J. Chem. Eng. Data 1995, 40, 31−33

Excess Molar Enthalpies and Excess Molar Volumes of Propylene Carbonate + Cyclic Ethers

Romolo Francesconi*

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

Fabio Comelli

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

Excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, have been determined as a function of mole fraction for propylene carbonate + oxane, oxolane, 1,4-dioxane, and 1,3-dioxolane at 298.15 K and at atmospheric pressure in a flow microcalorimeter and in a digital density meter. The experimental values have been correlated using the Redlich−Kister equation, and the parameters have been evaluated by least-squares analysis. The H_m^E values are positive for the propylene carbonate + oxane and oxolane mixtures and negative in the mixture with 1,3-dioxolane, while an inversion of sign has been noted for the propylene carbonate + 1,4-dioxane mixture. The H_m^E values range from a minimum of −170 J mol^{-1} to a maximum of 480 J mol^{-1}. The V_m^E values are all negative with a minimum varying from −0.21 up to −0.34 cm^3 mol^{-1} in the order dioxane < oxane < dioxolane < oxolane.

Introduction

We are engaged in a systematic study on the thermodynamic properties of esters of carbonic acids, which are indicated in the literature to have good properties as solvents in a variety of extractions of industrial interest and in pharmaceutical (*1, 2*) and electrochemical studies (*3, 4*).

In the present paper, the excess molar enthalpies, H_m^E, and the excess molar volumes, V_m^E, have been determined for propylene carbonate (component 1) + four cyclic ethers (component 2), namely, oxane, oxoloane, 1,4-dioxane, or 1,3-dioxolane, at 298.15 K and atmospheric pressure.

To our knownledge, no calorimetric or volumetric data have been reported in the literature.

In previous works (*5, 6*) we have determined the excess molar enthalpies and the excess molar volumes of dimethyl carbonate and diethyl carbonate + the same cyclic ethers here considered, and the purpose of our investigations is to have a more comprehensive thermodynamic understanding along these lines.

Experimental Section

Materials. All solvents were products from Aldrich and had stated purities equal to or exceeding 99 mol %: owing to their high purity grade, no further purification has been made. 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 compounds were checked by measuring their densities at 298.15 ± 0.01 K. Comparison with corresponding literature values (*7−10*) is reported in Table 1.

Table 1. Purity Grades and Densities, ϱ, of Pure Components and Comparison with Literature Data at 198.15 K

component	purity/%	ϱ/(g cm^{-3}) present work	ϱ/(g cm^{-3}) lit.
propylene carbonate	+99	1.199 15	1.198 83 (*2*)
oxane	99	0.879 06	0.879 10 (*7*)
oxolane	99.9	0.881 73	0.882 00 (*8*)
1,4-dioxane	99.9	1.027 98	1.027 97 (*9*)
1,3-dioxolane	+99.5	1.058 77	1.058 65 (*10*)

Measurements. Excess molar enthalpies, H_m^E, were determined using an LKB isothermal flow microcalorimeter (model 2107, LKB Produkter AB, Bromma, Sweden) as described in ref 11, while details of electrical calibration and analytical measurements are given in a previous paper (*12*). The performance of the calorimeter was checked by using the standard cyclohexane + hexane test mixture (*13*) over the whole composition range (about 0.5% is the agreement with the literature in the central range of composition). The uncertainty in H_m^E was estimated to be on the order of 0.5−1 J mol^{-1}.

Densities, ϱ, were measured to a precision of ±0.000 01 g cm^{-3} in an Anton Paar DMA 60 (Anton Paar, Graz, Austria) digital vibrating tube density meter with a DMA 602 measuring cell. Mixtures were prepared on a mass basis using a Mettler AE 160 analytical balance with a precision of ±0.0001 g. The nominal mass of the mixtures prepared was 8 g.

The operating procedure for determining mixtures by mass and densities is the same as described in ref 14. Temperature was kept at 298.15 ± 0.005 K by means of a Heto Therm ultrathermostat (Model 01 DTB 623).

Degassed, twice distilled water and dry air (*15*) were prepared daily as the calibrating and reference fluids.

