# Excess Molar Enthalpies and Excess Molar Volumes of Dialkyl Carbonates + Acetic or Propionic Acid at 298.15 K

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Excess molar enthalpies, $H_m^E$, and excess molar volumes, $V_m^E$, of the binary mixtures of dimethyl carbonate or diethyl carbonate + acetic acid or propionic acid have been determined at 298.15 K as a function of composition using a flow microcalorimeter and a digital density meter. Excess values have been correlated with the Redlich−Kister equation, and smoothed data plots are presented.

## Introduction

The excess properties of binary liquid mixtures are important to understand and interpret the nature of interactions between the molecules of the mixtures. Our research program involves esters of carbonic acid, used as solvents for a variety of extractions of industrial importance, in the synthesis of pharmaceuticals and in agricultural chemistry. In this paper we report measurements of excess molar enthalpies, $H_m^E$, and excess molar volumes, $V_m^E$, of dimethyl carbonate (DMC) or diethyl carbonate (DEC) + acetic or propionic acid at 298.15 K and at atmospheric pressure.

To our knowledge there are no published excess data on these systems.

## Experimental Section

***Chemicals.*** Dimethyl and diethyl carbonate, supplied by Aldrich Chemical Co., purity grade 99%, were fractionally distilled as indicated in a previous paper (Francesconi and Comelli, 1996), and after purification, GLC analysis revealed a purity grade of 99.9 mol % for both liquids. Acetic and propionic acid, a Fluka and a Merck product respectively, with stated purities 99.8 and 99.5 mol % were used as received.

Purities of components were also checked by comparing their measured densities, $\rho$, with those reported in the literature, as shown in Table 1.

Before measurements, the liquids were kept in dark bottles, dried over molecular sieves (Union Carbide, type 4A, $^1/_{16}$ in. pellets), and degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan).

***Procedure.*** Excess molar enthalpies, $H_m^E$, of binary mixtures were determined using an LKB flow microcalorimeter (LKB, model 2107, Produkter AB, Bromma, Sweden) equipped with two automatic burets (ABU, Radiometer, Copenhagen, Denmark) to pump pure liquids into the mixing cell of the calorimeter. Mole fractions $x_1$ of dialkyl carbonate (component 1) were measured from fluxes and the observed standard deviation was $\delta x \approx 0.0003$. The temperature in the apparatus was kept constant at (298.15 ± 0.01) K through an external circulator bath maintained at a temperature about 10 °C smaller than that of the calorimeter bath. Details of the equipment and its operating procedure have been described elsewere (Monk and Wadso, 1968; Francesconi and Comelli, 1986).

**Table 1. Densities, $\rho$, of Pure Components and Comparison with Literature Values**

| component | $\rho$(298.15 K)/g·cm$^{-3}$ exptl | lit. |
|---|---|---|
| dimethyl carbonate | 1.063 31 | 1.063 6[a]<br>1.063059[b] |
| diethyl carbonate | 0.969 25 | 0.969 26[c]<br>0.9694[a] |
| acetic acid | 1.043 78 | 1.043 92[c]<br>1.0437[d] |
| propionic acid | 0.987 96 | 0.988 08[c]<br>0.9879[e]<br>0.98787[f] |

[a] Cocero et al., 1991. [b] Negadi er al., 1993. [c] Riddick et al., 1986. [d] Kato, 1988. [e] Kato et al., 1990. [f] Comelli and Francesconi, 1996.

The reliability of the calorimeter was checked by measuring the $H_m^E$’s for the hexane + cyclohexane test mixture, which agree within experimental error (0.5%) with literature values (Gmehling, 1993).

Densities of pure liquids and binary mixtures were determined using an Anton Paar digital density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell type 602 (Anton Paar, Graz, Austria), following the procedure described elsewhere (Fermeglia and Lapasin, 1988).

The temperature was maintained constant at ±0.01 K by means of an external Hetotherm circulator bath (Heto, type 01 DBT 623, Birkerød, Denmark) showing a precision of ±0.005 K.

The accuracy of densities was $\pm 5 \times 10^{-5}$ g·cm$^{-3}$ leading to $V_m^E$ values with an estimated error of $\pm 0.003$ cm$^3$·mol$^{-1}$.

Mole fractions were prepared by weighting, using a Mettler balance (model AE 160) with a precision of ±0.0001 g.

The procedure adopted to prepare mixtures in airtight flasks is the same as that proposed by Fermeglia and Lapasin (1988).

