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Excess molar enthalpies of diethyl carbonate + fourteen *n*-alkyl alkanoates at 298.15 K

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Abstract

Excess molar enthalpies of binary mixtures containing diethyl carbonate + fourteen *n*-alkyl alkanoates (six acetates, four propanoates and four butyrates) have been determined at 298.15 K and at atmospheric pressure using an LKB flow microcalorimeter. The experimental data have been fitted to the Redlich–Kister equation to estimate the binary parameters. The results have been qualitatively discussed. © 1997 Elsevier Science B.V.

Keywords: Calorimeter; Data correlation; Enthalpy

1. Introduction

This contribution is part of a continuing research program of determination of the thermodynamic properties of binary mixtures containing dialkyl carbonates [1–3], used as solvents for a variety of extractions of industrial interest, in the synthesis of pharmaceuticals and agricultural chemistry. In this paper, we report experimental data on excess molar enthalpy, H_m^E, of diethyl carbonate, as common component (component 1), with fourteen *n*-alkyl alkanoates which are six acetates (methyl → hexyl acetate), four propanoates (methyl → butyl propanoate) and four butyrate (methyl → butyl butyrate).

No data have been found for these mixtures in literature.

2. Experimental

2.1. Chemicals

Table 1 collects the origin and the stated purities of the chemicals which were used as received. The stated purity of all chemicals is ≥ 99 mol% and no further purification was carried out: a GLC analysis did not detect any appreciable impurity peak. Purities were also checked by determining their densities, ρ, at 293.15 or 298.15 K and are reported in Table 2 in comparison with literature data [4–9].

Densities have been determined using a density meter (Anton Paar, model 60/602, Graz, Austria) with an accuracy of 1×10^{-5} g cm^{-3}.

Before measurements, the chemicals were kept in dark bottles, dried over molecular sieves (Union Carbide, type 4A, 1/16-in pellets) and degassed prior

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Table 1
Origins and stated purities of the pure components

Component	Origin	Stated purity/mol%
Diethyl carbonate	Aldrich	> 99
Methyl acetate	Fluka	> 99
Ethyl acetate	Fluka	> 99.5
Propyl acetate	Aldrich	99
Butyl acetate	Aldrich	99.7
Pentyl acetate	Aldrich	99
Hexyl acetate	Aldrich	99
Methyl propanoate	Aldrich	99
Ethyl propanoate	Aldrich	99
Propyl propanoate	Aldrich	99
Butyl propanoate	Aldrich	99
Methyl butyrate	Aldrich	99
Ethyl butyrate	Aldrich	99
Propyl butyrate	Aldrich	99
Butyl butyrate	Fluka	> 99

to actual measurements by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy).

2.2. *Calorimetric measurements*

Experimental excess molar enthalpies, H^E_m, have been determined at 298.15 K and at atmospheric pressure.

An LKB flow microcalorimeter (LKB Produkter, model 2107, Bromma, Sweden) equipped with two automatic solvent pumps (ABU, Radiometer, Copenhagen, Denmark) necessary to pump pure liquids into the mixing cell of the calorimeter, were used for the measurements of the excess molar enthalpies of the mixtures. Details of calibration and operating procedure have been previously reported [10,11]. The instrument was thermostated to 298.15 ± 0.01 K and controlled by calibrated transistors inside the calorimeter.

Table 2
Comparison between measured densities, ρ, and literature data for pure components

		ρ/g cm^{-3}	
Component	T/K	This paper	Lit.
Diethyl carbonate	298.15	0.96924	0.96926 [4]
Methyl acetate	298.15	0.92663	0.9270 [5]
Ethyl acetate	298.15	0.89438	0.8943 [6]
Propyl acetate	298.15	0.88333	0.8831 [7]
Butyl acetate	298.15	0.87620	0.87634 [4]
Pentyl acetate	298.15	0.87209	0.8719 [4]
Hexyl acetate	298.15	0.86856	0.86843 [8]
Methyl propanonate	293.15	0.91489	0.9150 [9]
Ethyl propanonate	298.15	0.88432	0.8840 [4]
Propyl propanonate	293.15	0.88111	0.8809 [9]
Butyl propanoate	293.15	0.87543	0.8754 [9]
Methyl butyrate	293.15	0.89850	0.8984 [9]
Ethyl butyrate	298.15	0.87356	0.87394 [4]
Propyl butyrate	293.15	0.87293	0.8730 [9]
Butyl butyrate	293.15	0.86960	0.8700 [9]

The mole fractions x_1 of diethyl carbonate were determined from fluxes and are accurate to ± 0.0002 and the errors in H^E_m are estimated to be in the range 0.5–1 J mol^{-1}.

