J. Chem. Eng. Data 1995, 40, 28−30

Excess Molar Enthalpies of Dimethyl Carbonate or Diethyl Carbonate + Cyclic Ethers at 298.15 K

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Excess molar enthalpies, H_m^E, of dimethyl carbonate or diethyl carbonate + oxane, oxolane, 1,4-dioxane, and 1,3-dioxolane are measured at 298.15 K in a flow microcalorimeter. Smooth representations of the results are presented. For all mixtures, the H_m^E values are positive with a maximum ranging from 25 to 550 J mol^{-1}.

Introduction

In the literature, esters of carbonic acid are indicated as good solvents for the separation of sour gases, for the synthesis of pharmaceuticals and agricultured chemicals, as solvents for many synthetic and natural resins and polymers, for nitrocellulose-manufactured radio tubes, and for fixing rare earths to cathode elements and gelling agents (*1−4*).

In spite of these evident applications there are no extensive studies on systems containing this class of substances, particularly on cyclic derivatives.

In particular, to our knowledge, no data exist on the calorimetric properties of binary mixtures of dialkyl carbonates + cyclic ethers. In this paper we report the excess molar enthalpies, H_m^E, of dimethyl carbonate (1) or diethyl carbonate (1) + oxane (2), + oxolane (2), +1,4-dioxane (2), and + 1,3-dioxolane (2) at 298.15 K and atmospheric pressure. In a previous work (*5*), we determined the excess molar volumes, V_m^E, of dimethyl carbonate + the same cyclic ethers considered in this paper, and the aim of this work is to obtain, by means of the calorimetric measurements, a better understanding of the thermodynamic properties of these systems.

Experimental Section

Dimethyl carbonate, diethyl carbonate, oxolane, 1,4-dioxane, 1,3-dioxolane, purity 99+, 99, 99.9+, 99.9, and 99 mass %, respectively, were from Aldrich, while oxane, purity 99+ mass %, was a Fluka product.

All products, owing to their high-grade purity, were used without further purification, and before measurements, all liquids were dried with molecular sieves (Union Carbide Type 4A, 1/16-in. pellets) and stored in dark bottles.

The purities of the solvents were ascertained by comparing their densities ϱ with the literature data (*6−8*); see Table 1.

Densities were determined by using a DMA 60/602 digital density meter (Anton Paar, Graz, Austria) with a resolution of 1 × 10^{-6} g cm^{-3}, thermostated by a Heto constant temperature bath circulator with a temperature control interval of ±0.005 K.

Details on the apparatus and its operating procedure are available elsewere (*9*).

Table 1. Densities, ϱ, of Pure Components and Comparison with Literature Data at 298.15 K

component	ϱ/(g cm^{-3}) this work	ϱ/(g cm^{-3}) lit.
dimethyl carbonate	1.063 49	1.063 5 (*6*)
diethyl carbonate	0.969 30	0.969 26 (*7*)
oxane	0.877 24	0.877 2 (*7*)
oxolane	0.882 70	0.882 69 (*8*)
1,4-dioxane	1.027 39	1.027 97 (*7*)
1,3-dioxolane	1.058 99	1.058 65 (*8*)

The H_m^E measurements were made at 298.15 ± 0.01 K with an LKB flow microcalorimeter, model 2107, LKB Produkter AB (Bromma, Sweden), described elsewere (*10*).

The microcalorimeter was electrically calibrated before use (*11*) and the calibration subsequently checked by using the standard cyclohexane + hexane test mixture (*12*). The precision of the H_m^E values is better than 0.5% over the central range of composition.

The experimental values of H_m^E for the eight mixtures are listed in Tables 1 and 2, where in all cases x_1 is the mole fraction of dimethyl carbonate or diethyl carbonate. Plots of the results are represented in Figures 1 and 2.

