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Excess Molar Enthalpies of Diethyl Carbonate + Four Butanol Isomers in the Range (288.15−318.15) K

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Excess molar enthalpies H_m^E of binary mixtures containing diethyl carbonate + 1-butanol, + 2-butanol, + 2-methyl-1-propanol, and + 2-methyl-2-propanol have been determined using a flow microcalorimeter in the range (288.15−318.15) K and at atmospheric pressure. All mixtures are strongly endothermic, with maxima of H_m^E varying from 1900 (mixture containing 1-butanol) to 2550 (mixture containing 2-butanol) J·mol^{-1}. The H_m^E curves are nearly symmetrical and show values increasing as the temperature increases. Data have been correlated using the Redlich−Kister equation, and experimental results have been qualitatively discussed.

Introduction

In this paper excess molar enthalpies H_m^E of binary mixtures containing diethyl carbonate + four butanol isomers, namely 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol, have been determined in the range (288.15−318.15) K and at atmospheric pressure. The aim of this article is to characterize the interactions when the hydroxyl (OH) groups of the alkanols are involved in a mixture with an ester and to emphasize the behavior of structural isomers.

This study continues our latest research program on mixtures containing dialkyl carbonates (Francesconi and Comelli, 1997; Francesconi and Comelli, in press; Comelli et al., in press), owing to their increasing interest as extractive solvents, in industry for the syntheses of many chemicals, in pharmaceuticals, and in agricultural chemistry.

To our knowledge, the H_m^E data presented in this paper are not reported in the literature with the exception of the mixture containing 1-butanol at 298.15 K, whose data have been previously determined (Francesconi and Comelli, 1997) and for which only the least-squares results are here reported. Values for the binary mixture of diethyl carbonate + 2-methyl-2-propanol have been determined only at temperatures ≥303.15 K, the melting point of 2-methyl-2-propanol being ≈298.15 K.

Experimental Section

Diethyl carbonate, an Aldrich product, stated purity +99 mol %, was fractionally distilled over sodium in a Vigreux 20-plates column, and only the middle fraction distilling at constant temperature was collected. The butanol isomers (all Aldrich products with the exception of 2-butanol, which was from Merck) were used without further purification, owing to their high grade of purity. The analyses of the products were performed on a Hewlett-Packard gas chromatograph model 5890 by using an HP (cross-linked 5% ME siloxane) capillary column.

Table 1. Mole Percent Purities, Densities ρ, and Refractive Indices n_D of Pure Components and Comparison with Literature Values at 298.15 K

component (purity, mol %)	ρ/kg·m^{-3} this paper	ρ/kg·m^{-3} lit.	n_D this paper	n_D lit.
diethyl carbonate (99.8)	969.23	969.26[a]	1.3829	1.38287[a]
1-butanol(99.8)	805.77	805.75[a] 805.85[b] 805.83[c]	1.3975	1.39742[a]
2-butanol (99.6)	802.53	802.41[a] 802.4[b] 802.5[c]	1.3952	1.3953[a]
2-methyl-1-propanol (99.5)	797.82	797.8[a] 797.88[b] 797.43[c]	1.3938	1.39389[a]
2-methyl-2-propanol (99.5)	764.84[d]	764.9[a,d]	1.3841[e]	1.3840[a,e]

[a] Riddick et al., 1986. [b] Artigas et al., 1994. [c] Smith and Srivastava, 1986. [d] At 313.15 K. [e] At 300.15 K.

Table 1 lists the purities, the experimental densities ρ, and the refractive indices n_D of all components at 298.15 K in comparison with literature values.

The densities and refractive indices were determined using a digital density meter (Anton Paar, model DMA 60/602, Graz, Austria) and an Abbe refractometer (Carl Zeiss, Jena, Switzerland) showing accuracies of 1×10^{-2} kg·m^{-3} and 1×10^{-4}, respectively.

Before the measurements, the pure liquids were degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy), kept in dark bottles, and dried over molecular sieves (Union Carbide, type 4A, $^{1}/_{16}$ in. pellets).

