.150 |
| 0.3347 | 0.90118 | 0.158 | 0.7299 | 0.99573 | 0.136 |
| 0.4006 | 0.91665 | 0.166 | 0.7944 | 1.01159 | 0.115 |
| 0.4403 | 0.92603 | 0.170 | 0.8899 | 1.03535 | 0.073 |
| 0.4709 | 0.93326 | 0.172 | 0.9472 | 1.04987 | 0.035 |
| | | | 1.0000 | 1.06328 | 0.000 |
| $a_0 = 0.6848$; $a_1 = -0.0523$; $a_2 = 0.0804$; $a_3 = 0.1018$; $\sigma(V_m^E/\text{cm}^3\cdot\text{mol}^{-1}) = 0.0014$ | | | | | |
| | | | $T = 313.15$ | | |
| 0.0000 | 0.80789 | 0.000 | 0.5078 | 0.92383 | 0.160 |
| 0.0666 | 0.82276 | 0.038 | 0.5399 | 0.93140 | 0.158 |
| 0.1219 | 0.83518 | 0.064 | 0.5819 | 0.94138 | 0.151 |
| 0.2083 | 0.85465 | 0.104 | 0.6306 | 0.95296 | 0.144 |
| 0.3057 | 0.87687 | 0.137 | 0.6668 | 0.96163 | 0.138 |
| 0.3347 | 0.88354 | 0.144 | 0.7299 | 0.97688 | 0.118 |
| 0.4006 | 0.89875 | 0.156 | 0.7944 | 0.99257 | 0.094 |
| 0.4403 | 0.90803 | 0.158 | 0.8899 | 1.01606 | 0.050 |
| 0.4709 | 0.91516 | 0.161 | 0.9472 | 1.03015 | 0.033 |
| | | | 1.0000 | 1.04336 | 0.000 |
| $a_0 = 0.6411$; $a_1 = -0.0453$; $a_2 = -0.1099$; $\sigma(V_m^E/\text{cm}^3\cdot\text{mol}^{-1}) = 0.0024$ | | | | | |

where $x_1$, $x_2$; $M_1$, $M_2$; and $\rho_1$ and $\rho_2$ are the mole fractions, the molecular weights, and the densities of dimethyl carbonate (component 1) and 1,2-epoxybutane (component 2), whereas $\rho$ is the density of the mixture.

The excess molar enthalpies, $H_m^E$, and the excess molar volumes, $V_m^E$, can be represented by the Redlich–Kister equation

$$Q_m^E = x_1x_2 \sum_{k\geq 0} a_k(x_1 - x_2)^k \tag{7}$$

where $Q_m^E = H_m^E$ or $V_m^E$.

The method of least squares, assuming unit statistical weight for the experimental points, was used to determine the values of the adjustable parameters $a_k$, following the procedure reported in previous papers (see, for example, Francesconi and Comelli, 1986). Some of parametrs $a_k$, reported in Table 3, are assumed to be zero, on account of their large uncertainties: the calculated objective function is sensibly reduced by putting to zero these parameters.

$H_m^E$ and $V_m^E$ data need nothing but a short comment, due to the small temperature dependence of these properties and the nearly symmetrical shape of the curves.

The $V_m^E$ term in the integral of eq 4, is found to contribute less than 10% to *I*.

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