The Redlich−Kister equation

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

was fitted to each set of results by the method of least squares with all points weighted equally. The a_k's are given in Table 3 together with the standard deviation $\sigma(H_m^E)$ defined as

$$\sigma(H_m^E) = |\Phi/(N - n)|^{0.5} \qquad (2)$$

where N is the number of the experimental points and n the number of adjustable parameters a_k. ϕ is the objective function defined as

$$\Phi = \sum_{k=0}^{N} \eta^2 \qquad (3)$$

where $\eta_k = H_{m,calcd}^E - H_m^E$; H_m^E is the experimental value,

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0021-9568/95/1740-0028$09.00/0

Table 2. Experimental Molar Enthalpies H_m^E, at 298.15 K for Dimethyl Carbonate or Diethyl Carbonate + Cyclic Ethers

x_1	H_m^E/ (J mol^{-1})	x_1	H_m^E/ (J mol^{-1})	x_1	H_m^E/ (J mol^{-1})
Dimethyl Carbonate (1) + Oxane (2)					
0.0461	70.1	0.3669	516.0	0.8226	283.3
0.0881	144.1	0.4359	547.0	0.8743	190.6
0.1266	217.9	0.5369	552.1	0.9027	136.0
0.1619	276.5	0.6349	513.2	0.9330	85.9
0.2247	375.9	0.6987	458.5	0.9653	38.1
0.2787	441.9	0.7767	358.2		
Dimethyl Carbonate (1) + Oxolane (2)					
0.0386	29.7	0.3251	270.6	0.7940	168.6
0.0743	62.3	0.3911	298.5	0.8525	107.6
0.1075	95.4	0.4907	309.8	0.8852	73.8
0.1383	128.6	0.5910	294.0	0.9204	41.0
0.1941	184.9	0.6583	268.3	0.9586	13.8
0.2431	221.8	0.7430	211.8		
Dimethyl Carbonate (1) + 1,4-Dioxane (2)					
0.0405	23.5	0.3361	146.9	0.8020	99.7
0.0778	44.3	0.4030	156.7	0.8587	73.8
0.1123	64.5	0.5031	166.3	0.8901	59.6
0.1444	80.8	0.6158	156.4	0.9240	39.8
0.2020	105.5	0.6694	141.5	0.9605	20.9
0.2523	123.8	0.7523	119.5		
Dimethyl Carbonate (1) + 1,3-Dioxolane (2)					
0.0333	1.6	0.2922	17.9	0.7676	20.6
0.0644	3.3	0.3551	20.9	0.8321	15.9
0.0936	5.4	0.4523	24.6	0.8686	12.5
0.1210	6.8	0.5474	26.2	0.9084	9.4
0.1711	9.8	0.6229	25.6	0.9520	5.3
0.2159	12.9	0.7125	23.2		
Diethyl Carbonate (1) + Oxane (2)					
0.0325	29.0	0.2872	210.5	0.7632	125.5
0.0629	54.6	0.3494	223.3	0.8286	84.8
0.0915	83.0	0.4462	231.5	0.8657	59.6
0.1184	110.0	0.5473	214.7	0.9063	37.1
0.1676	144.9	0.6171	191.1	0.9508	15.4
0.2117	172.7	0.7074	154.3		
Diethyl Carbonate (1) + Oxolane (2)					
0.0271	8.5	0.2508	89.1	0.7281	53.4
0.0528	17.5	0.3086	99.7	0.8007	32.5
0.0772	29.6	0.4010	105.7	0.8427	21.3
0.1004	40.0	0.5011	98.3	0.8894	9.2
0.1434	57.8	0.5725	91.8	0.9414	0.5
0.1824	70.4	0.6677	70.1		
Diethyl Carbonate (1) + 1,4-Dioxane (2)					
0.0285	32.9	0.2603	235.7	0.7379	198.9
0.0554	63.1	0.3193	259.9	0.8085	153.6
0.0808	93.0	0.4130	280.8	0.8492	125.1
0.1049	116.7	0.5270	282.9	0.8942	88.9
0.1496	157.5	0.5846	266.8	0.9441	50.0
0.1900	190.6	0.6786	233.5		
Diethyl Carbonate (1) + 1,3-Dioxolane (2)					
0.0234	15.4	0.2230	128.9	0.6966	128.5
0.0456	32.6	0.2767	148.0	0.7750	102.4
0.0669	45.3	0.3647	168.1	0.8212	83.0
0.0873	60.6	0.4567	173.3	0.8733	58.3
0.1255	82.6	0.5344	169.2	0.9323	31.4
0.1606	102.1	0.6326	148.5		

and $H_{m,calcd}^E$ is evaluated through eq 1. Curves calculated from eq 1 are included in Figures 1 and 2.

