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Excess molar enthalpies of binary mixtures containing dimethylcarbonate, diethylcarbonate or propylene carbonate + three chloroalkenes at 298.15 K

R. Francesconi[a,*], F. Comelli[b]

[a] *Dipartimento di Chimica "G. Ciamician", Università degli Studi, via Selmi 2, I-40126 Bologna, Italy*

[b] *Centro di Studio per la Fisica delle Macromolecole del CNR, via Selmi 2, I-40126 Bologna, Italy*

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Abstract

Excess molar enthalpies H_m^E of dimethylcarbonate, diethylcarbonate or propylene carbonate + *trans*-1,2-dichloroethylene, + trichloroethylene, and + tetrachloroethylene, respectively have been determined at 298.15 K using an LKB flow-microcalorimeter. Experimental data have been correlated by means of the Redlich–Kister equation and adjustable parameters have been evaluated by least-squares analysis. The H_m^E values range from a minimum value of -1000 J mol^{-1} for diethylcarbonate + *trans*-1,2-dichloroethylene up to a maximum of 920 J mol^{-1} for dimethylcarbonate + tetrachloroethylene. For each series of mixtures, a systematic increase in H_m^E with an increase in the number of Cl atoms in the chloroalkene molecule has been noted. The results are discussed in terms of the molecular interactions.

Keywords: Binary mixtures; Carbonic acid esters; Excess enthalpy

1. Introduction

Esters of carbonic acid such as dimethylcarbonate or diethylcarbonate are used in the synthesis of pharmaceuticals, agricultural chemicals, and as solvents for many synthetic and natural resins and polymers [1–4]. In recent years much interest has been shown in the electrochemical studies, battery systems and plating techniques of propylene carbonate [5, 6] and although these components have a wide range of

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* Corresponding author.

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technological applications, it appears that their thermodynamic properties have not been studied thoroughly. For these reasons we are engaged in a systematic study of the thermodynamic properties of mixtures containing dialkyl or propylene carbonates. This paper reports the excess molar enthalpies H_m^E of dimethylcarbonate, diethylcarbonate or propylene carbonate (component 1) + three chloroalkenes (component 2), namely *trans*-1,2-dichloroethylene, trichloroethylene or tetrachloroethylene, respectively. To our knowledge, no literature data exist on the properties of these mixtures.

2. Experimental

2.1. Materials

All chemicals were from Aldrich and had stated purities equal or exceeding 99 mol% with the exception of *trans*-1,2-dichloroethylene whose purity was 98 mol%. *trans*-1,2-dichloroethylene was further separated from the residual cis isomer contained in the commercial mixture by fractional distillation (Widmar 30-plate column) over 10% aqueous sodium hydroxide solution. In the case of the other compounds, owing to their high purity grade no further purification was made.

The purities of liquids were checked by comparing measured densities at 298.15 ± 0.005 K obtained by means of a digital density meter (Anton Paar model 60/602, Graz, Austria) [7] with those reported in the literature [8–13] and are listed in Table 1.

Before measurements, all chemicals were dried over molecular sieves (Union Carbide type 4A, 1/16-in. pellets) and stored in dark bottles.

2.2. Measurements

The H_m^E measurements were determined at 298.15 ± 0.01 K by means of an LKB flow microcalorimeter (model 2107, LKB Produkter, Bromma, Sweden) described elsewhere [14].

Table 1
Experimental densities ρ at 298.15 K and atmospheric pressure of pure liquids and comparison with literature data

Component	ρ/g cm^{-3}	
	This paper	Ref.
Dimethylcarbonate	1.06349	1.06350 [8]
Diethylcarbonate	0.96930	0.96926 [9]
Propylene carbonate	1.19915	1.19883 [10]
trans-1,2-Dichloroethylene	1.25032	1.2502 [11]
Trichloroethylene	1.45572	1.45544 [12] [a]
Tetrachloroethylene	1.61309	1.61432 [9]
		1.60682 [13]

[a] Interpolated from density equation.

Two identical automatic burets (ABU-Radiometer, Copenhagen, Denmark) were employed to pump liquids through the mixing cell of the calorimeter. Complete details of the operating procedure are reported in previous papers [14, 15].

