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Excess Molar Enthalpy of Binary Mixtures of Diethyl Carbonate + Nine Chloroalkanes at 298.15 K and Atmospheric Pressure

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Excess molar enthalpies, H^E_m, of binary mixtures of diethyl carbonate + nine chloroalkanes have been determined at 298.15 K and atmospheric pressure by using a flow isothermal microcalorimeter. The H^E_m values range from a minimum value of -2600 J mol^{-1} up to 340 J mol^{-1}. In the case of diethyl carbonate + dichloroalkanes, H^E_m increases with the increase of the chain length of the dichloro compound. Experimental data have been correlated by means of the Redlich−Kister equation, and adjustable parameters have been evaluated by the least-squares method.

Introduction

Esters of carbonic acid are used in the synthesis of pharmaceuticals and agricultural chemicals and as solvents for many synthetic and natural resins (*1*−*3*). Despite the extensive industrial applications of carbonic acid esters, few data are available and are increasing only in recent years.

The aim of this research is to determine and correlate a series of experimental data of binary mixtures containing carbonates, that is, diethyl carbonate (common component, component 1) + nine chloroalkanes (noncommon components, component 2), namely dichloromethane, 1,2-dichloroethane, 1,2-dichloropropane, 1,3-dichloropropane, 1,4-dichlorobutane, 1,6-dichlorohexane, 1,10-dichlorodecane, 1,1,1-trichloroethane and, 1,1,2,2-tetrachloroethane, respectively.

These measurements will improve the H^E_m data bank and further the understanding of the thermodynamic properties of the above mentioned-mixtures.

To our knowledge no data exist on calorimetric study of these systems: Garcia et al. (*4*) have determined the excess molar enthalpies of diethyl carbonate with alkanes, cyclohexane, benzene, toluene, and tetrachloromethane.

Experimental Section

Materials. All liquids were supplied from Aldrich with the exception of 1,2-dichloropropane, which was from Fluka: their purities were ≥99 mol % with the exception of 1,6-dichlorohexane (98 mol %), which was purified according to the method of Walden and Gloy (*5*). For the other components, owing to their high-grade purity, no further purification was made.

Before measurements, all liquids were stored in dark bottles over molecular sieves (Union Carbide type 4A, 1/16-in. pellets).

Apparatus and Procedure. All measurements were made at (298.15 ± 0.01) K and atmospheric pressure.

The experimental densities, ϱ, necessary to determine fluxes and hence mole fractions of mixtures, are given in Table 1 and are compared with literature values (*6*−*13*). All measurements were determined with an estimated accuracy of 5×10^{-5} g cm^{-3} by using a digital density meter (Anton Paar, Model 60/602, Graz, Austria) with a resolution of 1×10^{-6} g cm^{-3}. The apparatus and the operating procedure are well described elsewere (*14*).

Table 1. Densities, ϱ, of Pure Chemicals and Comparison with Literature Values at 298.15 K and Atmospheric Pressure

	ϱ/(g cm^{-3})	
component	exptl	lit.
diethyl carbonate	0.969 30	0.969 26 (*6*)
dichloromethane	1.316 11	1.316 3 (*7*)
1,2-dichloroethane	1.245 62	1.245 8 (*7*)
1,2-dichloropropane	1.149 47	1.149 36 (*6*)
1,3-dichloropropane	1.180 79	1.180 25 (*8*)
1,4-dichlorobutane	1.133 86	1.133 12 (*9*)
1,6-dichlorohexane	1.064 12	1.064 65 (*10*)
1,10-dichlorodecane	0.992 92	0.994 5 (*11*)
1,1,1-trichloroethane	1.329 72	1.329 93 (*12*)
1,1,2,2-tetrachloroethane	1.588 23	1.588 37 (*13*)

An LKB isothermal flow-microcalorimeter (LKB, Produckter AB, Bromma, Sweden) equipped with two solvent automatic burets ABU (ABU, Radiometer, Copenhagen, Denmark) was used for the calorimetric measurements. Details of the equipment and its operations have been given previously (*15*, *16*).

The microcalorimeter was calibrated before each set of measurements by employing the standard mixture cyclohexane + hexane (*17*). The errors in the excess molar enthalpy values were estimated to be less than 0.5% over the central mole fraction range and in the order of 0.5 J mol^{-1}.

The temperature in the circulator bath was kept constant to within ±0.01 K and the estimated error in the mole fraction is $\delta x = \approx 0.0005$.

Results and Discussion

The H^E_m values are reported in Table 2 and graphically represented in Figures 1 and 2.

