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Excess Molar Enthalpies, Densities, and Excess Molar Volumes of Diethyl Carbonate in Binary Mixtures with Seven *n*-Alkanols at 298.15 K

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The excess molar enthalpies, H_m^E, and the excess molar volumes, V_m^E, of diethyl carbonate + seven *n*-alkanols have been determined at 298.15 K and atmospheric pressure in order to investigate interactions between molecules. Mixtures show an endothermic effect which increases with the increase of the chain length of alkanols. The same positive pattern is observed for V_m^E. The experimental results have been correlated using the Redlich−Kister equation and have been qualitatively discussed.

Introduction

Literature reports only few thermodynamic studies on mixtures containing esters of carbonic acid, despite their importance as solvents used in industry, pharmaceuticals, and agricultural chemistry.

Continuing our research program, the present paper is undertaken to measure the excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, for diethyl carbonate + seven *n*-alkanols for which no literature data are available (that is, methanol, ethanol, propan-1-ol, butan-1-ol, hexan-1-ol, octan-1-ol, and decan-1-ol).

In previous papers (Comelli and Francesconi, 1995; Francesconi and Comelli, 1995) we have determined the excess molar enthalpies of diethyl carbonate with a series of dichloroalkanes and ketones, while other authors (Garcia et al., 1987) have measured the excess molar enthalpies of mixtures containing diethyl carbonate with some *n*-alkanes.

These series of data will contribute to a qualitative discussion.

Experimental Section

Materials. Origins and stated purities of liquids are shown in Table 1. All reagents were used without further purification, owing to their high purity grade, with the exception of diethyl carbonate which was fractionally distilled with sodium under reduced pressure and only the middle fraction was collected.

The purity tested by GLC was >99.8 mol %, and no appreciable peaks of impurities were detected.

Before use, all chemicals were kept in dark bottles over molecular sieves (Union Carbide type 4A, $^1/_{16}$-in. pellets) to reduce the water content and degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy).

In order to check the purity of compounds, also density values and refractive indices were determined and are reported in Table 2 in comparison with literature data.

Table 1. Origin and Stated Purity of the Pure Components

component	origin	stated purity/mol%
diethyl carbonate	Aldrich Chemical Co.	99%[a]; >99.8% (GLC)[b]
methanol	Aldrich Chemical Co.	99.8 (HPLC)
ethanol	E. Merck, D	99.8
propan-1-ol	Aldrich Chemical Co.	99.7
butan-1-ol	Aldrich Chemical Co.	99.8 (HPLC)
hexan-1-ol	Fluka Chemie, AG, CH	>99.5 (GC)
octan-1-ol	Fluka Chemie, AG, CH	>99.5 (GC)
decan-1-ol	Fluka Chemie, AG, CH	>99.5 (GC)

[a] As supplied. [b] After purification.

Table 2. Densities, ρ, Refractive Indices, n_D, of Pure Components and Comparison with Literature Values

	ρ/g·cm^{-3}		n_D	
component	exptl	lit.	exptl	lit.
diethyl carbonate	0.969 23	0.969 26[a]	1.3827	1.382 87[a]
		0.969 4[b]		1.3824[b]
methanol	0.786 56	0.786 37[a]	1.3264	1.326 52[a]
		0.7866[c]		1.3264[c]
		0.7868[d]		
ethanol	0.785 09	0.784 93[a]	1.3593	1.359 41[a]
		0.785 1[c]		1.3592[c]
		0.785 4[d]		
propan-1-ol	0.799 58	0.799 60[a]	1.3838	1.383 70[a]
		0.799 2[d]		
butan-1-ol	0.805 72	0.805 75[a]	1.3975	1.397 41[a]
		0.805 81[e]		
		0.805 93[f]		1.397 4[f]
hexan-1-ol	0.815 16	0.815 34[a]	1.4158	1.415 7[a]
		0.815 32[e]		
		0.815 26[f]		1.416 0[f]
octan-1-ol	0.821 64	0.821 57[a]	1.4274	1.427 6[a]
		0.821 62[e]		
		0.821 67[f]		1.4270[f]
decan-1-ol	0.826 33	0.826 42[f]	1.4348	1.4349[f]

[a] Riddick et al.,1986. [b] Cocero et al., 1989. [c] Arce et al., 1995. [d] Nikam et al., 1995. [e] Franjo et al., 1995. [f] Ortega, 1995.

Calorimetric Measurements. The excess molar enthalpies, H_m^E, were determined using a flow microcalorimeter (LKB Produkter, model 2107, Bromma, Sweden). Details of the apparatus and experimental procedure were described elsewere (Monk and Wadso, 1968; Francesconi and Comelli, 1986).

