Excess Molar Enthalpies and Excess Molar Volumes of Propylene Carbonate + Seven Pentanol Isomers at 298.15 K

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Excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, of propylene carbonate + seven pentanol isomers, namely, 1-, 2-, and 3-pentanol, 2-methyl-1-butanol, 2-methyl-2-butanol, 3-methyl-1-butanol, and 3-methyl-2-butanol, have been determined at 298.15 K and at atmospheric pressure using a flow microcalorimeter and a digital densimeter. H_m^E and V_m^E values are always positive, with the exception of the volumetric data for the mixture propylene carbonate + 3-methyl-2-butanol, showing a sign inversion of V_m^E. The Redlich−Kister equation, fitted to the experimental results, provides a satisfactory mathematical representation of H_m^E and V_m^E in all mixtures. Results have been qualitatively discussed.

Introduction

Propylene carbonate, an aprotic solvent with a high potential for industrial uses such as lithium batteries, has been the subject of several recent chemical and electrochemical studies (Tobishima et al., 1988; Pistoia, 1994). Binary mixtures containing propylene carbonate and other organic solvents, especially aprotic ones, have also great technological and theoretical interest (Gabano, 1983). This paper continues our research program on binary mixtures containing propylene carbonate as the common component (Righetti et al., 1997; Comelli et al., 1998) and reports experimental excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, of propylene carbonate + seven pentanol isomers, namely, 1-, 2-, and 3-pentanol, 2-methyl-1-butanol, 2-methyl-2-butanol, 3-methyl-1-butanol, and 3-methyl-2-butanol at 298.15 K.

Experimental values have been fitted to the Redlich−Kister (1948) equation to determine the binary coefficients and standard deviation. A qualitative discussion of the results is given.

To our knowledge, mixtures of propylene carbonate with pentanol isomers have not been previously studied.

Experimental Section

Materials. Chemicals were Aldrich and Fluka products, listed in Table 1. Propylene carbonate, showing a stated purity of 99.7 mol % was used as received. Pentanols were purified by refluxing over CaO, then distilled in a 30-plate column and stored in dark bottles over molecular sieves (Union Carbide, type 4A, $^1/_{16}$ in. pellets).

The GLC analyses were done on a gas chromatograph, Hewlett-Packard model. 5890 and an HP (cross-linked 5% ME siloxane) capillary column. Purities, density values, and comparison with literature results are also reported in Table 1.

Before measurements, pure liquids were degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy).

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Table 1. Mole Percent Purities, Sources, and Densities, ρ, of Pure Compounds Compared with Literature Values

		ρ (g cm^{-3})	
component	source	this paper	lit.
propylene carbonate(99.7)	Aldrich	1.199 52	1.1995[a]
			1.1998[b]
			1.1988[c]
1-pentanol(99.7)	Fluka	0.810 86	0.81080[d]
			0.81104[e]
			0.81108[c]
2-pentanol(99.8)	Aldrich	0.817 20	0.8160[d]
3-pentanol(99.7)	Fluka	0.815 24	0.81412[e]
2-methyl-1-butanol(99.9)	Aldrich	0.815 02	0.8150[d]
2-methyl-2-butanol(99.8)	Aldrich	0.804 61	0.8050[d]
			0.80443[e]
3-methyl-1-butanol(99.9)	Fluka	0.801 33[h]	0.80182[f,g]
3-methyl-2-butanol(99.8)	Fluka	0.815 24	0.81412[e]

[a] Moumouzias et al., 1991. [b] Ue, 1994. [c] Muhuri and Hazra, 1994. [d] Riddick et al., 1986. [e] Smith and Srivastava, 1986 (calculated from density equation). [f] Ortega and Paz-Andrade, 1986. [g] Sreenivasulu and Naidu, 1993. [h] At 303.15 K.

Apparatus and Procedure. The excess molar enthalpies, H_m^E, have been determined using a differential microcalorimeter (model 2107 from LKB, Bromma, Sweden) operating on the heat-leakage principle (Monk and Wadso, 1968) under flow conditions using two automatic burets (ABU from Radiometer, Copenhagen, Denmark) that pump continuously the required flow of each liquid into the mixing cell of the calorimeter.

Mole fractions were determined by fluxes showing errors less than ±0.0002.