H_m^E values were determined using a flow microcalorimeter (LKB Produkter, model 2107, Bromma, Sweden). Details about the equipment, the electrical calibration, and the experimental procedure were described previously (Monk and Wadso, 1968; Francesconi and Comelli, 1986).

Two identical automatic burets (ABU, Radiometer, Copenhagen, Denmark) were employed to pump liquids into the

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Table 2. Excess Molar Enthalpies H_m^E for Diethyl Carbonate + Butanol Isomers in the Range (288.15−318.15) 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	$H_m^E/J\cdot mol^{-1}$
Diethyl Carbonate (1) + 1-Butanol (2)							
T/K = 288.15							
0.0305	223	0.5315	1801	0.2012	1139	0.8581	1079
0.0592	412	0.6019	1771	0.2743	1391	0.9007	817
0.0863	586	0.6940	1658	0.3350	1546	0.9558	404
0.1119	723	0.7515	1523	0.4305	1731		
0.1589	962	0.8194	1274				
T/K = 293.15							
0.0305	234	0.5313	1870	0.2012	1219	0.8580	1106
0.0592	434	0.6017	1844	0.2742	1455	0.9007	832
0.0863	607	0.6939	1721	0.3349	1607	0.9477	478
0.1118	748	0.7514	1554	0.4304	1799		
0.1589	1005	0.8193	1295				
T/K = 303.15							
0.0304	260	0.5308	2087	0.2008	1344	0.8578	1215
0.0591	485	0.6013	2056	0.2738	1617	0.9005	914
0.0861	675	0.6934	1903	0.3344	1839	0.9476	521
0.1116	847	0.7510	1723	0.4299	1996		
0.1586	1113	0.8190	1423				
T/K = 308.15							
0.0304	263	0.5306	2106	0.2007	1337	0.8577	1195
0.0591	490	0.6011	2068	0.2736	1643	0.9004	903
0.0841	671	0.6933	1924	0.3343	1825	0.9474	522
0.1115	839	0.7509	1731	0.4297	2045		
0.1585	1144	0.8189	1431				
T/K = 313.15							
0.0304	269	0.5305	2211	0.2006	1412	0.8576	1250
0.0590	496	0.6009	2164	0.2735	1741	0.8972	943
0.0860	707	0.6931	1979	0.3341	1932	0.9476	524
0.1115	886	0.7507	1793	0.4295	2145		
0.1584	1178	0.8188	1474				
T/K = 318.15							
0.0304	278	0.5303	2229	0.2005	1437	0.8575	1254
0.0590	519	0.6008	2178	0.2734	1764	0.9003	921
0.0860	727	0.6930	1987	0.3339	1954	0.9475	529
0.1114	908	0.7506	1804	0.4293	2168		
0.1583	1231	0.8187	1473				
Diethyl Carbonate (1) + 2-Butanol (2)							
T/K = 288.15							
0.0306	308	0.5324	2200	0.2018	1515	0.8786	1029
0.0594	568	0.6027	2140	0.2750	1803	0.9157	761
0.0866	784	0.6947	1937	0.3358	1954	0.9560	419
0.1122	975	0.7521	1734	0.4314	2162		
0.1594	1277	0.8199	1408				
T/K = 293.15							
0.0306	327	0.5322	2210	0.2018	1539	0.8585	1138
0.0594	591	0.6026	2145	0.2749	1840	0.9010	838
0.0866	826	0.6946	1936	0.3357	2049	0.9479	465
0.1122	1022	0.7520	1719	0.4313	2182		
0.1594	1325	0.8198	1370				
T/K = 298.15							
0.0306	319	0.5320	2288	0.2016	1582	0.8584	1241
0.0594	589	0.6025	2227	0.2748	1910	0.9009	930
0.0865	834	0.6945	2008	0.3355	2083	0.9479	529
0.1121	1028	0.7519	1816	0.4310	2239		
0.1593	1342	0.8197	1478				
T/K = 303.15							
0.0306	336	0.5320	2436	0.2016	1670	0.8583	1296
0.0594	623	0.6023	2330	0.2816	2038	0.9009	965
0.0865	866	0.6944	2138	0.3354	2211	0.9479	553
0.1121	1085	0.7518	1907	0.4310	2384		
0.1592	1414	0.8197	1552				
T/K = 308.15							
0.0306	343	0.5319	2446	0.2015	1705	0.8583	1270
0.0595	637	0.6023	2355	0.2746	2060	0.9009	955
0.0865	869	0.6943	2128	0.3354	2254	0.9478	542
0.1120	1100	0.7518	1885	0.4309	2418		
0.1592	1432	0.8196	1548				