Liquids were pumped into the mixing cell of the calorimeter using two automatic burets (ABU, Radiometer, Copenhagen, Denmark), and the temperature was kept constant to ±0.01K by an isothermal control unit. Mole fractions of mixtures were determined from calibrated flow rates and fluid densities: we estimate mole fractions

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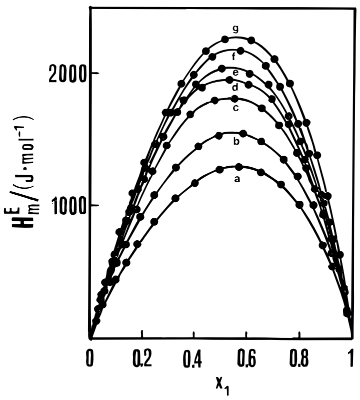

Figure 1. Excess molar enthalpies, H_m^E, of diethyl carbonate (1) with methanol (2) (a), ethanol (2) (b), propan-1-ol (2) (c), butan-1-ol (2) (d), hexan-1-ol (2) (e), octan-1-ol (2) (f), and decan-1-ol (2) (f) at 298.15 K: (●), experimental points; (solid curves), calculated from eq 2.

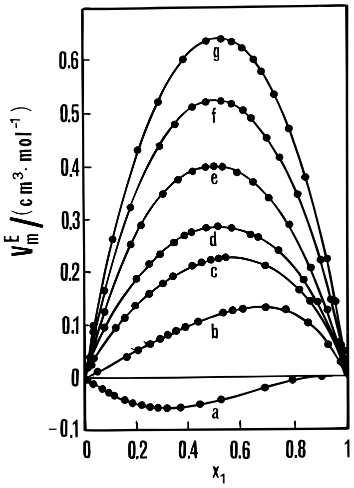

Figure 2. Excess molar volumes, V_m^E, of diethyl carbonate (1) with methanol (2) (a), ethanol (2) (b), propan-1-ol (2) (c), butan-1-ol (2) (d), hexan-1-ol (2) (e), octan-1-ol (2) (f), and decan-1-ol (2) (g) at 298.15 K: (●), experimental points; (solid curves), calculated from eq 2.

precise to 1 × 10^{-4}, and the accuracy of the excess molar enthalpies is less than 1%.

Before measurements, the mixing cell was calibrated electrically with an integral resistance heater.

The calorimeter was tested by using the reference cyclohexane + hexane mixture (Gmehling, 1993) at 298.15 K: the deviation of our measurements from the literature was less than 0.5% over the central range of mole fraction of cyclohexane.

Density Measurements. Densities of the pure components and binary mixtures were determined using a vibrating density meter (model DMA 60, Anton Paar, Graz, Austria) equipped with a density measuring cell (Type 602) with a precision for the measured period τ of 1 × 10^{-6} s, which leads to a precision in densities and excess molar volumes of ±5 × 10^{-5} g·cm^{-3} and 3 × 10^{-3}cm^3·mol^{-1}, respectively.

The densities, ρ, of mixtures were used to calculate the excess molar volumes, V_m^E, according to

$$V_m^E/\mathrm{cm^3{\cdot}mol^{-1}} = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \qquad (1)$$

where x_i, M_i, and ρ_i are the mole fraction, molar mass, and density of component i, respectively.

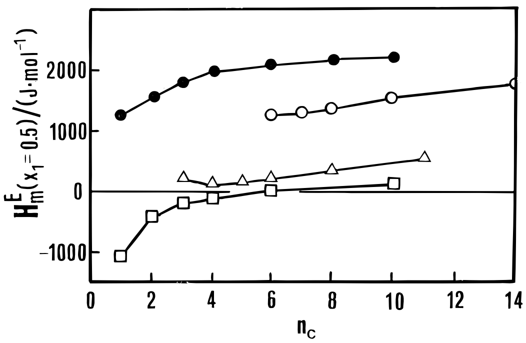

Figure 3. Values of equimolar excess enthalpies, H_m^E(x_1=0.5), at 298.15 K as a function of the number of carbon atoms n_c of n-alkanols for the binary mixtures with diethyl carbonate: (closed circles) this paper; (open points) comparison with other functional groups from literature; (○), n-alkanes (Garcia et al., 1987); (△) methyl n-alkyl ketones (Francesconi and Comelli, 1995); (□), chloroalkanes (Comelli and Francesconi, 1995).