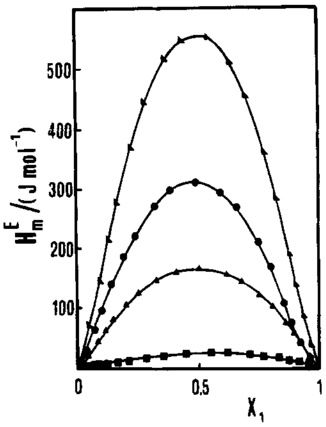

Figure 1. Excess molar enthalpies, H_m^E, of dimethyl carbonate + four cyclic ethers plotted against the mole fraction x_1 of dimethyl carbonate. Experimental results: (right triangle) oxane, (circle) oxolane, (equilateral triangle) 1,4-dioxane, (square) 1,3-dioxolane, (solid line) curves calculated from eq 1 using the parameters of Table 3.

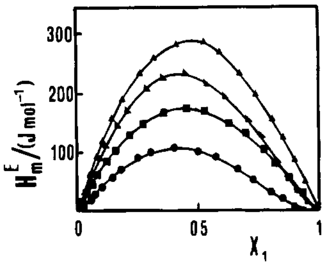

Figure 2. Excess molar enthalpies, H_m^E, of diethyl carbonate + four cyclic ethers plotted against the mole fraction x_1 of diethyl carbonate. Experimental results: (right triangle) oxane, (circle) oxolane, (equilateral triangle) 1,4-dioxane, (square) 1,3-dioxolane, (solid line) curves calculated from eq 1 using the parameters of Table 3.

Table 3. Parameters a_k and Standard Deviations $\sigma(H_m^E)$ for the Representation of H_m^E at 298.15 K for Dimethyl Carbonate or Diethyl Carbonate + Cyclic Ether Mixtures by Eq 1

mixture	a_0	a_1	a_2	a_3	a_4	$\sigma(H_m^E)$/ (J mol^{-1})
dimethyl carbonate						
+ oxane	2222.6	−258.2	0	0	−1211.6	1.1
+ oxolane	1238.7	−56.7	−128.5	−227.0	−794.8	1.4
+ 1,4-dioxane	663.8	−23.8	−79.3			1.5
+ 1,3-dioxolane	103.0	32.6	−24.4			1.6
diethyl carbonate						
+ oxane	894.7	−341.4	0	0	−399.9	1.7
+ oxolane	398.7	−220.2	−60.0	0	−262.4	1.2
+ 1,4-dioxane	1339.2	−183.5	−71.9			1.7
+ 1,3-dioxolane	690.2	−145.1	−95.7			1.2

Discussion

Some interesting conclusions may be drawn from the graphs of Figures 1 and 2. Both dimethyl and diethyl carbonate in mixtures with mono- and dicyclic ethers show positive H_m^E with nearly symmetric curves. An increase in the number of ring atoms in both mono- and diethers leads to increased values of H_m^E for both alkyl carbonates, with a more marked difference for dimethyl carbonate mixtures. Instead, the alkyl carbonates display an opposite behavior in going from mono- to diethers, and again dimethyl carbonate shows a (negative) variation larger than the (positive) one of diethyl carbonate.

A qualitative interpretation of the above results was tried in terms of interaction energies between C=O groups of ester and H atoms of ether, but no useful correlation was obtained. Also dipole moments and the acid character of esters (pK_a) failed in the attempt to explain the observed trends.

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Received for review June 21, 1994. Revised September 20, 1994. Accepted September 28, 1994.[⊗]

JE940113W

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1994.