Table 2 (Continued)

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
Diethyl Carbonate (1) + 2-Butanol (2)							
T/K = 313.15							
0.0306	346	0.5318	2526	0.2015	1744	0.8583	1308
0.0593	642	0.6022	2426	0.2746	2118	0.9008	972
0.0864	898	0.6943	2181	0.3353	2302	0.9478	548
0.1120	1125	0.7517	1938	0.4308	2509		
0.1591	1483	0.8196	1573				
T/K = 318.15							
0.0306	339	0.5318	2541	0.2014	1758	0.8582	1266
0.0593	631	0.6022	2455	0.2745	2118	0.9008	936
0.0864	887	0.6942	2164	0.3353	2366	0.9478	521
0.1120	1096	0.7517	1926	0.4308	2552		
0.1591	1470	0.8195	1537				
Diethyl Carbonate (1) + 2-Methyl-1-Propanol (2)							
T/K = 288.15							
0.0308	267	0.5340	2015	0.2029	1338	0.8593	1147
0.0598	491	0.6043	1985	0.2763	1618	0.9016	865
0.0871	682	0.6961	1810	0.3373	1773	0.9563	425
0.1129	836	0.7534	1632	0.4330	1961		
0.1603	1116	0.8209	1371				
T/K = 293.15							
0.0308	280	0.5338	2099	0.2028	1405	0.8592	1155
0.0598	519	0.6041	2032	0.2762	1699	0.9016	873
0.0871	733	0.6960	1891	0.3371	1881	0.9482	499
0.1128	891	0.7532	1684	0.4328	2067		
0.1602	1186	0.8208	1389				
T/K = 298.15							
0.0308	285	0.5335	2148	0.2026	1423	0.8591	1183
0.0597	526	0.6039	2088	0.2759	1713	0.9015	894
0.0870	734	0.6958	1911	0.3369	1882	0.9482	510
0.1127	924	0.7530	1705	0.4325	2081		
0.1601	1203	0.8206	1412				
T/K = 303.15							
0.0308	308	0.5335	2268	0.2026	1537	0.8591	1265
0.0597	570	0.6038	2217	0.2828	1871	0.9014	954
0.0870	784	0.6957	2025	0.3368	2034	0.9482	544
0.1127	988	0.7530	1817	0.4191	2176		
0.1600	1308	0.8206	1503				
T/K = 308.15							
0.0307	309	0.5333	2340	0.2025	1567	0.8590	1256
0.0597	573	0.6037	2279	0.2758	1903	0.9014	943
0.0869	821	0.6956	2073	0.3367	2090	0.9481	531
0.1126	988	0.7529	1848	0.4323	2298		
0.1600	1337	0.8205	1497				
T/K = 313.15							
0.0307	312	0.5333	2410	0.2024	1616	0.8583	1269
0.0596	583	0.6036	2325	0.2757	1974	0.9013	938
0.0869	818	0.6955	2095	0.3366	2158	0.9481	527
0.1126	1022	0.7528	1861	0.4322	2374		
0.1599	1355	0.8204	1514				
T/K = 318.15							
0.0307	317	0.5331	2440	0.2023	1631	0.8589	1256
0.0596	590	0.6034	2360	0.2756	1998	0.9013	941
0.0868	827	0.6954	2101	0.3364	2191	0.9481	530
0.1125	1035	0.7527	1902	0.4321	2404		
0.1598	1372	0.8203	1532				
Diethyl Carbonate (1) + 2-Methyl-2-Propanol (2)							
T/K = 303.15							
0.0315	343	0.5391	2342	0.2063	1673	0.8618	1221
0.0610	635	0.6092	2245	0.2875	2000	0.9034	910
0.0888	866	0.7005	2024	0.3419	2169	0.9493	519
0.1150	1092	0.7572	1809	0.4381	2349		
0.1631	1425	0.8239	1472				
T/K = 308.15							
0.0315	337	0.5393	2338	0.2064	1638	0.8619	1212
0.0610	623	0.6094	2245	0.2806	1978	0.9035	897
0.0889	841	0.7006	2015	0.3420	2159	0.9493	507
0.1150	1070	0.7573	1793	0.4382	2326		
0.1632	1409	0.8240	1435				