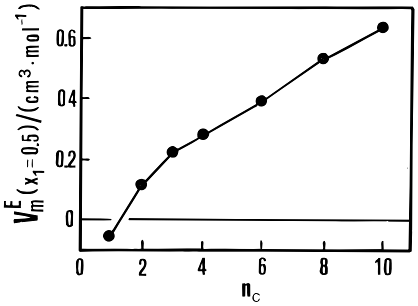

Figure 4. Values of equimolar excess volumes, V_m^E(x_1 = 0.5), at 298.15 K as a function of the number of carbon atoms n_c of n-alkanols for the binary mixtures with diethyl carbonate.

The temperature of the U-shaped tube was checked using a calibrated digital thermometer (Anton Paar, DT-25) with an accuracy of ±0.01 K. An external Hetotherm bath circulator (Heto, type 01 DBT 623) was used with a temperature control interval of ±0.005 K.

The apparatus, the measuring method of densities, and the procedure to prepare samples by mass have been described elsewhere (Fermeglia and Lapasin, 1988).

Corrections for buoyancy and evaporation of the components were carried out, showing only a negligible contribution to the mole fraction, on the order of 1 × 10^{-4} at the worst.

Before measurements, the apparatus was calibrated with redistilled, degassed water and dry air.

The test mixture benzene + cyclohexane (Wilhelm, 1985) at 298.15 K was used to check the density meter and our measurements show a discrepancy less than 0.5% over the central range of mole fraction of benzene with respect to literature values.

Results and Discussion

The experimental values H_m^E and V_m^E as a function of mole fraction of diethyl carbonate (1) are shown in Tables 3 and 4 and are graphically represented in Figures 1 and 2. For each binary mixture, H_m^E and V_m^E values were fitted to the Redlich−Kister equation to correlate the composition dependence of both excess properties

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

where Q_m^E = H_m^E/J·mol^{-1} or V_m^E/cm^3·mol^{-1}, a_k are the adjustable parameters and x_1 and x_2 are the mole fractions of diethyl carbonate and alkanols, respectively.

Table 3. Excess Molar Enthalpies, H^E_m, of Diethyl Carbonate + *n*-Alkanol at 298.15 K

x_1	H^E_m/J·mol^{-1}	x_1	H^E_m/J·mol^{-1}
Diethyl Carbonate (1) + Methanol (2)			
0.0271	124	0.5007	1253
0.0527	236	0.5721	1281
0.1002	425	0.6673	1250
0.1432	569	0.7278	1167
0.1821	701	0.8005	1023
0.2505	879	0.8892	698
0.3339	1055	0.9146	552
0.4006	1168	0.9750	191
Diethyl Carbonate (1) + Ethanol (2)			
0.0386	213	0.4905	1526
0.0742	404	0.5908	1539
0.1074	558	0.6582	1491
0.1382	684	0.7428	1352
0.1940	905	0.7938	1230
0.2428	1065	0.8524	992
0.3248	1279	0.9203	638
0.4194	1444		
Diethyl Carbonate (1) + Propan-1-ol (2)			
0.0488	304	0.5521	1801
0.0931	564	0.6490	1727
0.1335	785	0.7114	1602
0.1704	966	0.7872	1391
0.2356	1251	0.8314	1197
0.2911	1440	0.8809	944
0.3813	1661	0.9367	569
0.4805	1777		
Diethyl Carbonate (1) + Butan-1-ol (2)			
0.0592	386	0.5310	1943
0.0862	556	0.6015	1900
0.1117	712	0.6936	1782
0.1587	980	0.7512	1612
0.2010	1196	0.8191	1359
0.2740	1506	0.8579	1144
0.3346	1699	0.9006	882
0.4300	1890	0.9477	526
Diethyl Carbonate (1) + Hexan-1-ol (2)			
0.0411	289	0.6067	1978
0.0789	547	0.6729	1902
0.1463	980	0.7552	1686
0.2045	1278	0.8044	1494
0.2553	1505	0.8606	1222
0.3396	1782	0.8916	1019
0.4066	1915	0.9250	757
0.5069	2022	0.9611	431
Diethyl Carbonate (1) + Octan-1-ol (2)			
0.0514	327	0.6611	2054
0.0978	623	0.7223	1905
0.1398	889	0.7960	1634
0.1781	1120	0.8387	1415
0.2453	1470	0.8864	1094
0.3024	1713	0.9123	892
0.3940	1996	0.9389	663
0.4642	2124	0.9690	347
0.5652	2174		
Diethyl Carbonate (1) + Decan-1-ol (2)			
0.0468	316	0.5115	2250
0.0614	410	0.6111	2240
0.1158	780	0.7022	2100
0.1641	1088	0.7586	1908
0.2075	1314	0.8250	1620
0.2820	1718	0.8628	1383
0.3437	1930	0.9041	1070
0.4400	2175	0.9497	630