The temperature of the apparatus was electronically controlled and kept constant to ±0.01 K.

Details of the experimental procedure have been described elsewere (Francesconi and Comelli, 1986). The uncertainty in H_m^E did not exceed 1 J mol^{-1}. The apparatus has been checked before measurements with the standard mixture cyclohexane + hexane, and our results, when compared with those of literature (Gmehling, 1993),

10.1021/je9801718 CCC: $18.00 © 1999 American Chemical Society
Published on Web 12/16/1998

Table 2. Excess Molar Enthalpies, H_m^E, of Propylene Carbonate + Pentanol Isomers at 298.15 K

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
Propylene Carbonate (1) + 1-Pentanol (2)			
0.0505	699	0.5609	1987
0.0962	1094	0.6571	1930
0.1377	1326	0.7187	1847
0.1755	1471	0.7930	1636
0.2420	1619	0.8846	1201
0.2986	1734	0.9109	994
0.3897	1882	0.9388	747
0.4598	1930	0.9684	427
Propylene Carbonate (1) + 2-Pentanol (2)			
0.0509	728	0.6588	2263
0.0968	1201	0.7201	2142
0.1385	1521	0.7942	1860
0.1765	1705	0.8373	1628
0.2433	1982	0.8853	1296
0.3001	2108	0.9114	1041
0.3914	2232	0.9392	756
0.4616	2294	0.9686	415
0.5626	2323		
Propylene Carbonate (1) + 3-Pentanol (2)			
0.0501	702	0.6554	2468
0.0955	1170	0.7171	2312
0.1368	1498	0.7918	2007
0.1744	1704	0.8352	1698
0.2406	2013	0.8838	1299
0.2970	2174	0.9102	1053
0.3879	2403	0.9383	766
0.4579	2471	0.9682	407
0.5589	2545		
Propylene Carbonate (1) + 2-Methyl-1-butanol (2)			
0.0503	678	0.6560	2067
0.0957	1118	0.7172	2015
0.1371	1405	0.7922	1823
0.1748	1591	0.8356	1613
0.2411	1781	0.8841	1286
0.2975	1916	0.9104	1063
0.3885	2009	0.9385	784
0.4585	2054	0.9683	436
0.5596	2098		
Propylene Carbonate (1) + 2-Methyl-2-butanol (2)			
0.0509	700	0.6589	2167
0.0969	1135	0.7202	1994
0.1386	1398	0.7943	1695
0.1766	1583	0.8374	1433
0.2435	1827	0.8854	1073
0.3002	1991	0.9115	879
0.3916	2168	0.9390	617
0.4617	2221	0.9686	336
0.5628	2278		
Propylene Carbonate (1) + 3-Methyl-1-butanol (2)			
0.0462	546	0.6590	1914
0.0969	999	0.7203	1851
0.1386	1278	0.7944	1696
0.1767	1455	0.8374	1523
0.2435	1701	0.8854	1238
0.3003	1795	0.9115	1035
0.3917	1910	0.9392	772
0.4618	1966	0.9687	435
0.5629	1953		
Propylene Carbonate (1) + 3-Methyl-2-butanol (2)			
0.0503	651	0.6559	2252
0.0956	1096	0.7176	2143
0.1370	1410	0.7922	1837
0.1747	1626	0.8356	1600
0.2410	1924	0.8840	1243
0.2975	2081	0.9104	1003
0.3885	2286	0.9384	728
0.4585	2345	0.9682	396
0.5596	2369		

show a discrepancy lower than 0.5% at the maximum of the thermal effect.

Table 3. Densities, ρ, and Excess Molar Volumes, V_m^E, of Propylene Carbonate + Seven Pentanol Isomers at 298.15 K

