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Excess Molar Enthalpies for Propylene Carbonate + Linear and Cyclic Ketones at 298.15 K

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Excess molar enthalpies, $H^{\mathrm{E}}_{\mathrm{m}}$, have been determined for propylene carbonate + five linear ketones (2-propanone, 2-butanone, 2-hexanone, 2-octanone, or 2-undecanone) and + three cyclic ketones (cyclohexanone, 2-methylcyclohexanone, or 2,6-dimethylcyclohexanone) at 298.15 K and atmospheric pressure by means of an LKB flow microcalorimeter. Results have been correlated using the Redlich–Kister equation, and the adjustable parameters have been evaluated by the least-squares analysis. $H^{\mathrm{E}}_{\mathrm{m}}$ values are found to be positive for all mixtures with the exception of propylene carbonate + 2-propanone, which shows a sign inversion of $H^{\mathrm{E}}_{\mathrm{m}}$.

Introduction

In recent years much interest has been shown in the solvent properties and electrochemical studies of propylene carbonate (*1–3*). This work is undertaken to determine the excess molar enthalpies, $H^{\mathrm{E}}_{\mathrm{m}}$, for propylene carbonate (component 1) + five linear and + three cyclic ketones (component 2), namely, 2-propanone, 2-butanone, 2-hexanone, 2-octanone, 2-undecanone, cyclohexanone, 2-methylcyclohexanone, and 2,6-dimethylcyclohexanone, respectively. Measurements have been made at 298.15 K and atmospheric pressure. There appear to be no results published previously.

Previous papers (*4, 5*) report excess molar enthalpies of dimethyl carbonate or diethyl carbonate + linear and cyclic ketones. Calorimetric and phase equilibrium data for mixtures of linear carbonates + hydrocarbons or + carbon tetrachloride are given in the paper of Gonzalez et al. (*6*), reporting also revised data on mixtures of linear carbonates + aromatic hydrocarbons or + cyclohexane. Excess molar heat capacities and excess molar volumes of propylene carbonate + aromatic hydrocarbons have been measured by Wilhelm et al. (*7*). The purpose of the investigations is to obtain more information on the thermodynamic properties of the mixtures.

Experimental Section

Chemicals. All substances were from Aldrich, and their purities were better than 99 mass % with the exception of 2-octanone and 2,6-dimethylcyclohexanone whose purities were +98 mass %. 2-Octanone was purified following the method of Collerson et al. (*8*). 2,6-Dimethylcyclohexanone, a mixture of isomers, was used as received. The purities of the compounds were checked by density determinations at (298.15 ± 0.01) K by using a vibrating digital density meter (Anton Paar, model DMA 60/602, Graz, Austria), and the values obtained are reported in Table 1 and compared with literature values (*9–12*). Before measurements, the liquids were dried over molecular sieves (Union Carbide, type 4A, 1/16-in. pellets) and kept in dark bottles.

Table 1. Purity Grades and Densities, ϱ, of the Pure Compounds and Comparison with Literature Data at 298.15 K and Atmospheric Pressure

		$\varrho/(\mathrm{g\ cm^{-3}})$	
component	purity/%	present work	lit
propylene carbonate	+99	1.199 15	1.199 3 (*9*)
2-propanone	+99.9	0.784 37	0.784 4 (*10*)
2-butanone	+99.5	0.799 71	0.799 70 (*10*)
2-hexanone	+99	0.806 74	0.806 7 (*10*)
2-octanone	98	0.814 34	0.814 3 (*10*)
2-undecanone	99	0.822 31	0.822 15 (*11*)
cyclohexanone	99.8	0.942 20	0.942 21 (*12*)
2-methylcyclohexanone	99	0.921 54	0.921 48 (*11*)
2,6-dimethylcyclohexanone	98	0.912 12[a]	

[a] No literature value at 298.15 K.

Apparatus. Excess molar enthalpies, $H^{\mathrm{E}}_{\mathrm{m}}$, were measured at (298.15 ± 0.01) K (IPTS-68) using an LKB flow microcalorimeter (*13*) (model 2107, AB Produkter, LKB Bromma, Sweden) equipped with two identical automatic burets (ABU-Radiometer, Copenhagen, Denmark) which pumped the liquids through the mixing cell of the calorimeter. Further details on the apparatus and experimental procedure are described in a previous paper (*14*). The test system cyclohexane + hexane was used to evaluate the accuracy of the experimental technique, and the results obtained agree with those in the literature (*15*), within 0.5% over the central range of concentration.