Before measurements, the apparatus was checked with a benzene + cyclohexane mixture, the density of which is accurately known from the literature (*16*): our value for V_m^E at 0.5 mole fraction is 0.652 cm^3 mol^{-1} (lit. value, 0.6514). All measurements were corrected for buoyancy and for evaporation of components. The estimated uncertainty in V_m^E was determined from variance analysis (*17*) and shows a maximum value of 3.0 × 10^{-3} cm^3 mol^{-1} for all mixtures.

Results and Discussion

The experimental values of H_m^E and V_m^E are listed in Tables 2 and 3 as a function of the mole fraction of

---

* To whom correspondence should be addressed.

0021-9568/95/1740-0031$09.00/0

Table 2. Excess Molar Enthalpies, H_m^E, for Propylene Carbonate + Cyclic Ethers at 298.15 K

x_1	H_m^E/(J mol^{-1})	x_1	H_m^E/(J mol^{-1})
Propylene Carbonate (1) + Oxane (2)			
0.0458	87.2	0.6332	452.7
0.0875	163.0	0.6971	409.9
0.1258	223.1	0.7754	335.7
0.1609	272.0	0.8215	268.1
0.2234	349.6	0.8735	193.7
0.2773	404.1	0.9020	141.6
0.3653	455.0	0.9325	90.0
0.4341	480.2	0.9651	40.9
0.5351	480.0		
Propylene Carbonate (1) + Oxolane (2)			
0.0385	17.5	0.5904	205.9
0.0741	36.3	0.6577	192.7
0.1072	58.1	0.7424	156.1
0.1380	80.0	0.7935	127.3
0.1937	111.2	0.8522	85.3
0.2426	138.5	0.8849	60.7
0.3245	175.9	0.9202	33.9
0.3904	194.9	0.9584	11.5
0.4900	210.5		
Propylene Carbonate (1) + 1,4-Dioxane (2)			
0.0272	41.5	0.5018	−49.1
0.0403	54.1	0.6146	−68.9
0.0774	74.3	0.6683	−72.4
0.1118	76.0	0.7514	−68.8
0.1437	70.0	0.8012	−60.9
0.2012	49.7	0.8590	−47.9
0.2514	31.0	0.8896	−39.9
0.3350	−1.0	0.9236	−29.9
0.4018	−22.5	0.9606	−16.1
Propylene Carbonate (1) + 1,3-Dioxolane (2)			
0.0331	−24.3	0.5521	−162.3
0.0641	−45.0	0.6216	−154.5
0.0931	−63.0	0.7114	−131.5
0.1204	−79.2	0.7667	−111.2
0.1704	−103.9	0.8314	−88.2
0.2145	−122.5	0.8679	−70.0
0.2911	−144.8	0.9079	−48.4
0.3538	−158.4	0.9517	−25.6
0.4510	−167.8		

Table 3. Excess Molar Volumes, V_m^E, for Propylene Carbonate + Cyclic Ethers at 298.15 K

x_1	V_m^E/(cm^3 mol^{-1})	x_1	V_m^E/(cm^3 mol^{-1})
Propylene Carbonate (1) + Oxane (2)			
0.0191	−0.034	0.5756	−0.241
0.0834	−0.124	0.6066	−0.235
0.1888	−0.209	0.6681	−0.210
0.3337	−0.254	0.7288	−0.183
0.3992	−0.261	0.7993	−0.144
0.4553	−0.258	0.8839	−0.086
0.4954	−0.256	0.9431	−0.043
0.5459	−0.248	0.9868	−0.008
Propylene Carbonate (1) + Oxolane (2)			
0.0123	−0.028	0.5218	−0.314
0.0717	−0.139	0.5713	−0.297
0.1303	−0.217	0.6256	−0.271
0.2296	−0.295	0.6897	−0.237
0.3172	−0.330	0.7705	−0.182
0.4007	−0.336	0.8692	−0.107
0.4589	−0.329	0.9233	−0.062
0.4979	−0.323	0.9881	−0.007
Propylene Carbonate (1) + 1,4-Dioxane (1)			
0.0191	−0.020	0.5449	−0.202
0.0838	−0.079	0.5827	−0.194
0.1531	−0.129	0.6376	−0.181
0.2481	−0.175	0.7126	−0.154
0.3069	−0.194	0.7742	−0.127
0.3590	−0.204	0.8703	−0.077
0.4210	−0.207	0.9371	−0.038
0.4610	−0.211	0.9847	−0.008
0.498	−0.207		
Propylene Carbonate (1) + 1,3-Dioxolane (2)			
0.0158	−0.027	0.4902	−0.270
0.0593	−0.094	0.5342	−0.260
0.1220	−0.168	0.5903	−0.243
0.2075	−0.2316	0.6454	−0.220
0.2706	−0.260	0.7500	−0.167
0.3130	−0.272	0.8475	−0.106
0.3713	−0.280	0.9271	−0.052
0.4092	−0.280	0.9867	−0.009
0.4534	−0.278		