The test mixture hexane + cyclohexane was used to check the calorimeter and our results show a discrepancy of less than 0.5% from those of literature [12].

3. Correlation of the calorimetric data

Table 3 summarizes the experimental data of x_1 and H^E_m while Figs. 1–3 show their graphical representation.

The Redlich–Kister polynomial

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

was fitted to each set of results in Table 3 by the

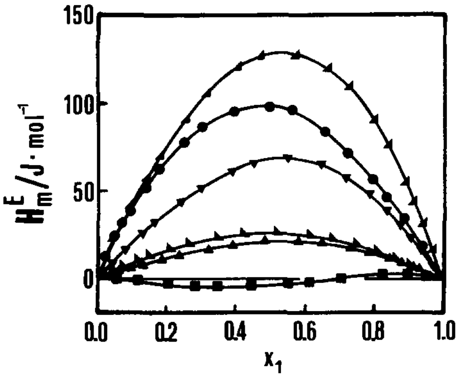

Fig. 1. Excess molar enthalpies, H^E_m, of diethyl carbonate(1) + methyl acetate(2)(●), + ethyl acetate(2)(■), + propyl acetate(2)(▲), + butyl acetate(2)(◣), + pentyl acetate(2)(▼), + Hexyl Acetate(2)(◢) at 298.15 K. Solid curves, calculated by Eq. (1).

Table 3
Mole fractions, x_1, and excess molar enthalpies, H^E_m, of diethyl carbonate(1) + *n*-alkyl alkanoates(2) at 298.15 K

x_1	H^E_m/J mol^{-1}	x_1	H^E_m/J mol^{-1}
Diethyl carbonate(1) + methyl acetate(2)			
0.0266	12	0.4960	98
0.0518	22	0.5674	95
0.0758	32	0.6631	82
0.0985	39	0.7240	71
0.1409	53	0.7974	56
0.1794	62	0.8399	46
0.2470	78	0.8873	34
0.3042	86	0.9403	19
0.3961	94		
Diethyl carbonate(1) + ethyl acetate(2)			
0.0326	−0.3	0.5480	−2.8
0.0631	−1.1	0.6178	−1.7
0.1187	−1.7	0.7080	0.4
0.2122	−3.6	0.8291	2.3
0.2878	−4.4	0.9065	2.3
0.3501	−4.3	0.9510	1.6
0.4470	−4.0		
Diethyl carbonate(1) + propyl acetate(2)			
0.0380	1.6	0.5873	21.0
0.0732	3.6	0.6548	19.9
0.1060	5.6	0.7400	17.7
0.1365	7.3	0.7914	15.1
0.1917	10.5	0.8506	11.1
0.2402	12.2	0.8836	8.6
0.3217	16.3	0.9193	6.4
0.3874	18.2	0.9579	3.4
0.4868	20.9		
Dietyl carbonate(1) + butyl acetate(2)			
0.0433	3.1	0.6200	23.9
0.0831	6.3	0.6850	22.0
0.1197	9.6	0.7492	18.3
0.1534	12.2	0.8131	15.8
0.2138	15.7	0.8671	11.5
0.2660	19.0	0.8969	8.6
0.3522	22.7	0.9288	6.3
0.4203	24.3	0.9631	3.3
0.5210	25.4		
Diethyl carbonate(1) + pentyl acetate(2)			
0.0485	9	0.6474	64
0.0926	17	0.7100	59
0.1327	25	0.7860	48
0.1694	32	0.8304	40
0.2343	42	0.8802	30
0.2898	51	0.9073	23
0.3797	62	0.9363	16
0.4493	65	0.9671	9
0.5504	68		