Results and Discussion

The experimental excess molar enthalpies, $H^{\mathrm{E}}_{\mathrm{m}}$, for the eight binary mixtures as a function of mole fraction x_1 of propylene carbonate were fitted to the Redlich–Kister equation

$$H^{\mathrm{E}}_{\mathrm{m}}/(\mathrm{J{\cdot}mol^{-1}}) = x_1x_2\sum_{k\geq 0} a_k(x_1 - x_2)^k \qquad (1)$$

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Table 2. Excess Molar Enthalpies, H_m^E, of Binary Mixtures and Adjustable Parameters a_k of Eq 1 Along with Standard Deviations $\sigma(H_m^E)$ at 298.15 K

x_1	$H_m^E/(J \cdot mol^{-1})$	x_1	$H_m^E/(J \cdot mol^{-1})$	x_1	$H_m^E/(J \cdot mol^{-1})$	x_1	$H_m^E/(J \cdot mol^{-1})$	x_1	$H_m^E/(J \cdot mol^{-1})$
Propylene Carbonate (1) + 2-Propanone (2)									
0.035	−4.3	0.1786	−5.2	0.4652	15.5	0.7767	15.7	0.9543	2.1
0.0676	−6.5	0.2247	−2.3	0.5662	19.6	0.8392	11.2		
0.0981	−7.3	0.3031	3.9	0.6530	20.2	0.8743	8.4		
0.1266	−7.1	0.3670	9.0	0.7229	18.4	0.9126	5.0		
$a_0 = 69.8$, $a_1 = 93.4$, $a_2 = -88.0$, $a_3 = 0$, $a_4 = -48.8$									
$\sigma(H_m^E) = 0.1$ J·mol^{-1}									
Propylene Carbonate (1) + 2-Butanone (2)									
0.0423	12.4	0.2093	101.6	0.5144	188.8	0.8090	119.6	0.9622	22.6
0.0811	28.3	0.2609	128.7	0.6138	183.2	0.8640	87.5		
0.1169	48.1	0.3462	158.6	0.6793	169.9	0.8944	65.7		
0.1500	66.1	0.4138	174.1	0.7606	143.6	0.9271	44.1		
$a_0 = 743.9$, $a_1 = 122.8$, $a_2 = 0$, $a_3 = 67.0$, $a_4 = -420.1$									
$\sigma(H_m^E) = 1.3$ J·mol^{-1}									
Propylene Carbonate (1) + 2-Hexanone (2)									
0.0573	80.7	0.2672	371.3	0.5932	522.5	0.8537	302.8	0.9722	57.1
0.1083	158.5	0.3271	430.2	0.6863	492.3	0.8974	216.2		
0.1542	228.4	0.4217	491.3	0.7447	445.5	0.9211	169.0		
0.1955	287.0	0.4929	522.9	0.8140	361.4	0.9460	115.8		
$a_0 = 2079.4$, $a_1 = 457.9$, $a_2 = 384.1$, $a_3 = 0$, $a_4 = -832.8$									
$\sigma(H_m^E) = 2.3$ J·mol^{-1}									
Propylene Carbonate (1) + 2-Octanone (2)									
0.0715	119.7	0.3162	587.9	0.6490	780.8	0.8809	420.6	0.9780	94.1
0.1335	235.2	0.3814	681.2	0.7350	701.4	0.9315	269.8		
0.1878	353.2	0.4804	773.4	0.7872	624.0	0.9367	249.8		
0.2356	447.1	0.5521	794.4	0.8473	504.9	0.9569	173.2		
$a_0 = 3131.4$, $a_1 = 966.5$, $a_2 = -203.6$, $a_3 = 584.0$									
$\sigma(H_m^E) = 2.6$ J·mol^{-1}									
Propylene Carbonate (1) + 2-Undecanone (2)									
0.0920	291.8	0.3782	939.3	0.7087	953.1	0.9068	546.6	0.9832	129.9
0.1685	499.8	0.4478	1009.1	0.7849	850.7	0.9359	419.0		
0.2332	663.0	0.5488	1045.2	0.8295	770.4	0.9511	344.4		
0.2885	796.2	0.6186	1030.7	0.8795	641.4	0.9669	246.0		
$a_0 = 4170.8$, $a_1 = 608.2$, $a_2 = 0$, $a_3 = 1844.3$, $a_4 = 1843.2$									
$\sigma(H_m^E) = 4.1$ J·mol^{-1}									
Propylene Carbonate (1) + Cyclohexanone (2)									
0.0485	47.3	0.2342	215.5	0.5503	312.9	0.8304	195.9	0.9671	42.6
0.0925	92.4	0.2897	254.3	0.6484	301.0	0.8801	145.6		
0.1327	131.7	0.3796	290.5	0.7099	277.9	0.9073	115.4		
0.1694	168.1	0.4492	309.1	0.7859	229.2	0.9362	79.7		
$a_0 = 1256.4$, $a_1 = 128.1$, $a_2 = 233.7$, $a_3 = 56.9$, $a_4 = -397.3$									
$\sigma(H_m^E) = 1.5$ J·mol^{-1}									
Propylene Carbonate (1) + 2-Methycyclohexanone (2)									
0.0562	72.0	0.2633	350.5	0.5884	489.0	0.8512	285.2	0.9717	61.8
0.1064	141.0	0.3227	406.1	0.6821	452.6	0.8956	213.1		
0.1516	205.4	0.4169	465.1	0.7409	409.7	0.9196	171.0		
0.1924	262.5	0.4880	489.5	0.8109	339.7	0.9449	119.3		
$a_0 = 1962.9$, $a_1 = 301.0$, $a_2 = 113.6$, $a_3 = 301.7$, $a_4 = -385.2$									
$\sigma(H_m^E) = 1.8$ J·mol^{-1}									
Propylene Carbonate (1) + 2,6-Dimethylcyclohexanone (2)									
0.0634	115.5	0.2889	487.0	0.6191	625.6	0.8667	354.1	0.9750	76.3
0.1193	210.1	0.3514	562.2	0.7092	570.6	0.9070	264.1		
0.1688	300.7	0.4483	629.7	0.7647	523.9	0.9286	213.6		
0.2131	372.1	0.5200	648.9	0.8298	428.7	0.9512	148.9		
$a_0 = 2576.6$, $a_1 = 254.9$, $a_2 = 0$, $a_3 = 1510.3$, $a_4 = 0$, $a_5 = -1219.4$									
$\sigma(H_m^E) = 2.7$ J·mol^{-1}									