The performance of the calorimeter was checked using the standard cyclohexane + hexane test mixture [16]. The precision of the H_m^E values is better than 0.5% over the central range of composition.

3. Results and discussion

The experimental values of H_m^E for the nine mixtures are listed in Table 2 as a function of composition and are represented graphically in Figs. 1–3.

The Redlich–Kister equation

$$H_m^E/x_1x_2 = \sum_{k\geq 0} a_k(x_1 - x_2)^k \qquad (1)$$

Table 2

Excess molar enthalpies H_m^E, adjustable parameters a_k (in J mol^{-1}), and standard deviations $\sigma(H_m^E)$ (in J mol^{-1}), at 298.15 K for the binary mixtures containing dimethylcarbonate, diethylcarbonate or propylene carbonate + chloroalkenes

x_1	H_m^E/J mol^{-1}	x_1	H_m^E/J mol^{-1}
Dimethylcarbonate(1) + *trans*-1,2-dichloroethylene(2)			
0.0367	−77.2	0.5787	−420.4
0.0709	−146.8	0.6467	−363.2
0.1027	−207.5	0.7331	−267.0
0.1323	−256.3	0.7855	−198.2
0.1862	−320.5	0.8460	−120.6
0.2330	−373.7	0.8798	−78.2
0.3140	−425.7	0.9166	−40.9
0.3790	−450.7	0.9565	−12.0
0.4779	−463.1		
$a_0 = -1829.5$; $a_1 = 586.3$; $a_2 = 624.7$; $a_3 = 618.9$; $\sigma(H_m^E) = 3.9$			
Dimethylcarbonate(1) + trichloroethylene(2)			
0.0425	−36.0	0.6152	5.8
0.0815	−63.1	0.6806	26.3
0.1175	−83.2	0.7617	45.8
0.1508	−96.6	0.8100	49.0
0.2102	−109.0	0.8648	40.4
0.2621	−106.0	0.8950	33.3
0.3476	−89.7	0.9275	23.3
0.4153	−69.3	0.9624	11.5
0.5159	−32.5		
$a_0 = -155.5$; $a_1 = 764.0$; $a_2 = 0$; $a_3 = 264.2$; $a_4 = -189.6$; $a_5 = -463.6$; $\sigma(H_m^E) = 1.2$			

Table 2 (*continued*)

x_1	$H_m^E/\mathrm{J\,mol^{-1}}$	x_1	$H_m^E/\mathrm{J\,mol^{-1}}$
Dimethylcarbonate(1) + tetrachloroethylene(2)			
0.0481	195.1	0.6456	817.7
0.0918	353.7	0.7082	721.1
0.1317	475.5	0.7845	564.0
0.1682	571.6	0.8292	462.1
0.2328	714.4	0.8797	326.7
0.2880	792.2	0.9066	245.0
0.3777	880.2	0.9358	159.2
0.4472	911.3	0.9668	79.3
0.5483	891.6		
$a_0 = 3635.3$; $a_1 = -321.7$; $a_2 = 447.7$; $a_3 = -744.8$; $a_4 = -856.4$; $\sigma(H_m^E) = 3.4$			
Diethylcarbonate(1) + *trans*-1, 2-dichloroethylene(2)			
0.0258	−105.9	0.4884	−972.0
0.0503	−210.9	0.5599	−915.9
0.0737	−296.9	0.6562	−752.7
0.0958	−385.7	0.7179	−571.0
0.1372	−535.3	0.7924	−322.3
0.1749	−646.0	0.8358	−192.5
0.2413	−822.0	0.8842	−114.6
0.2978	−911.6	0.9385	−70.9
0.3888	−964.7		
$a_0 = -3833.9$; $a_1 = 872.6$; $a_2 = 0$; $a_3 = 6071.6$; $a_4 = 7559.0$; $a_5 = -6398.2$; $a_6 = -7534.8$; $\sigma(H_m^E) = 5.5$			
Diethylcarbonate(1) + trichloroethylene(2)			
0.0299	−102.5	0.5264	−604.4
0.0581	−186.6	0.5970	−538.6
0.0847	−270.9	0.6896	−413.2
0.1098	−337.9	0.7476	−327.9
0.1562	−443.5	0.8163	−218.6
0.1980	−520.4	0.8556	−161.3
0.2702	−611.0	0.8989	−96.2
0.3305	−654.2	0.9467	−48.8
0.4255	−667.6		
$a_0 = -2521.2$; $a_1 = 1442.4$; $a_2 = 358.5$; $\sigma(H_m^E) = 3.6$			
Diethylcarbonate(1) + tetrachloroethylene(2)			
0.0330	82.6	0.5587	421.2
0.0657	143.4	0.6278	386.2
0.0954	197.1	0.7168	318.5
0.1232	246.3	0.7714	264.6
0.1741	315.2	0.8350	185.5
0.2194	365.7	0.8709	147.5
0.2966	420.1	0.9101	94.5
0.3599	443.8	0.9529	46.3
0.4576	457.5		
$a_0 = 1782.1$; $a_1 = -472.3$; $a_2 = 119.8$; $a_3 = -352.0$; $a_4 = -231.5$; $\sigma(H_m^E) = 3.2$			