Table 3 (*Continued*)

x_1	H^E_m/J mol^{-1}	x_1	H^E_m/J mol^{-1}
Dietyl carbonate(1) + hexyl acetate(2)			
0.0537	23	0.6714	120
0.1019	42	0.7315	108
0.1455	57	0.8034	89
0.1850	70	0.8449	76
0.2540	90	0.8910	53
0.3123	105	0.9159	44
0.4052	120	0.9424	30
0.4759	128	0.9703	15
0.5767	127		
Diethyl carbonate(1) + methyl propanoate(2)			
0.0318	6	0.5425	49
0.0617	11	0.6125	48
0.0898	16	0.7033	43
0.1163	19	0.7596	36
0.1648	25	0.8258	28
0.2085	30	0.8634	21
0.2832	36	0.9046	15
0.3450	41	0.9499	8
0.4415	47		
Diethyl carbonate(1) + ethyl propanoate(2)			
0.0732	−0.6	0.6546	−2.9
0.1364	−1.1	0.7398	−1.7
0.2400	−3.0	0.7912	−1.2
0.3215	−3.8	0.8504	−0.5
0.3871	−4.5	0.8835	−0.2
0.4865	−4.4	0.9192	−0.1
0.5870	−3.7		
Diethyl carbonate(1) + propyl propanoate(2)			
0.0431	7	0.6187	46
0.0827	14	0.6839	41
0.1191	19	0.7644	33
0.1527	23	0.8123	27
0.2128	31	0.8665	18
0.2650	36	0.8964	14
0.3510	43	0.9285	9
0.4190	46	0.9629	4
0.5196	48		
Diethyl carbonate(1) + butyl propanoate(2)			
0.0342	12	0.6468	94
0.0923	30	0.7093	87
0.1323	44	0.7854	72
0.1690	54	0.8299	60
0.2338	69	0.8798	43
0.2891	80	0.9071	33
0.3789	93	0.9361	26
0.4486	99	0.9670	14
0.5497	103		

Table 3 (*Continued*)

x_1	H_m^E/J mol^{-1}	x_1	H_m^E/J mol^{-1}
Diethyl carbonate(1) + methyl butyrate(2)			
0.0721	1.3	0.5831	8.2
0.1345	2.8	0.6510	8.6
0.2371	4.5	0.7367	7.9
0.3180	5.8	0.8484	5.5
0.3834	6.4	0.9180	3.4
0.4826	8.1	0.9572	1.9
Diethyl carbonate(1) + ethyl butyrate(2)			
0.0435	6	0.6208	33
0.0833	11	0.6857	31
0.1200	15	0.7660	25
0.1538	19	0.8136	21
0.2143	24	0.8675	16
0.2667	28	0.8972	12
0.3530	33	0.9290	9
0.4211	34	0.9632	5
0.5219	35		
Diethyl carbonate(1) + propyl butyrate(2)			
0.0485	18	0.6473	94
0.0925	32	0.7099	88
0.1327	45	0.7859	71
0.1694	54	0.8304	60
0.2342	70	0.8801	47
0.2897	83	0.9073	34
0.3796	96	0.9362	26
0.4493	101	0.9671	14
0.5503	101		
Diethyl carbonate(1) + butyl butyrate(2)			
0.0536	25	0.6712	144
0.1018	48	0.7313	131
0.1454	66	0.8032	107
0.1848	85	0.8448	88
0.2538	111	0.8909	65
0.3120	131	0.9159	50
0.4049	151	0.9423	35
0.4756	160	0.9703	18
0.5764	157		

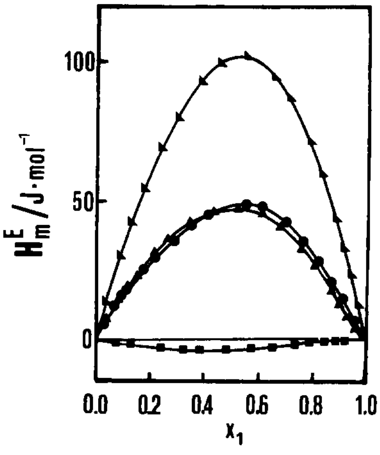

Fig. 2. Excess molar enthalpies, H_m^E, of diethyl carbonate(1) + methyl propanoate(2)(●), + ethyl propanoate(2)(■), + propyl propanoate(2)(▲), + butyl propanoate(2)(◣) at 298.15 K. Solid curves, calculated by Eq. (1).