Table 4. Excess Molar Volumes, V^E_m, of Diethyl Carbonate + *n*-Alkanol at 298.15 K

x_1	ρ/g·cm^{-3}	V^E_m/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V^E_m/cm^3·mol^{-1}
Diethyl Carbonate (1) + Methanol (2)					
0.0054	0.789 56	−0.003	0.2783	0.885 23	−0.058
0.0356	0.805 00	−0.014	0.3170	0.893 54	−0.059
0.0663	0.818 98	−0.024	0.3726	0.904 18	−0.058
0.0932	0.830 09	−0.033	0.4430	0.915 81	−0.054
0.1194	0.839 90	−0.037	0.5284	0.927 78	−0.047
0.1610	0.853 92	−0.046	0.6946	0.946 03	−0.022
0.1883	0.862 15	−0.050	0.7905	0.954 44	−0.010
0.2219	0.871 46	−0.055	0.9031	0.962 91	−0.001
0.2527	0.879 21	−0.056			
Diethyl Carbonate (1) + Ethanol (2)					
0.0507	0.803 37	0.009	0.4439	0.898 87	0.104
0.0900	0.816 23	0.018	0.5428	0.924 22	0.120
0.1712	0.839 99	0.032	0.5734	0.919 46	0.126
0.2135	0.850 89	0.050	0.6104	0.924 73	0.129
0.2593	0.861 91	0.062	0.6975	0.936 24	0.130
0.2924	0.869 35	0.070	0.7737	0.945 42	0.124
0.3201	0.875 28	0.077	0.8489	0.953 81	0.105
0.3594	0.883 27	0.086	0.9335	0.962 63	0.061
0.4032	0.891 62	0.094			
Diethyl Carbonate (1) + Propan-1-ol (2)					
0.0202	0.804 89	0.018	0.4535	0.894 91	0.216
0.0432	0.810 76	0.037	0.4948	0.901 66	0.222
0.1249	0.830 53	0.093	0.5224	0.906 05	0.224
0.1563	0.837 64	0.113	0.5490	0.910 17	0.225
0.2008	0.847 34	0.136	0.6954	0.931 34	0.211
0.2550	0.858 57	0.161	0.8145	0.946 94	0.168
0.3094	0.869 25	0.179	0.8531	0.951 76	0.145
0.3461	0.876 11	0.193	0.9806	0.966 94	0.030
0.4185	0.888 97	0.212			
Diethyl Carbonate (1) + Butan-1-ol (2)					
0.0297	0.811 79	0.035	0.5214	0.89 94	0.283
0.0821	0.822 26	0.091	0.5706	0.907 65	0.282
0.2039	0.845 54	0.186	0.6474	0.919 38	0.268
0.2517	0.854 29	0.213	0.6648	0.921 99	0.264
0.2936	0.861 79	0.232	0.7391	0.932 89	0.236
0.3505	0.871 73	0.254	0.8371	0.946 84	0.179
0.3860	0.877 78	0.265	0.8826	0.953 16	0.144
0.4170	0.882 99	0.272	0.9562	0.963 25	0.064
0.4702	0.891 73	0.280			
Diethyl Carbonate (1) + Hexan-1-ol (2)					
0.0251	0.818 63	0.043	0.5422	0.894 78	0.392
0.0776	0.826 00	0.123	0.5883	0.901 93	0.385
0.1872	0.841 65	0.252	0.6481	0.911 30	0.366
0.2258	0.847 25	0.286	0.7052	0.920 37	0.337
0.3136	0.860 16	0.345	0.7840	0.933 06	0.281
0.3667	0.868 07	0.370	0.8671	0.946 67	0.202
0.4239	0.876 68	0.386	0.9265	0.956 62	0.124
0.4706	0.883 77	0.393	0.9721	0.964 37	0.053
0.5024	0.888 65	0.395			
Diethyl Carbonate (1) + Octan-1-ol (2)					
0.0401	0.825 79	0.084	0.6097	0.898 86	0.503
0.0797	0.830 00	0.162	0.6399	0.903 57	0.491
0.1845	0.841 73	0.320	0.7021	0.913 63	0.453
0.2960	0.855 18	0.435	0.7469	0.921 16	0.417
0.3627	0.863 72	0.479	0.8154	0.933 16	0.344
0.4314	0.872 90	0.511	0.8994	0.948 82	0.220
0.4800	0.879 67	0.521	0.9388	0.956 58	0.145
0.5284	0.886 63	0.520	0.9824	0.965 49	0.048
0.5586	0.891 09	0.518			
Diethyl Carbonate (1) + Decan-1-ol (2)					
0.0391	0.829 50	0.097	0.6513	0.900 22	0.602
0.1126	0.835 83	0.258	0.6854	0.905 70	0.578
0.2157	0.845 55	0.430	0.7344	0.913 97	0.534
0.2902	0.853 23	0.521	0.7880	0.923 60	0.469
0.3894	0.864 42	0.600	0.8441	0.934 44	0.375
0.4806	0.875 76	0.634	0.9188	0.950 18	0.219
0.5307	0.882 48	0.639	0.9511	0.957 49	0.139
0.5704	0.888 06	0.634	0.9817	0.964 75	0.052
0.6072	0.893 45	0.623			