Table 2 (Continued)

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
			Diethyl Carbonate (1) + 2-Methyl-2-Propanol (2)				
			T/K = 313.15				
0.0315	318	0.5395	2358	0.2065	1614	0.8620	1220
0.0611	592	0.6096	2268	0.2808	1967	0.9036	902
0.0889	840	0.7008	2033	0.3422	2158	0.9493	504
0.1151	1031	0.7574	1799	0.4384	2337		
0.1633	1368	0.8214	1449				
			T/K = 318.15				
0.0323	321	0.5461	2336	0.2109	1623	0.8651	1182
0.0626	597	0.6159	2241	0.2862	1965	0.9059	864
0.0911	811	0.7064	1993	0.3482	2157	0.9506	486
0.1179	1027	0.7623	1769	0.4450	2333		
0.1670	1371	0.8279	1421				

Table 3. Adjustable Parameters a_k of Eq 1 and Standard Deviation $\sigma(H_m^E)$ in the Range (288.15−318.15) K for Diethyl Carbonate + Butanol Isomers

T/K	a_0	a_1	a_2	a_3	$\sigma(H_m^E)$/J·mol^{-1}	T/K	a_0	a_1	a_2	a_3	$\sigma(H_m^E)$/J·mol^{-1}
					Diethyl Carbonate (1) + 1-Butanol (2)						
288.15	7139.3	1077.5	1740.5	120.2	5.6	308.15	8401.1	949.4	1509.2		8.5
293.15	7431.0	1011.1	1675.0		9.4	313.15	8825.9	843.0	1309.7		7.5
298.15	7774.5[a]	676.0[a]	1176.4[a]	1652.7[a]	7.6[a]	318.15	8892	698.7	1458.4		8.6
303.15	8305.0	1002.2	1681.8		9.4						
					Diethyl Carbonate (1) + 2-Butanol (2)						
288.15	8795.3	376.5	1621.0	−715.5	9.3	308.15	9833.2	−239.4	1666.2		8.4
293.15	8893.3	82.6	1523.3	−1013.5	6.8	313.15	10140.7	−270.6	1546.0		6.5
298.15	9164.1	59.0	1970.6		6.9	318.15	10298.1	−459.0	833.7		9.2
303.15	9724.5	12.4	1849.7		8.5						
					Diethyl Carbonate (1) + 2-Methyl-1-propanol (2)						
288.15	8041.4	748.9	1708.8		8.9	308.15	9374.9	334.7	1511.5		8.9
293.15	8408.0	497.4	1626.2		9.1	313.15	9652.3	157.1	1200.1	6.4	
298.15	8521.1	558.4	1700.7		9.3	318.15	9781.6	121.1	1130.6	8.6	
303.15	9044.7	489.9	2037.2		8.0						
					Diethyl Carbonate (1) + 2-Methyl-2-propanol (2)						
303.15	9422.5	−183.5	1877.7		8.4	313.15	9476	21.5	1213.5		7.4
308.15	9404.1	−162.4	1583.3		7.6	318.15	9428	94.5	1.28.0		8.1

[a] Francesconi and Comelli, 1997.

mixing cell of the apparatus. The temperature inside the equilibrium cell was measured with a precision of ±0.01 K by means of an electronic unit. Mole fractions x_1 of diethyl carbonate (component 1) were determined from the calibrated flow rates and were estimated to be precise to 1 $\times$ 10^{-4}, which lead to errors in H_m^E less than 1%.