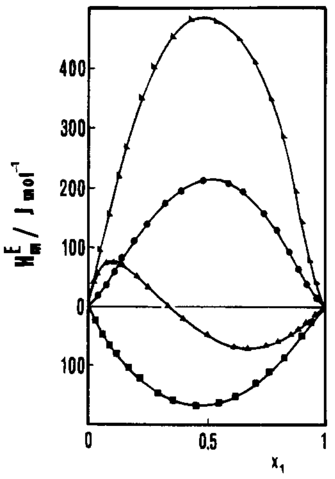

Figure 1. Excess molar enthalpies, H_m^E, at 298.15 K plotted against the mole fraction x_1 of propylene carbonate. Experimental values: (right triangle) oxane; (circle) oxolane; (equilateral triangle) 1,4-dioxane; (square) 1,3-dioxolane, (solid line) curves calculated from eq 1 using the parameters of Table 4.

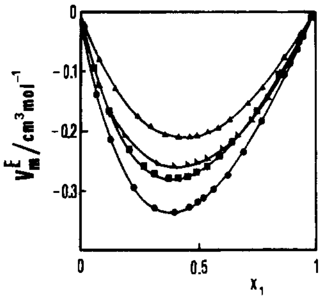

Figure 2. Excess molar volumes, V_m^E, at 298.15 K plotted against the mole fraction x_1 of propylene carbonate. Experimental results: (right triangle) oxane; (circle) oxolane; (equilateral triangle) 1,4-dioxane; (square) 1,3-dioxolane, (solid line) curves calculated from eq 1 using the parameters of Table 5.

propylene carbonate. Plots of the results are represented in Figures 1 and 2.

The Redlich–Kister equation

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

where $Q_m^E = H_m^E$/(J mol^{-1}) or V_m^E/(cm^3 mol^{-1}) was fitted to the results by a least-squares method, with all points weighted equally. The adjustable parameters a_k and standard deviations $\sigma(Q_m^E)$ are given in Tables 4 and 5. Curves calculated from eq 1 are included in Figures 1 and 2.

The main features of cyclic ethers with propylene carbonate can be inferred from the graphs of Figures 1 and 2. The excess enthalpy H_m^E increases when both the number of oxygen atoms and the ring size of the ethers are decreased. Furthermore, 1,4-dioxane shows a sign inversion of H_m^E at a mole fraction of propylene carbonate of about 0.35. The same sign inversion is shown by 1,4-dioxane + water (*18*) and, to a smaller extent, by 1,3-dioxolane + water (*19, 20*) and, in aqueous mixtures, has

Table 4. Adjustable Parameters, a_k, and Standard Deviations, σ, for the Representation of H_m^E at 298.15 K for Propylene Carbonate + Cyclic Ether Mixtures by Eq 1

	propylene carbonate +			
a_k, σ	oxane	oxolane	1,4-dioxane	1,3-dioxolane
a_0	1934.1	841.5	−194.8	−671.3
a_1	28.7	113.9	−468.1	91.8
a_2	384.7	−61.6	193.4	
a_3	−454.7	−239.2	−105.1	
a_4	−887.3	−569.8	719.9	
a_5			−613.5	
σ	3.2	1.3	0.5	1.3