Table 2 (*Continued*)

x_1	H_m^E/J mol^{-1}	x_1	H_m^E/J mol^{-1}
Propylene carbonate(1) + *trans*-1,2-dichloroethylene(2)			
0.0277	84.9	0.4766	80.9
0.0366	105.2	0.5775	38.0
0.0705	159.1	0.6456	13.0
0.1022	184.1	0.7321	−3.9
0.1318	193.8	0.7846	−11.3
0.1854	190.8	0.8453	−12.6
0.2329	177.7	0.8793	−12.7
0.3129	151.9	0.9162	−8.8
0.3778	125.3	0.9563	−6.2
$a_0 = 284.1$; $a_1 = -884.4$; $a_2 = 356.3$; $a_3 = -92.3$; $a_4 = 1097.7$; $a_5 = -982.3$; $\sigma(H_m^E) = 1.3$			
Propylene carbonate(1) + trichloroethylene(2)			
0.0423	140.2	0.6140	346.0
0.0812	230.9	0.6795	305.2
0.1170	286.6	0.7608	243.5
0.1501	323.3	0.8092	196.2
0.2095	361.7	0.8642	134.1
0.2611	372.3	0.8945	96.4
0.3464	383.8	0.9271	57.1
0.4141	383.7	0.9622	27.3
0.5146	372.4		
$a_0 = 1495.0$; $a_1 = -287.0$; $a_2 = 727.5$; $a_3 = -1412.1$; $\sigma(H_m^E) = 2.3$			
Propylene carbonate(1) + tetrachloroethylene(2)			
0.0479	94.8	0.6444	639.9
0.0914	146.3	0.7072	672.5
0.1311	191.5	0.7837	648.4
0.1675	226.9	0.8285	576.9
0.2319	300.1	0.8787	439.3
0.2870	350.8	0.9062	340.6
0.3675	432.6	0.9355	223.7
0.4460	490.3	0.9664	100.3
0.5470	575.7		
$a_0 = 2124.5$; $a_1 = 1487.9$; $a_2 = 2634.1$; $a_3 = 2797.2$; $a_4 = -2272.2$; $a_5 = -4542.3$; $\sigma(H_m^E) = 4.3$			

was fitted to each set of data by the method of least-squares. The a_k values are given in Table 2 together with the standard deviation $\sigma(H_m^E)$ defined as