Before measurements, the apparatus with its equipment was tested with the standard mixture cyclohexane + hexane, and our results, compared with those of the literature (Gmehling, 1993), showed an accuracy better than 0.5% at the maximum of the thermal effect.

Results and Discussion

Results of the H_m^E measurements are shown in Table 2. Correlation of the binary mixtures was carried out using the Redlich−Kister polynomial

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

and a least-squares procedure with all points weighted equally was used to obtain the adjustable parameters a_k and the standard deviations $\sigma(H_m^E)$, which are reported in Table 3.

Figure 1 shows a graphical example of the four mixtures at 313.15 K while Figure 2 represents the equimolar H_m^E (x = 0.5) as a function of the temperature for all binary mixtures.

As can be seen, all experimental data are positive, showing symmetrical curves with maximum values of H_m^E varying in the range (1900−2550) J·mol^{-1} . All H_m^E values increase strongly as the temperature increases, with the exception of those for the mixture containing 2-methyl-2-propanol, for which this increase is negligible.

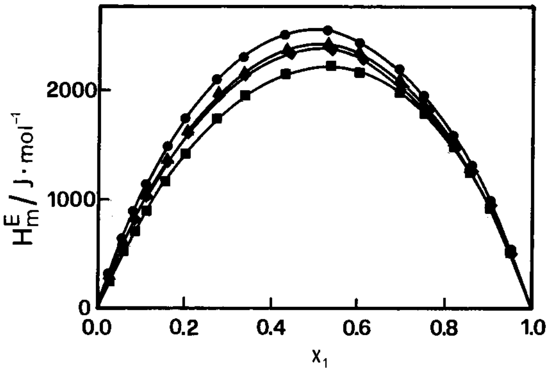

Figure 1. Excess molar enthalpies H_m^E for binary mixtures of diethyl carbonate + butanol isomers at 313.15 K. ■, ◆, ▲, and ● refer to mixtures containing 1-butanol, 2-methyl-2-propanol, 2-methyl-1-propanol, and 2-butanol, respectively. Solid curves, Redlich−Kister equation.

The mixtures containing unbranched 1-butanol and 2-butanol have H_m^E values in the order 2-butanol > 1-butanol, whereas the values for branched isomers are in between those for 2-butanol and 1-butanol. These results match the ones referring to mixtures containing dimethyl carbonate and the same butanol isomers (Francesconi and Comelli, in press).

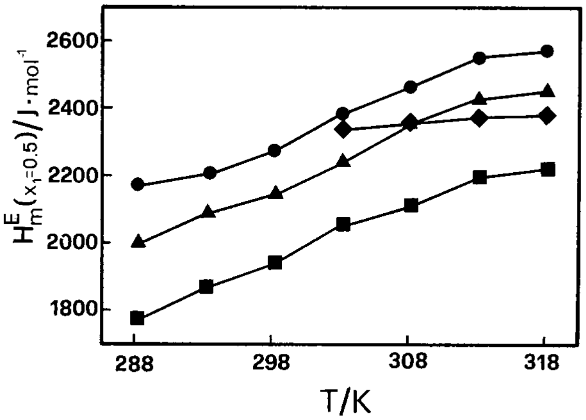

Figure 2. Values of equimolar excess molar enthalpies H_m^E ($x_1 = 0.5$) as a function of the temperature of experience of diethyl carbonate + butanol isomers. ■, ▲, ◆, and ● refer to mixtures containing 1-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, and 2-butanol, respectively.

If we consider that the molecular interactions such as dipole−dipole and hydrogen bond interactions and also steric hindrances, which are surely present in the mixtures of this paper, are negatively influenced by a temperature increase, then the positive dependence observed for H_m^E seems to indicate a larger influence of temperature on the ester−alkanol interaction energy E_{12}, if the approximate expression $H_m^E \propto E_{11} + E_{22} - 2E_{12}$ is assumed for the overall thermal effect, with *ij* referring to molecules *i* and *j*.

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