Buoyancy corrections due to air and evaporation of solvents were allowed to achieve greater accuracy in measurements, but only a variation of one unit in the fourth decimal value of the mole fraction has been observed.

For each experimental set of measurements, the apparatus was calibrated with doubly fresh distilled water and dry air.

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**Table 2. Mole Fractions, $x_1$, and Excess Molar Enthalpies, $H_m^E$, of Dialkyl Carbonates + Acetic or Propionic Acid at 298.15 K**

| $x_1$ | $H_m^E$/J·mol$^{-1}$ | $x_1$ | $H_m^E$/J·mol$^{-1}$ |
|---|---|---|---|
| Dimethyl Carbonate (1) + Acetic Acid (2) | | | |
| 0.0275 | 23 | 0.5046 | 321 |
| 0.0536 | 49 | 0.5760 | 327 |
| 0.0783 | 71 | 0.6708 | 331 |
| 0.1017 | 87 | 0.7309 | 320 |
| 0.1451 | 131 | 0.8030 | 298 |
| 0.1846 | 163 | 0.8446 | 266 |
| 0.2535 | 209 | 0.8907 | 223 |
| 0.3116 | 244 | 0.9422 | 140 |
| 0.4044 | 289 | | |
| Dimethyl Carbonate (1) + Propionic Acid (2) | | | |
| 0.0355 | 71 | 0.5704 | 581 |
| 0.0687 | 134 | 0.6390 | 562 |
| 0.0996 | 197 | 0.7264 | 510 |
| 0.1285 | 255 | 0.7798 | 468 |
| 0.1812 | 331 | 0.8416 | 388 |
| 0.2278 | 404 | 0.8762 | 331 |
| 0.3068 | 482 | 0.9140 | 259 |
| 0.3711 | 538 | 0.9550 | 151 |
| 0.4695 | 569 | | |
| Diethyl Carbonate (1) + Acetic Acid (2) | | | |
| 0.0378 | 25 | 0.4856 | 246 |
| 0.0729 | 48 | 0.5861 | 265 |
| 0.1056 | 71 | 0.6538 | 273 |
| 0.1360 | 92 | 0.7391 | 268 |
| 0.1910 | 124 | 0.7906 | 256 |
| 0.2394 | 151 | 0.8500 | 226 |
| 0.3207 | 191 | 0.9189 | 158 |
| 0.4146 | 228 | | |
| Diethyl Carbonate (1) + Propionic Acid (2) | | | |
| 0.0250 | 23 | 0.4799 | 302 |
| 0.0488 | 45 | 0.5517 | 317 |
| 0.0714 | 67 | 0.6486 | 316 |
| 0.0930 | 87 | 0.7111 | 306 |
| 0.1333 | 127 | 0.7869 | 281 |
| 0.1702 | 153 | 0.8311 | 255 |
| 0.2353 | 197 | 0.8807 | 210 |
| 0.2909 | 229 | 0.9366 | 133 |
| 0.3808 | 272 | | |

The benzene + cyclohexane test mixture was used to check the density meter: our $V_m^E$ values are in agreement with those of literature (Wilhelm, 1985) within experimental error (0.5%).

$V_m^E$ values were obtained using the following equation

$$V_m^E/\text{cm}^3\cdot\text{mol}^{-1} = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \qquad (1)$$

where $x_i$, $M_i$, and $\rho_i$ are the molar fraction, molar mass, and density of component $i$, respectively.

## Results and Discussion

Tables 2 and 3 report $H_m^E$ and $V_m^E$ which are also graphically represented in Figures 1 and 2.

The excess values have been correlated using the Redlich−Kister polynomial

$$Q_m^E = x_1x_2\sum_{k\geq 0} a_k(x_1 - x_2)^k \qquad (2)$$

where $Q_m^E = H_m^E$/(J·mol$^{-1}$) or $V_m^E$/(cm$^3$·mol$^{-1}$), $x_1$, $x_2$ are the mole fractions of components, and $a_k$ are the adjustable parameters, obtained by fitting eq 2 to the experimental $H_m^E$ or $V_m^E$ by unweighted least-squares regression.