x_1	ρ (g cm^{-3})	V_m^E (cm^3 mol^{-1})	x_1	ρ (g cm^{-3})	V_m^E (cm^3 mol^1)
Propylene Carbonate (1) + 1-Pentanol (2)					
0.0458	0.824 62	0.042	0.6256	1.029 43	0.154
0.1504	0.857 32	0.105	0.6933	1.057 52	0.145
0.2486	0.889 67	0.134	0.7946	1.101 64	0.117
0.3195	0.914 02	0.145	0.8702	1.136 24	0.085
0.3894	0.938 87	0.151	0.9304	1.164 95	0.049
0.4964	0.978 54	0.160	0.9863	1.192 59	0.010
0.5624	1.004 12	0.160			
Propylene Carbonate (1) + 2-Pentanol (2)					
0.0537	0.821 08	0.090	0.6145	1.020 81	0.236
0.1415	0.848 45	0.180	0.6675	1.043 06	0.217
0.2092	0.870 54	0.219	0.7392	1.074 11	0.194
0.3046	0.903 11	0.247	0.8819	1.140 18	0.106
0.3477	0.918 35	0.253	0.9171	1.157 42	0.078
0.4568	0.958 50	0.256	0.9810	1.189 66	0.021
0.5215	0.983 40	0.255			
Propylene Carbonate (1) + 3-Pentanol (2)					
0.0372	0.828 06	0.059	0.6035	1.022 53	0.301
0.0841	0.842 05	0.122	0.6607	1.045 59	0.285
0.1830	0.872 79	0.218	0.7456	1.081 20	0.244
0.2327	0.888 87	0.247	0.8305	1.118 63	0.183
0.3165	0.916 89	0.287	0.9201	1.160 29	0.098
0.4087	0.919 47	0.308	0.9841	1.191 50	0.023
0.5228	0.991 22	0.313			
Propylene Carbonate (1) + 2-Methyl-1-butanol (2)					
0.0462	0.828 75	0.050	0.6169	1.028 37	0.144
0.1052	0.846 84	0.095	0.6825	1.055 16	0.133
0.2452	0.892 06	0.143	0.7888	1.100 65	0.104
0.3622	0.932 31	0.156	0.8851	1.144 26	0.063
0.4354	0.958 73	0.156	0.9381	1.169 29	0.037
0.4962	0.981 33	0.156	0.9795	1.189 38	0.014
0.5569	1.004 61	0.153			
Propylene Carbonate (1) + 2-Methyl-2-butanol (2)					
0.0542	0.822 32	−0.115	0.6424	1.033 93	0.066
0.0982	0.836 55	−0.148	0.6872	1.052 79	0.071
0.2755	0.895 27	−0.072	0.7531	1.081 47	0.073
0.3752	0.930 36	−0.013	0.8210	1.112 15	0.066
0.4484	0.957 28	0.019	0.9325	1.165 44	0.031
0.5287	0.988 08	0.043	0.9861	1.192 40	0.006
0.5798	1.008 32	0.056			
Propylene Carbonate (1) + 3-Methyl-1-butanol (2)					
0.0222	0.811 14	0.009	0.5945	1.014 39	0.032
0.1130	0.839 65	0.034	0.6669	1.044 49	0.030
0.2198	0.874 92	0.044	0.7513	1.081 11	0.025
0.3234	0.910 91	0.046	0.8556	1.128 72	0.016
0.3671	0.926 64	0.045	0.9381	1.168 43	0.010
0.4573	0.960 25	0.041	0.9729	1.185 75	0.005
0.5293	0.988 14	0.039			
Propylene Carbonate (1) + 3-Methyl-2-butanol (2)					
0.0405	0.827 32	0.035	0.6089	1.024 56	0.210
0.1043	0.846 76	0.091	0.6925	1.058 76	0.191
0.2150	0.882 04	0.160	0.7731	1.093 21	0.161
0.3169	0.926 25	0.197	0.8750	1.139 16	0.104
0.4191	0.952 35	0.214	0.9316	1.165 95	0.061
0.5031	0.983 42	0.222	0.9830	1.191 04	0.018
0.5574	1.004 30	0.214			

Excess molar volumes, V_m^E, were determined from densities using a digital densimeter (from Anton Paar, model DMA 60/602, Graz, Austria) operating in the static mode and capable of an accuracy of $\pm 1 \times 10^{-5}$ g cm^{-3} for density, which leads to an error in V_m^E less than $\pm 3 \times 10^{-3}$ cm^3 mol^{-1}.

Liquid mixtures, from which volumes were determined, were prepared by mass using an electronic balance (Mettler, model AE 160, Switzerland with a resolution of ±0.0001 g and a maximum capacity of 150 g).