$$\sigma(H_m^E) = |\phi_{\min}/(N - n)|^{0.5} \tag{2}$$

where $\phi_{\min}$ is the minimum value of the objective function ϕ defined as

$$\phi = \sum_{k=1}^{N} \eta_k^2 \tag{3}$$

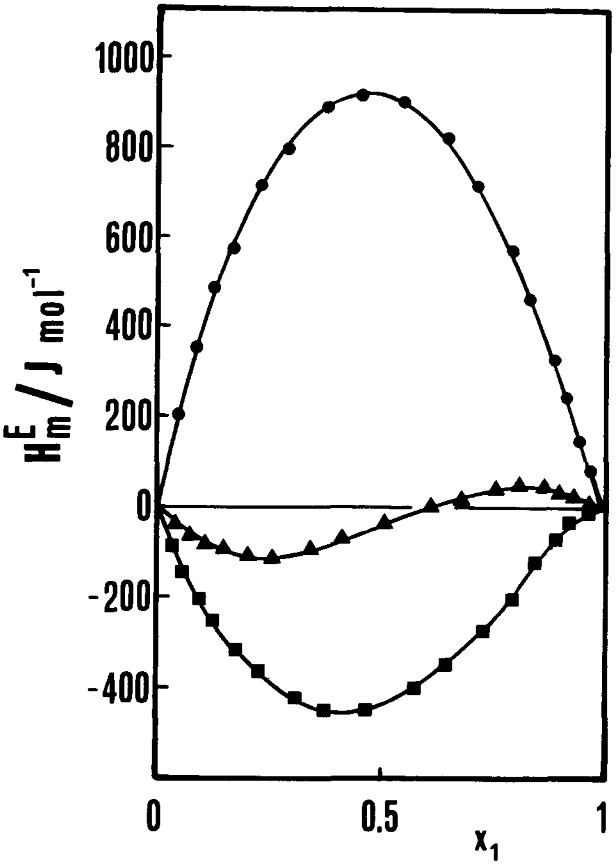

Fig. 1. Excess molar enthalpies H^E_m at 298.15 K for dimethylcarbonate + *trans*-1,2-dichloroethylene (■), + trichloroethylene (▲), and + tetrachloroethylene (●). Solid curves are the least-squares representation of results by Eq. (1).

where $\eta_k = H^E_{m,calc} - H^E_m$; H^E_m is the experimental value and $H^E_{m,calc}$ is evaluated through Eq. (1).

Curves calculated from Eq. (1) are included in Figs. 1–3.

Fig. 4 shows H^E_m ($x_1 = 0.5$), the equimolar excess enthalpy, plotted against n_{Cl}, the number of chlorine atoms in the chloroalkenes molecule. The cyclic molecule of propylene carbonate leads to more asymmetric H^E_m vs. x_1 curves, with partial overlapping for ester-poor mixtures.

Sign inversion of H^E_m as a function of composition is shown for the mixtures dimethyl carbonate + trichloroethylene and propylene carbonate + *trans*-1,2-dichloroethylene.

Chloroalkenes display the same trend in mixtures with all three esters of carbonic acid, i.e. increased values of H^E_m with increasing Cl atoms and this effect may be explained qualitatively by considering that H^E_m is nearly proportional to $E_{11} + E_{22} - 2E_{12}$, E_{ij} representing the interaction energy between i and j molecules. In fact, the hydrogen bonding between H atoms of chloroalkenes and the C=O groups of esters

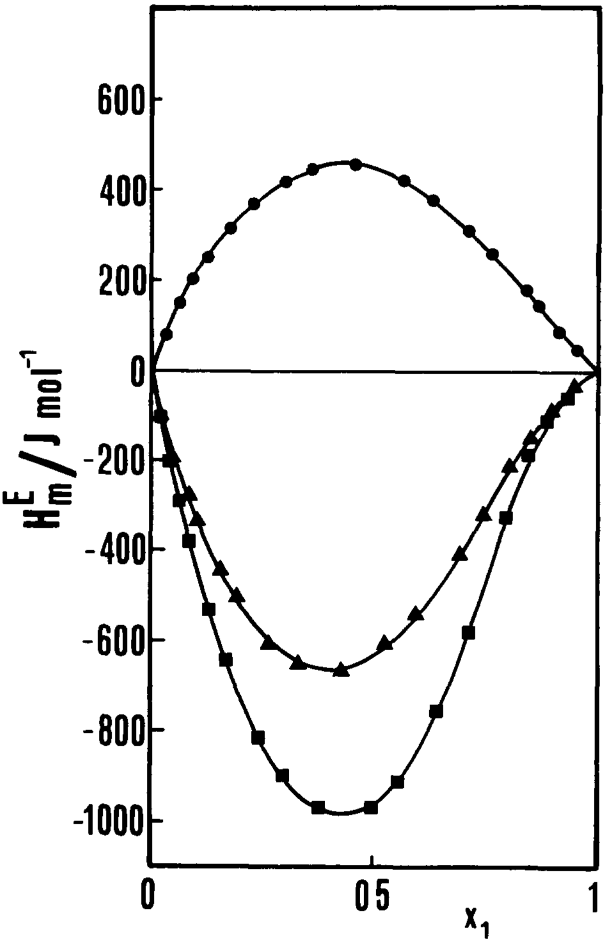

Fig. 2. Excess molar enthalpies H_m^E at 298.15 K for diethylcarbonate + *trans*-1,2-dichloroethylene (■), + trichloroethylene (▲), and + tetrachloroethylene (●). Solid curves are the least-squares representation of results by Eq. (1).

will represent the main contribution to E_{12} and this effect will decrease in passing from dichloro- to trichloroalkenes (fewer H atoms are available) and vanish for the tetrachloroalkenes.