**Table 3. Mole Fractions, $x_1$, Densities, $\rho$, and Excess Molar Volumes, $V_m^E$, of Dialkyl Carbonates + Acetic or Propionic Acid at 298.15 K**

| $x_1$ | $\rho$/ g·cm$^{-3}$ | $V_m^E$/ cm$^3$·mol$^{-1}$ | $x_1$ | $\rho$/ g·cm$^{-3}$ | $V_m^E$/ cm$^3$·mol$^{-1}$ |
|---|---|---|---|---|---|
| Dimethyl Carbonate (1) + Acetic Acid (2) | | | | | |
| 0.0338 | 1.044 66 | 0.004 | 0.4482 | 1.054 42 | 0.001 |
| 0.0507 | 1.045 09 | 0.006 | 0.4823 | 1.055 13 | −0.002 |
| 0.1229 | 1.046 91 | 0.013 | 0.5476 | 1.056 45 | −0.010 |
| 0.1649 | 1.047 94 | 0.014 | 0.6280 | 1.058 01 | −0.020 |
| 0.2203 | 1.049 28 | 0.015 | 0.7055 | 1.059 41 | −0.028 |
| 0.2736 | 1.050 56 | 0.012 | 0.7997 | 1.060 99 | −0.037 |
| 0.3248 | 1.051 73 | 0.010 | 0.8574 | 1.061 87 | −0.038 |
| 0.3660 | 1.052 65 | 0.008 | 0.9679 | 1.063 11 | −0.016 |
| 0.4021 | 1.053 43 | 0.005 | | | |
| Dimethyl Carbonate (1) + Propionic Acid (2) | | | | | |
| 0.0181 | 0.989 47 | −0.002 | 0.5111 | 1.029 62 | −0.068 |
| 0.0881 | 0.995 50 | −0.013 | 0.5519 | 1.032 71 | −0.071 |
| 0.1533 | 1.001 02 | −0.024 | 0.6140 | 1.037 32 | −0.076 |
| 0.1986 | 1.004 79 | −0.030 | 0.6655 | 1.041 09 | −0.078 |
| 0.2665 | 1.010 37 | −0.040 | 0.7507 | 1.047 21 | −0.080 |
| 0.3339 | 1.015 80 | −0.048 | 0.8596 | 1.054 65 | −0.068 |
| 0.3843 | 1.019 80 | −0.055 | 0.9161 | 1.058 31 | −0.052 |
| 0.4445 | 1.024 52 | −0.0620 | 0.9798 | 1.062 16 | −0.016 |
| 0.4676 | 1.026 29 | −0.064 | | | |
| Diethyl Carbonate (1) + Acetic Acid (2) | | | | | |
| 0.0192 | 1.040 31 | 0.028 | 0.3609 | 1.000 57 | 0.211 |
| 0.0466 | 1.035 69 | 0.063 | 0.3901 | 0.998 37 | 0.209 |
| 0.0883 | 1.029 32 | 0.108 | 0.4443 | 0.994 59 | 0.201 |
| 0.1149 | 1.025 62 | 0.131 | 0.4567 | 0.992 77 | 0.199 |
| 0.1673 | 1.019 03 | 0.167 | 0.5200 | 0.989 90 | 0.181 |
| 0.2089 | 1.014 38 | 0.186 | 0.6301 | 0.984 02 | 0.140 |
| 0.2553 | 1.009 67 | 0.201 | 0.7538 | 0.978 42 | 0.085 |
| 0.2911 | 1.006 36 | 0.207 | 0.8463 | 0.974 78 | 0.041 |
| 0.3238 | 1.003 55 | 0.211 | 0.9703 | 0.970 30 | 0.002 |
| Diethyl Carbonate (1) + Propionic Acid (2) | | | | | |
| 0.0215 | 0.987 35 | −0.003 | 0.4230 | 0.978 37 | −0.055 |
| 0.0496 | 0.986 58 | −0.006 | 0.4645 | 0.977 63 | −0.059 |
| 0.1039 | 0.985 21 | −0.017 | 0.5289 | 0.976 52 | −0.063 |
| 0.1543 | 0.983 98 | −0.024 | 0.5813 | 0.975 66 | −0.067 |
| 0.2080 | 0.982 74 | −0.031 | 0.6833 | 0.974 09 | −0.072 |
| 0.2615 | 0.981 57 | −0.038 | 0.8022 | 0.972 35 | −0.070 |
| 0.3112 | 0.980 54 | −0.044 | 0.8892 | 0.971 08 | −0.055 |
| 0.3521 | 0.979 72 | −0.048 | 0.9556 | 0.970 04 | −0.029 |
| 0.3737 | 0.979 31 | −0.051 | | | |

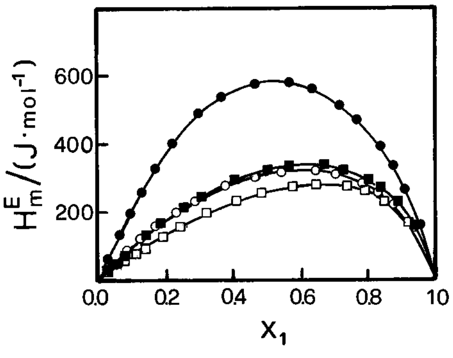

**Figure 1.** Excess molar enthalpies, $H_m^E$, of dialkyl carbonates + acetic or propionic acid. Symbols, experimental points: (■), DMC + acetic acid; (●), DMC + propionic acid; (□), DEC + acetic acid; (○) DEC + propionic acid mixtures. Solid lines, eq 2.