Table 4. Adjustable Parameters, a_k, Eq 2, and Standard Deviations, $\sigma(Q_m^E)$, of Propylene Carbonate + Pentanol Isomers at 298.15 K

function	a_0	a_1	a_2	a_3	a_4	$\sigma(Q_m^E)$
			Propylene Carbonate + 1-Pentanol			
H_m^E (J mol^{-1})	7876.1	1190.0	3778.0	−2245.9	4709.6	9.5
V_m^E (cm^3 mol^{-1})	0.6355	0.0389	0.3911	−0.1961		0.0011
			Propylene Carbonate + 2-Pentanol			
H_m^E (J mol^{-1})	9244.5	828.58	6179.4	−2108.5		8.8
V_m^E (cm^3 mol^{-1})	1.0146	−0.1748	0.4534	−0.2891		0.0019
			Propylene Carbonate + 3-Pentanol			
H_m^E (J mol^{-1})	10095	1528.1	4768.4	−2931.6		12.0
V_m^E (cm^3 mol^{-1})	1.2582	−0.0477	0.2903	−0.1570		0.0011
			Propylene Carbonate + 2-Methyl-1-butanol			
H_m^E (J mol^{-1})	8283.8	1004.7	7080.2	−1449.8		9.9
V_m^E (cm^3 mol^{-1})	0.6214	−0.0919	0.3054	−0.2304		0.0011
			Propylene Carbonate + 2-Methyl-2-butanol			
H_m^E (J mol^{-1})	9067.5	1109.9	3318.2	−3618.2	1378.1	12.4
V_m^E (cm^3 mol^{-1})	0.1591	0.5746	−0.5143	1.1860	−0.9783	0.0006
			Propylene Carbonate + 3-Methyl-1-butanol			
H_m^E (J mol^{-1})	7792.2	316.82	6421.9	729.70		11.3
V_m^E (cm^3 mol^{-1})	0.1557	−0.1136	0.1345			0.0012
			Propylene Carbonate + 3-Methyl-2-butanol			
H_m^E (J mol^{-1})	9460.4	690.90	4592.2	−1366.7		10.7
V_m^E (cm^3 mol^{-1})	0.8797	−0.1778	−0.1423			0.0020

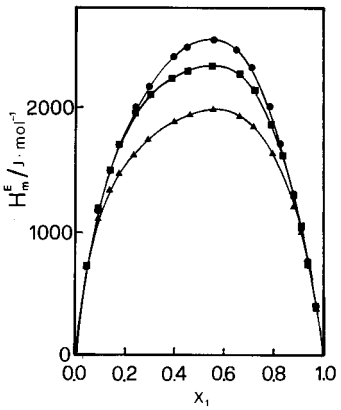

Figure 1. Excess molar enthalpies, H_m^E, of propylene carbonate (1) + 1-pentanol (2) (▲), + 2-pentanol (2) (■), + 3-pentanol (2) (●) at 298.15 K. Solid curves are calculated with eq 2.

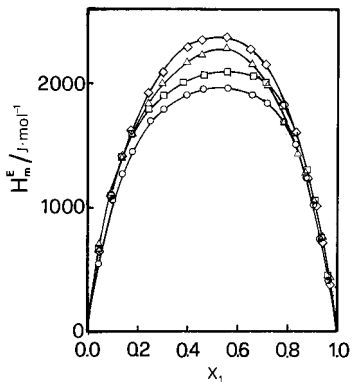

Figure 2. Excess molar enthalpies, H_m^E, of propylene carbonate (1) + 2-methyl-2-butanol (2) (△), + 3-methyl-2-butanol (2) (◇), + 2-methyl-1-butanol (2) (□), + 3-methyl-1-butanol (2) (○) at 298.15 K. Solid curves are calculated with eq 2.

The error in preparing mole fractions of propylene carbonate (component 1) was estimated to be on the order of $\pm 1 \times 10^{-4}$.

Details of experimental procedure has been previously described (Fermeglia and Lapasin, 1988).

To minimize the error due to evaporation of chemicals, the denser component was charged first in preparing solutions.

Before measurements, the apparatus has been calibrated with twice-distilled water (Wagenbreth and Blanke, 1971) and dry air (Kohlrausch, 1968). The temperature of the densimeter cell was measured with an Anton Paar DT 100-25 digital thermometer and maintained constant to ±0.01 K using a Heto external bath (type 01 DBT 623, Birkerød, Denmark) whose temperature was controlled to ±0.005 K.