The composition dependence of H^E_m was correlated by the Redlich−Kister equation

$$H^E_m/(\mathrm{J\ mol^{-1}}) = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \qquad (1)$$

where x_1 is the mole fraction of diethyl carbonate. The a_k

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Table 2. Excess Molar Enthalpies, H_m^E, Adjustable Parameters, a_k, and Standard Deviation, $\sigma(H_m^E)$, at 298.15 K for Diethyl Carbonate + Chloroalkanes

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) + Dichloromethane (2)							
0.0216	−82	0.1500	−558	0.5144	−1087	0.8641	−426
0.0423	−172	0.2093	−736	0.6137	−985	0.9271	−233
0.0621	−250	0.2609	−847	0.6793	−871		
0.0811	−317	0.3462	−994	0.7606	−712		
0.1169	−459	0.4428	−1089	0.8227	−570		
$a_0 = -4334.2$; $a_1 = 489.5$; $a_2 = 634.0$; $\sigma(H_m^E)/(J\ mol^{-1}) = 9.9$							
Diethyl Carbonate (1) + 1,2-Dichloroethane (2)							
0.0264	−36	0.1785	−248	0.5659	−431	0.8867	−139
0.0515	−72	0.2458	−323	0.6617	−382	0.9399	−78
0.0753	−108	0.3029	−371	0.7228	−333		
0.0980	−142	0.3946	−432	0.7964	−255		
0.1401	−196	0.4945	−442	0.8391	−203		
$a_0 = -1791.2$; $a_1 = 107.6$; $a_2 = 461.2$; $\sigma(H_m^E)/(J\ mol^{-1}) = 3.0$							
Diethyl Carbonate (1) + 1,2-Dichloropropane (2)							
0.0317	−52	0.2074	−284	0.6109	−359	0.9041	−105
0.0614	−101	0.2819	−347	0.7020	−299	0.9496	−53
0.0894	−140	0.3436	−386	0.7585	−252		
0.1157	−177	0.4398	−401	0.8249	−189		
0.1641	−236	0.5409	−386	0.8627	−147		
$a_0 = -1601.0$; $a_1 = 334.7$; $a_2 = 213.4$; $\sigma(H_m^E)/(J\ mol^{-1}) = 2.3$							
Diethyl Carbonate (1) + 1,3-Dichloropropane (2)							
0.0317	−24	0.2074	−143	0.6109	−197	0.9041	−59
0.0614	−47	0.2819	−174	0.7020	−169	0.9496	−31
0.0894	−69	0.3436	−195	0.7585	−143		
0.1157	−87	0.4398	−216	0.8249	−104		
0.1641	−115	0.5409	−212	0.8627	−86		
$a_0 = -860.6$; $a_1 = 90.5$; $a_2 = 154.4$; $\sigma(H_m^E)/(J\ mol^{-1}) = 1.5$							
Diethyl Carbonate (1) + 1,4-Dichlorobutane (2)							
0.0369	−18	0.2345	−109	0.6477	−158	0.9169	−51
0.0711	−33	0.3149	−136	0.7339	−138	0.9567	−27
0.1030	−51	0.3799	−153	0.7862	−117		
0.1328	−68	0.4789	−171	0.8466	−89		
0.1868	−89	0.5797	−167	0.8803	−73		
$a_0 = -681.7$; $a_1 = -87.4$; $a_2 = 112.6$; $\sigma(H_m^E)/(J\ mol^{-1}) = 1.1$							
Diethyl Carbonate (1) + 1,6-Dichlorohexane (2)							
0.0474	−3.0	0.2850	13.5	0.7051	42.1	0.9349	13.5
0.0906	−2.9	0.3742	20.9	0.7820	38.7	0.9663	7.4
0.1300	−0.7	0.4435	28.2	0.8271	33.4		
0.1661	1.5	0.5446	36.5	0.8777	26.9		
0.2301	7.7	0.6421	41.6	0.9054	21.2		
$a_0 = 131.5$; $a_1 = 167.2$; $a_2 = 45.5$; $a_3 = 0$; $a_4 = -130.6$; $\sigma(H_m^E)/(J\ mol^{-1}) = 0.5$							
Diethyl Carbonate (1) + 1,10-Dichlorodecane (2)							
0.0678	53	0.3678	273	0.7773	283	0.9544	84
0.1271	96	0.4660	315	0.8396	231	0.9767	45
0.1791	143	0.5378	333	0.8747	194		
0.2253	182	0.6357	333	0.9129	146		
0.3038	235	0.7237	314	0.9332	118		
$a_0 = 1304.6$; $a_1 = 573.7$; $a_2 = 74.9$; $\sigma(H_m^E)/(J\ mol^{-1}) = 3.3$							
Diethyl Carbonate (1) + 1,1,1-Trichloroethane (2)							
0.0331	−29	0.2153	−149	0.6221	−177	0.9081	−43
0.0686	−55	0.2916	−176	0.7118	−145	0.9518	−21
0.0933	−78	0.3543	−193	0.7670	−119		
0.1206	−98	0.4515	−206	0.8440	−78		
0.1707	−124	0.5526	−192	0.8682	−66		
$a_0 = -807.0$; $a_1 = 167.0$; $a_2 = 139.9$; $a_3 = 98.1$; $\sigma(H_m^E)/(J\ mol^{-1}) = 1.6$							
Diethyl Carbonate (1) + 1,1,2,2-Tetrachloroethane (2)							
0.0349	−322	0.2242	−1885	0.6343	−2266	0.9123	−626
0.0674	−617	0.3024	−2280	0.7223	−1832	0.9542	−344
0.0978	−893	0.3663	−2537	0.7762	−1539		
0.1262	−1141	0.4644	−2606	0.8388	−1163		
0.1782	−1563	0.5655	−2476	0.8740	−924		
$a_0 = -10417.8$; $a_1 = 2172.9$; $a_2 = 1972.1$; $a_3 = -1425.4$; $\sigma(H_m^E)/(J\ mol^{-1}) = 13.9$							

adjustable parameters were obtained by least-squares method and are collected in Table 2, together with the standard deviation $\sigma(H_m^E)$ defined as in ref 16.