Table 5. Adjustable Parameters, a_k, and Standard Deviations, σ, for the Representation of V_m^E at 298.15 K for Propylene Carbonate + Cyclic Ether Mixtures by Eq 1

	propylene carbonate +			
a_k, σ	oxane	oxolane	1,4-dioxane	1,3-dioxolane
a_0	−1.019	−1.283	−0.829	−1.074
a_1	0.254	0.524	0.183	0.426
a_2	−0.279	−0.252	−0.030	−0.180
a_3	0.331	0.249	0.073	0.128
$10^3\sigma$	1.1	1.2	1.0	0.5

been ascribed to partial hydrogen bond formation between dissimilar molecules. Really, the molecular structure of propylene carbonate, with an electronegative C=O group, may give rise to interactions with positively charged H atoms of ethers in agreement with the sign inversion for H_m^E. Instead, the curve H_m^E vs x_1 for propylene carbonate + 1,3-dioxolane has no sign inversion and is everywhere negative.

The smaller interactions between monocyclic ethers and propylene carbonate explain the positive H_m^E values. Also the negative V_m^E values are in agreement with the interaction pattern given above, since $V_m^E < 0$ may be associated with the prevailing interactions between ethers and carbonate.

Propylene carbonate, a five-atom ring molecule, displays a behavior quite different from that of the noncyclic molecules of dimethyl or diethyl carbonate, whose excess properties have been measured in previous papers (*5*, *6*). In fact, both the H_m^E and V_m^E values are always positive for the noncyclic carbonates, which may suggest a smaller interaction energy with ethers, probably because the ring molecule is responsible for an enhancement in the electrostatic induction of the C=O group on side H atoms.

The larger interactions of propylene carbonate are confirmed by its very low vapor pressure at 298.15 K (0.015 kPa) (*1*) when compared with those of dimethyl or diethyl carbonate (7.19 and 1.43 kPa, respectively) (*1*, *9*, *21*).

Literature Cited

(1) Annesini, M. C.; De Sanctis, R.; Kikic, I.; Manelli, L. *J. Chem. Eng. Data* **1984**, *29*, 39.
(2) Muhuri, P. K.; Hazra, D. K. *J. Chem. Eng. Data* **1994**, *39*, 375.
(3) *Martindale, the Extra Pharmacopea*, 29th ed.; Parfitt, K., Ed.; The Pharmaceutical Press: London, 1989.
(4) Al-Najor, A. A.; Alami, K. M. H.; Ebrahem, A. M. *J. Chem. Eng. Data* **1992**, *37*, 443.
(5) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1994**, *39*, 106.
(6) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **1995**, *40*, 28.
(7) Inglese, A.; Grolier, J-P. E.; Wilhelm, E. *J. Chem. Eng. Data* **1983**, *28*, 124.
(8) Fenclova, D.; Donhal, V. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1992**, *4*, 224.
(9) Riddik, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986; Vol. 2.
(10) Inglese, A. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1986**, 178.
(11) Monk, P.; Wadso, I. *Acta Chem. Scand.* **1968**, *22*, 1842.
(12) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1986**, *31*, 250.
(13) Benson, G. C. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1974**, 19.
(14) Fermeglia, M; Lapasin, J. *J. Chem. Eng. Data* **1988**, *33*, 415.
(15) Weast, R. C. *Handbook of Chemistry and Physics*, 67th ed.; Chemical Rubber Co.: Cleveland, OH, 1986.
(16) Wilhelm, E. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1985**, 164.
(17) Green, J. R.; Margerison, D. *Statistical Treatment of Experimental Data*; Elsevier: Amsterdam, 1977.
(18) Rowlinson, J. S. *Liquids and Liquid Mixtures*; Butterworth: London, 1959.
(19) Blandamer, H. J.; Nidden, N. J.; Morcom, K. W.; Smith, R. W.; Trelor, N. C.; Wootten, M. J. *Trans. Faraday Soc.* **1939**, *65*, 2633.
(20) *Beilstein*, Springer-Verlag: Berlin, 1961; Dritter Band, Erster Teil p 3.
(21) Cocero, M. J.; Mato, F.; Garcia, I.; Cobos, J. C.; Kehiaian, H. V. *J. Chem. Eng. Data* **1989**, *34*, 73.

Received for review July 11, 1994. Accepted September 28, 1994.[⊗]

JE940139N

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