Buoyancy corrections were made for density measurements, but only a variation of about 1×10^{-4} g cm^{-3} in the mole fraction has been observed.

Before measurements were made, the densimeter was checked against literature data of the mixture benzene + cyclohexane (Wilhelm, 1985); an agreement of our data to better than 0.5% in the central range of mole fraction of benzene was found.

Results and Discussion

The experimental excess molar enthalpies, H_m^E, and volumes, V_m^E, of the seven mixtures at 298.15 K are listed in Tables 2 and 3, respectively.

The excess molar volumes, V_m^E, were calculated from densities by the following equation

$$V_m^E = (x_1M_1 + x_2M_2)/\rho_m - x_1M_1/\rho_1 - x_2M_2/\rho_2 \qquad (1)$$

where x_i, M_i, and ρ_i ($i = 1, 2$) are the mole fractions, molar mass, and densities of the pure compounds, respectively, and ρ_m is the density of the mixture.

The experimental H_m^E and V_m^E values were correlated by the Redlich−Kister (1948) equation

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

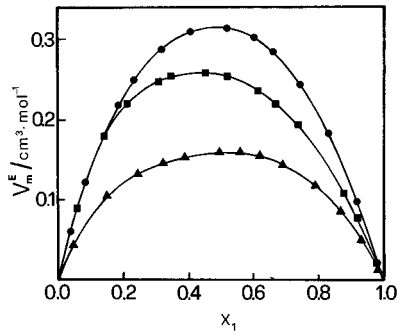

Figure 3. Excess molar volumes, V_m^E, of propylene carbonate (1) + 1-pentanol (2) (▲), + 2-pentanol (2) (■), + 3-pentanol (2) (●) at 298.15 K. Solid curves are calculated with eq 2.

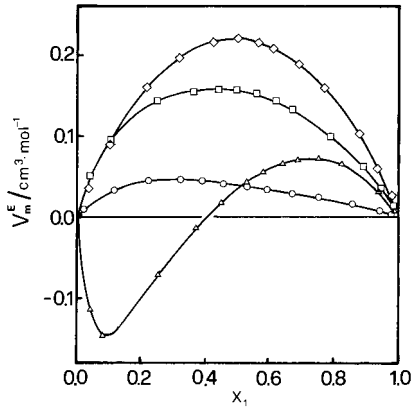

Figure 4. Excess molar volumes, V_m^E, of propylene carbonate (1) + 3-methyl-2-butanol (1) (◇), + 2-methyl-1-butanol (2) (□), + 3-methyl-1-butanol (2) (○), + 2-methyl-2-butanol (2) (△) at 298.15 K. Solid curves are calculated with eq 2.

where $Q_m^E = H_m^E/(\text{J mol}^{-1})$ or $V_m^E/(\text{cm}^3\ \text{mol}^{-1})$ and the adjustable parameters a_k were determined by the nonweighted least-squares fit. Adjustable parameters a_k and standard deviation $\sigma(Q_m^E)$ are listed in Table 4.

The experimental values and those correlated through eq 2 are represented in Figures 1−4.

The large positive values of H_m^E for all mixtures are consistent with the associations of alkanols. Moreover, the linear increase of H_m^E when going from 1-pentanol to 3-pentanol, Figure 1, may be due to the increased branching of the alkanols with a consequent increased steric effect of the C_5H_{11}group. The H-bonding alkanol−propylene carbonate is accordingly decreased, and then $H_m^E \approx H_{11} + H_{22} - 2H_{12}$, with H_{ij} the interaction energy between molecules i and j, must increase. The contribution H_{22} of alkanols to H_m^E is less influenced by the steric effect, since the vaporization heats of 1-, 2-, 3-pentanol vary in the range 56.9−53.1 kJ mol^{-1}.

If we exclude the mixture propylene carbonate + 2-methyl-2-butanol showing a sign inversion of H_m^E around $x_1 = 0.4$, all the V_m^E's are positive in accordance with breaking of alkanols associates during mixing.

3-Methyl-1-butanol and 2-methyl-2-butanol have the less and more branched C_5H_{11} chain, respectively, and, as can be seen from Table 1, have the smaller values of density. Moreover, their mixtures with propylene carbonate show the lower V_m^E's, with a sign inversion for propylene carbonate + 2-methyl-2-butanol.

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JE9801718