Curves calculated from eq 1 are included in Figures 1 and 2 with a solid line.

Figure 1 shows the gradual increase of H_m^E when the number of carbon atoms passes from 1 to 10. Curves c and d compare the data of 1,2-dichloro- and 1,3-dichloropropane and emphasize the larger values of H_m^E for the latter dichloro compound.

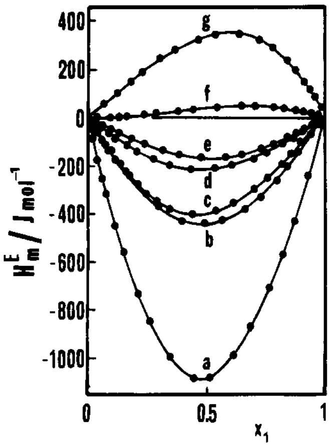

Figure 1. Excess molar enthalpies, H^E_m, at 298.15 K for the binary mixtures containing diethyl carbonate + dichloroalkanes: a–g refer to diethyl carbonate + dichloromethane, + 1,2-dichloroethane, + 1,2-dichloropropane, + 1,3-dichloropropane, + 1,4-dichlorobutane, + 1,6-dichlorohexane, + 1,10-dichlorodecane, respectively. (●) Experimental points; solid curves, calculated from eq 1 using parameters a_k of Table 2.

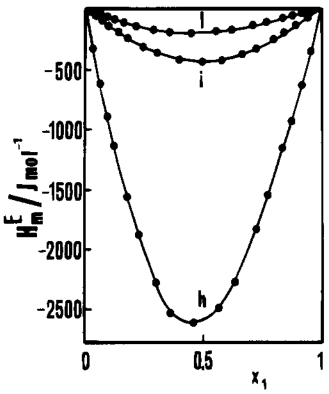

Figure 2. Excess molar enthalpies, H^E_m, at 298.15 K for the binary mixtures containing diethyl carbonate + chloroethanes: h, i, and l refer to diethyl carbonate + 1,1,2,2-tetrachloroethane, + 1,2-dichloroethane, and + 1,1,1-trichloroethane, respectively. (●) Experimental points; solid curves, calculated from eq 1 using parameters a_k of Table 2.

As can be seen from Figure 2, substitution of Cl atoms in the ethane molecule leads to decreased values of H^E_m in the order tetra- < di- < trichloroethane.

Figure 3 shows H^E_m ($x_1 = 0.5$), the equimolar excess enthalpies for diethyl carbonate + dichloroalkanes against the number of carbon atoms, n_C, of dichloroalkanes. This figure shows the H^E_m data for the 1,3-dichloropropane and not for the 1,2-dichloropropane. The dashed line refers to diethyl carbonate + alkanes (*4*).

We see that substitution of the two H atoms by Cl atoms at chain ends causes the same H^E_m decrease, at least for $n_C \geq 5$.

The complexity in the molecular structure of the mixtures here studied may justify our failure in the attempts of giving even a qualitative explanation of the above results.

In fact, hydrogen bonding of the type O–H–C, existing between the O atom of the ester and the C atom of the chloroalkanes, is too feeble (*18*) as to give rise to H^E_m values up to 2500 J mol^{-1}, even if the inductive effect of Cl atoms is allowed.

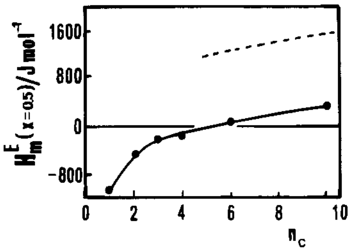

Figure 3. Values of equimolar enthalpies, H^E_m ($x = 0.5$) at 298.15 K as a function of the number of carbon atoms in the dichloroalkanes, n_C, for the binary mixtures containing diethyl carbonate + dichloroalkanes. This figure shows the H^E_m data for 1,3-dichloropropane and not for 1,2-dichloropropane. Dashed lines refer to diethyl carbonate + alkanes, see ref 4.

Also, an analysis of the dipole moments of the compounds was unable to account for the large H^E_m values (*6, 19*).

Most probably, both hydrogen bonding and dipole–dipole interactions, in addition to a deep change in the molecular structure on mixing, occur, which also makes difficult a qualitative insight into the molecular interpretation of the results.

Finally, it is interesting to compare the data of Figures 1 and 2 with the H^E_m data of diethyl carbonate + tetrachloromethane, the latter mixture showing a very small calorimetric effect, not exceeding 80 J mol^{-1}, in agreement with the zero dipole moment of tetrachloromethane and the absence of hydrogen bonding between this molecule and diethyl carbonate.

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