The adjustable parameters a_k were evaluated by fitting H_m^E to eq 1 by the method of least squares. Table 2 collects the experimental H_m^E values and the adjustable parameters a_k along with the standard deviations $\sigma(H_m^E)$.

A graphical representation of the results is given in Figures 1 and 2, and excess molar enthalpies at $x_1 = 0.5$, $H_m^E(x_1{=}0.5)$, have been reported in Figure 3, as a function of the number n_c of carbon atoms, only for linear ketones. All excess enthalpies are nearly symmetrical in mole fraction, with the exception of the mixture containing 2-propanone, which has the smallest values of H_m^E and shows a minor sign inversion of the excess enthalpy.

$H_m^E(x{=}0.5)$ increases regularly with the chain length of the ketones for mixtures of propylene carbonate + linear ketones, as shown in Figures 1 and 3. Also, increasing the number of CH_3 groups in the cyclohexanone molecule leads to an increase in $H_m^E(x{=}0.5)$, as shown in Figure 2, reporting for comparison the H_m^E values of 2-hexanone (dashed line). Thus, cyclization of the molecule leads to smaller H_m^E, and an increase in molecular size leads to larger H_m^E. The same trends are observed for the excess enthalpy of dimethyl or diethyl carbonate with cyclic or

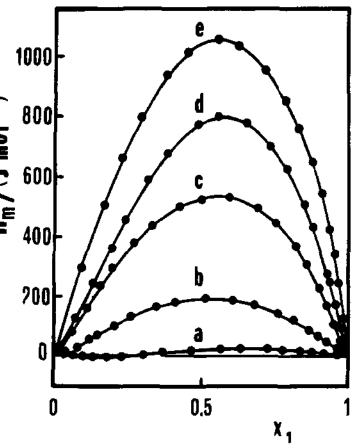

Figure 1. Excess molar enthalpies, H_m^E, of propylene carbonate + 2-propanone (a), + 2-butanone (b), + 2-hexanone (c), + 2-octanone (d), and +2-undecanone (e) at 298.15 K: (○) experimental points; (—) curves calculated from eq 1 using the parameters of Table 1.