As to the influence of the carbonate substituting groups on the same chloroalkene, we note that a CH_3 group leads to increased values of H_m^E with respect to a C_2H_5 group, whereas the behavior of the cyclic carbonate is not comparable with that of the other carbonates.

In passing from dimethyl to diethylcarbonates, most probably both the interaction energies E_{11} and E_{12} are changed and it is hazardous to make qualitative predictions on H_m^E since the distinct amounts of the two effects are not known.

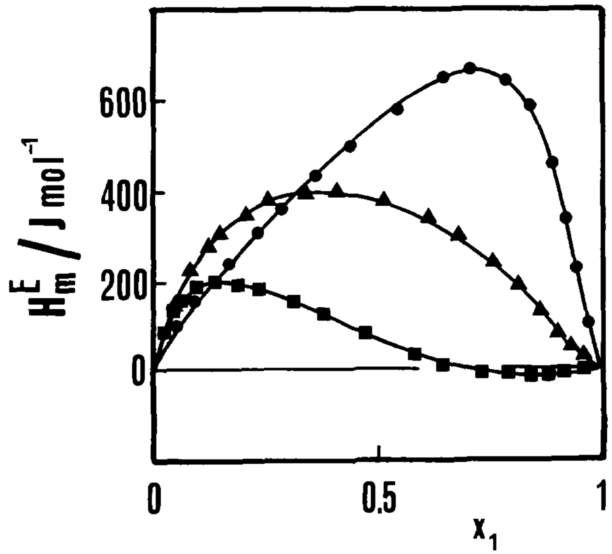

Fig. 3. Excess molar enthalpies H_m^E at 298.15 K for propylene carbonate + *trans*-1,2-dichloroethylene (■), + trichloroethylene (▲), and + tetrachloroethylene (●). Solid curves are the least-squares representation of results by Eq. (1).

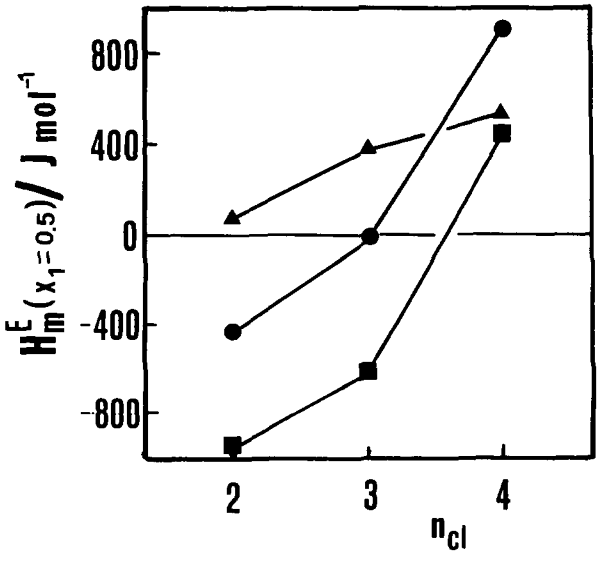

Fig. 4. Values of equimolar enthalpy H_m^E (x_1 = 0.5) at 298.15 K as a function of the number of Cl atoms n_{Cl} in the chloroalkene molecule for the binary mixtures with carbonates: ●, ■, ▲ refer to dimethylcarbonate, diethylcarbonate and propylene carbonate + chloroalkenes, respectively.

Our attempt to interpret the experimental data by means of thermodynamic theories, such as the extended cell model of Prigogine [17], led to unsatisfactory results, due not to the high values of H_m^E but rather to the marked skewness of the H_m^E vs. x_1 curves.

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