The values of a_k, obtained by a least-squares method with all points weighted equally, correspond to the minimum value of the standard deviation $\sigma(Q^E_m)$ defined as

$$\sigma(Q^E_m) = |\Phi/(N - n)|^{0.5} \tag{3}$$

where N is the number of experimental points, n is the number of adjustable parameters, and Φ is the objective function defined as

$$\phi = \sum_{k \geq 0}^{N} {\eta_k}^2 \tag{4}$$

where $\eta = Q^E_{m,calcd} - Q^E_m$, with $Q^E_{m,calcd}$ determined from the right-hand side of eq 2.

Table 5. Adjustable Parameters, a_k, and Standard Deviations, $\sigma(Q_m^E)$, Eq 4, for H_m^E and V_m^E of Diethyl Carbonate (1) + *n*-Alkanols (2) at 298.15 K

alkanol	function	a_0	a_1	a_2	a_3	$\sigma(Q_m^E)$
methanol	H_m^E/J·mol^{-1}	5030.5	1249.8	1354.6	401.3	6.1
	V_m^E/cm^3·mol^{-1}	−0.1922	0.2215	0.2333		0.0008
ethanol	H_m^E/J·mol^{-1}	6092.7	1174.9	1554.0	707.8	6.1
	V_m^E/cm^3·mol^{-1}	0.4571	0.3292	0.1549	0.1619	0.0017
propan-1-ol	H_m^E/J·mol^{-1}	7177.7	804.99	1213.4	1156.2	4.6
	V_m^E/cm^3·mol^{-1}	0.8899	0.2072			0.0017
butan-1-ol	H_m^E/J·mol^{-1}	7777.4	675.99	1176.4	1652.7	7.6
	V_m^E/cm^3·mol^{-1}	1.1261	0.1124	0.2590		0.0017
hexan-1-ol	H_m^E/J·mol^{-1}	8062.8	754.31	1710.5	1709.5	6.4
	V_m^E/cm^3·mol^{-1}	1.5762	0.0283	0.2581		0.0018
octan-1-ol	H_m^E/J·mol^{-1}	8638.3	1309.1	708.99	1764.5	5.8
	V_m^E/cm^3·mol^{-1}	2.0802	0.0720	0.3352	0.1436	0.0020
decan-1-ol	H_m^E/J·mol^{-1}	8991.2	1530.6	1391.3	2280.5	8.4
	V_m^E/cm^3·mol^{-1}	2.5545	0.2167	0.3284		0.0018

Results of least-squares analysis are reported in Table 5.

Both H_m^E and V_m^E increase with the increase of the chain length of alkanol: these results are also shown in Figures 3 and 4 where the equimolar excess functions are plotted against n_c, the number of carbon atoms of alkanol.

Large positive values of H_m^E are in agreement with breaking of hydrogen bonding of alkanols during mixing.

The consequent loosening of intermolecular interactions is also responsible for the positive values of V_m^E, with the exception of methanol, due to its smaller molecular dimensions.

The same results have been observed for the binary mixtures of epoxybutane + alkanols (Comelli and Francesconi, 1996a) and propylene carbonate + alkanols (Comelli and Francesconi, 1996b).

Figure 3 allows drawing some interesting conclusions as to the H_m^E values for different series of compounds in mixtures with dimethyl carbonate. In fact, the curves are nearly parallel to each other, with the highest values for alkanols and lower values for dichloroalkanes and ketones, capable of interactions with alkanols, which reduces the endothermic effect during mixing.

The same figure shows that the contribution to H_m^E of different substituting groups in a linear chain tends to become independent of chain length.

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