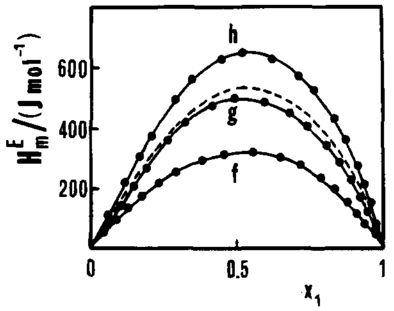

Figure 2. Excess molar enthalpies, H_m^E, of propylene carbonate + cyclohexanone (f), + 2-methylcyclohexanone (g), and + 2,6-dimethylcyclohexanone (h): (●) experimental points; (—) curves calculated from eq 1 using the parameters of Table 1; (- - -) propylene carbonate + 2-hexanone, taken from Figure 1 and shown for comparison.

linear ketones (*4*, *5*). However, the magnitude of the cyclization effect is smaller.

The regular increase of H_m^E with the increase of the chain length in linear ketones and with the increase of the CH$_3$ groups in cyclic ketones may be explained, at most qualitatively, by the prevailence of the interaction energy between molecules of ketones, E_{22}, over that between molecules of ketone and cyclic ester, E_{12}, in the approximate expression for

$$H_m^E \approx E_{11} + E_{22} - 2E_{12} \tag{2}$$

In fact, alkyl chains and CH$_3$ groups exert an electron donor effect on the neighbor C=O groups of ketones with an increased negative charge induced on the O atom of C=O and consequent larger interactions between ketones molecules.

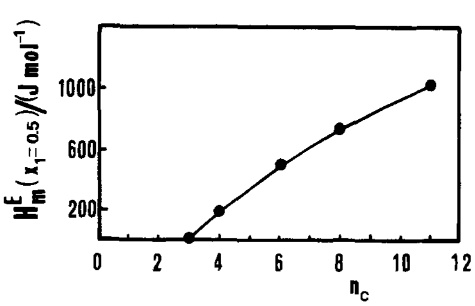

Figure 3. Values of $H_m^E(x_1=0.5)$ at 298.15 K for the five binary mixtures of propylene carbonate + linear ketones as a function of the number n_c of carbon atoms in the ketone.

Literature Cited

(1) Annesini, M. C., De Sanctis, R.; Kikic, I.; Marrelli, L. *J. Chem. Eng. Data* **1984**, *29*, 39.
(2) Muhuri, P. K.; Hazra, D. K. *J. Chem. Eng. Data* **1994**, *39*, 375.
(3) Al-Najar, A. A.; Alami, K. M. H.; Ebraheem, A. M. *J. Chem. Eng. Data* **1992**, *37*, 443.
(4) Francesconi, R.; Comelli, F. *Thermochim. Acta*, in press.
(5) Francesconi, R.; Comelli, F. *J. Thermal Anal.*, in press.
(6) Gonzalez, J. A.; Garcia, I.; Cobos, J. C.; Casanova, C.; Kehiaian, H. V. *Thermochim. Acta* **1993**, *217*, 57.
(7) Wilhelm, E.; Jmenez, E. *J. Solution Chem.* **1991**, *20*, 17.
(8) Collerson, R. R.; Counsell, J. F.; Handley, R.; Martin, J. F.; Sprake, C. H. S. *J. Chem. Soc.* **1965**, 3697.
(9) Jansen, M. L.; Yeager, H. L. *J. Phys. Chem.* **1973**, *77*, 3089.
(10) Riddik, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; Wiley-Interscience: New York, 1986.
(11) Smith, B. D.; Srivastava, R. S. *Thermodynamic Data for Pure Compounds*; Elsevier: Amsterdam, 1986; Part A.
(12) Dernini, S.; Polcaro, A. M.; Ricci, P. F.; Marongiu, B. *J. Chem. Eng. Data* **1987**, *32*, 194.
(13) Monk, P.; Wadso, I. *Acta Chem. Scand.* **1968**, *22*, 1842.
(14) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1986**, *31*, 250.
(15) Benson, G. C. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1974**, 19.

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