Table 4 shows the resulting $a_k$ together with the standard deviation $\sigma(Q_m^E)$ defined as

$$\sigma(Q_m^E) = |\Phi/(N - n)|^{0.5} \qquad (3)$$

with $N$ = number of experimental points and $n$ = number of adjustable parameters $a_k$.

Figures 1 and 2 show a singular behavior if $H_m^E$ and $V_m^E$ curves are compared. In fact, in passing from DMC to DEC, mixtures containing acetic acid present a small

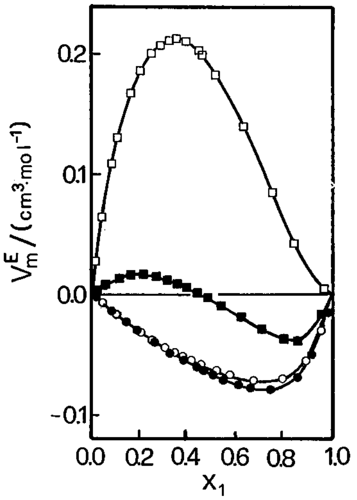

**Figure 2.** Excess molar volumes, $V_m^E$, of dialkyl carbonates + acetic or propionic acid. Symbols, experimental points: (■), DMC + acetic acid; (●), DMC + propionic acid; (□), DEC + acetic acid; (○), DEC + propionic acid. Solid lines, eq 2.

**Table 4. Adjustable Parameters, $a_k$, and Standard Deviation, $\sigma(Q_m^E)$, Eqs 2 and 3, of Dialkyl Carbonates + Acetic or Propionic Acid at 298.15 K**

| function | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $\sigma(Q_m^E)$ |
|---|---|---|---|---|---|
| | Dimethyl Carbonate (1) + Acetic Acid (2) | | | | |
| $H_m^E$/J·mol$^{-1}$ | 1259.4 | 426.9 | 602.7 | 618.1 | 2.9 |
| $V_m^E$/cm$^3$·mol$^{-1}$ | −0.0151 | −0.2139 | −0.1665 | −0.1558 | 0.0008 |
| | Dimethyl Carbonate (1) + Propionic Acid (2) | | | | |
| $H_m^E$/J·mol$^{-1}$ | 2314.8 | 194.8 | 583.1 | 654.2 | 3.9 |
| $V_m^E$/cm$^3$·mol$^{-1}$ | −0.2660 | −0.1811 | −0.2009 | −0.1829 | 0.0008 |
| | Diethyl Carbonate (1) + Acetic Acid (2) | | | | |
| $H_m^E$/J·mol$^{-1}$ | 994.1 | 457.7 | 575.0 | 506.2 | 1.8 |
| $V_m^E$/cm$^3$·mol$^{-1}$ | 0.7506 | −0.5636 | 0.0390 | −0.1780 | 0.0007 |
| | Diethyl Carbonate (1) + Propionic Acid (2) | | | | |
| $H_m^E$/J·mol$^{-1}$ | 1221.5 | 374.6 | 513.0 | 412.2 | 2.3 |
| $V_m^E$/cm$^2$·mol$^{-1}$ | −0.2438 | −0.1510 | −0.1983 | −0.1590 | 0.0006 |

decrease of $H_m^E$ with a corresponding large increase of $V_m^E$, whereas mixtures containing propionic acid have a large decrease of $H_m^E$ with a small increase of $V_m^E$.

Moreover, acetic acid + DMC mixture shows a sign inversion of $V_m^E$ at $x_1 \approx 0.45$, acetic acid + DEC mixture has positive $V_m^E$, and negative $V_m^E$ are observed for propionic acid + alkyl carbonates.

These results seems to indicate a very complex pattern for the interactions between molecules, where hydrogen bondings of acids are broken during mixing and new (less strong) hydrogen bondings are formed between OH groups of acids and C=O groups of esters. This, however, may explain the positive $H_m^E$'s found for all the four mixtures but makes it impossible to interpret the small differences among the curves of Figure 1.

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