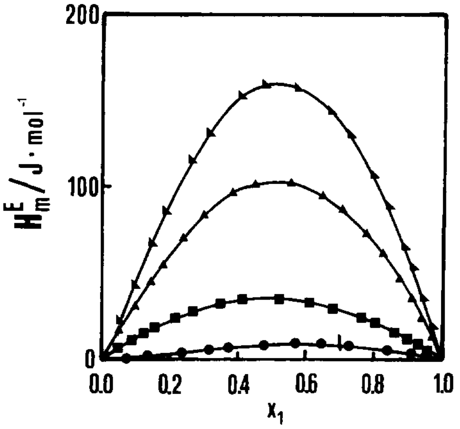

Fig. 3. Excess molar enthalpies, H_m^E, of diethyl carbonate(1) + methyl butyrate(2)(●), + ethyl butyrate(2)(■), + propyl butyrate(2)(▲), + butyl butyrate(2)(◣) at 298.15 K. Solid curves, calculated by Eq. (1).

least-squares method with all points assigned equal weight. The values of the adjustable parameters a_k obtained from the least-squares analysis are shown in Table 4, together with the standard deviation $\sigma(H_m^E)$ defined as

$$\sigma(H_m^E) = |\Phi/(N-n)|^{0.5} \qquad (2)$$

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

$$\Phi = \sum_{k \geq 0}^{N} \eta_k^2 \qquad (3)$$

with $\eta = H_{m,calcd}^E - H_m^E$, $H_{m,calcd}^E$ being determined from the right-hand side of Eq. (1).

Table 4
Adjustable parameters, a_k, and standard deviations, $\sigma(H_m^E)$, of a least-squares fit of H_m^E for diethyl carbonate(1) + n-alkyl alkanoates (2) by Eq. (1) at 298.15 K

Mixture	a_0	a_1	a_2	a_3	$\sigma(H_m^E)$/J mol^{-1}
Diethyl carbonate					
+ methyl acetate	387.9	−61.0			1.0
+ ethyl acetate	−14.3	27.1	28.8		0.2
+ propyl acetate	83.8	19.6	−17.5		0.3
+ butyl acetate	101.5	5.1	−13.5		0.3
+ pentyl acetate	271.8	42.2	−41.8		0.4
+ hexyl acetate	513.5	75.6			1.1
+ methyl propanoate	194.3	41.9	−20.5	−79.8	0.3
+ ethyl propanoate	−17.5	9.7	19.8	−8.3	0.1
+ propyl propanoate	192.8	12.9	−43.4	−50.5	0.4
+ butyl propanoate	403.4	31.0			1.3
+ methyl butyrate	32.4	15.4			0.2
+ ethyl butyrate	140.9	−4.3			0.3
+ propyl butyrate	409.3	26.9			0.9
+ butyl butyrate	642.4	82.6	−71.8		1.5

4. Conclusions

Figs. 1–3 show a regular increase of H_m^E with the increase of molecular size of the n-alkyl alcanoates, with the exception of mixtures diethyl carbonate + methyl acetate and diethyl carbonate + methyl propionate. In these latter cases, the first element of the series has an irregular behaviour, with values of H_m^E more larger than those corresponding to pentyl- and ethyl- members, respectively.

Considering that no strong hydrogen bonding may occur between diethyl carbonate and esters and that dipole moment of esters have not a regular trend [4], molecular interactions cannot be invoked to explain the exceptional behaviour of the methyl acetate and methyl propionate molecules which is probably due to their unfavourable packing leading to less interaction energy between molecules after mixing.

This effect is not present in mixtures containing dimethyl carbonate. In fact, it must be pointed out that the mixtures dimethyl carbonate + n-alkyl acetates previously measured [13], show a regular increase of H_m^E with the molecular size of acetates.

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