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Excess molar enthalpies of binary mixtures containing dialkylcarbonates + cyclic ketones at 298.15 or 313.15 K

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Abstract

Excess molar enthalpies H_m^E for the binary mixtures containing dimethylcarbonate or diethylcarbonate + cyclohexanone, 2-methylcyclohexanone and 2,6-dimethylcyclohexanone have been determined at 298.15 and 313.15 K and at atmospheric pressure, utilizing an isothermal flow microcalorimeter. The experimental values have been correlated by the Redlich–Kister equation and the parameters have been evaluated by least-squares analysis. For all the mixtures, the H_m^E values are positive with a maximum ranging from + 190 up to 700 J mol^{-1}. All curves present a regular trend decreasing with an increase in temperature. The experimental data have been examined by an extended cell model.

Keywords: Binary system; Enthalpy; Microcalorimetry; Redlich–Kister

1. Introduction

Following our systematic study on the thermodynamic properties of binary liquid mixtures containing dialkylcarbonates [1–4] as common component (component 1), we report in this paper the excess molar enthalpies H_m^E of dimethylcarbonate or diethylcarbonate + three cyclic ketones (component 2), namely cyclohexanone, 2-methylcyclohexanone and 2,6-dimethylcyclohexanone at 298.15 and 313.15 K and atmospheric pressure.

In a previous paper [3] we determined the excess molar volume V_m^E of the same mixtures at 298.15 K and the aim of this work is to obtain, by means of calorimetric measurements, a better understanding of the thermodynamic properties of these systems.

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To our knowledge, no enthalpy data for these mixtures are reported in the literature.

2. Experimental

2.1. Chemicals and apparatus

Dimethylcarbonate (99 mass%), diethylcarbonate (+ 99 mass%), cyclohexanone (99.8 mass%), 2-methylcyclohexanone (99 mass%) and 2,6-dimethylcyclohexanone (a mixture of isomers, 98 mass%) were purchased from Aldrich and all substances were used without further purification. The purity of the solvents was ascertained by comparing their densities ρ and refractive indices n(D) with the literature data [5–10], see Table 1.

Densities ρ were determined using a DMA 60/602 digital density meter (A. Paar, Graz, Austria) with a resolution of 1×10^{-6} g cm^{-3}, thermostated by a Heto constant temperature bath circulator with a temperature control interval of ± 0.005 K. Details of the apparatus and procedure are available elsewhere [11].

Refractive indices n(D) were obtained using an Abbe refractometer (Carl Zeiss-Jena, precision 0.0001); a refractometer check was first carried out with standard liquids, supplied with the instrument, with known index values.

An LKB flow microcalorimeter (model 2107, LKB, Bromma, Sweden) was used to measure the excess molar enthalpies H_m^E. Flows of the components were produced by infusion automatic burets (ABU, Radiometer, Copenhagen, Denmark). The two calorimetric flow cells were thermostated with a precision of ± 0.01 K by an internal circulator bath. Details of the equipment and operating procedure have been described previously [12, 13]. The calorimeter was checked against n-hexane + cyclohexane test system at 298.15 K, the agreement with the data of Ref. [14] being better than 0.5% over the central range of concentration.

3. Correlation of the calorimetric data

Excess molar enthalpies H_m^E at 298.15 and 313.15 K are collected in Tables 2 and 3 and are represented graphically in Figs. 1 and 2.

Table 1
Densities ρ and refractive indices n(D) of pure components and comparison with literature data

Component	ρ(298.15 K)/g cm^{-3}		n(D, 298.15 K)	
	Obsd.	Lit.	Obsd.	Lit.
Dimethylcarbonate	1.06349	1.06350 [50]	1.3671	1.3670 [16]
Diethylcarbonate	0.96930	0.96926 [7]	1.3827	1.38287 [7]
Cyclohexanone	0.94220	0.94221 [8]	1.4499	1.4500 [7]
2-Methylcyclohexanone	0.92154	0.92148 [9]	1.4483 [a]	1.4485 [a] [10]
2,6-Dimethylcyclohexanone	0.91212	–	1.4470 [a]	1.4470 [a] [10]

[a] At 291.15 K.

Table 2
Experimental excess molar enthalpies H_m^E of dialkylcarbonates + cyclic ketones at 298.15 K

x_1	H_m^E/J mol^{-1}	x_1	H_m^E/J mol^{-1}	x_1	H_m^E/J mol^{-1}
Dimethylcarbonate(1) + cyclohexanone(2)					
0.0487	88.1	0.3808	482.4	0.8311	281.8
0.0929	163.7	0.4505	495.8	0.8807	212.2
0.1332	229.3	0.5515	490.5	0.9077	168.3
0.1701	286.3	0.6486	449.4	0.9366	122.6
0.2351	366.1	0.7110	407.1	0.9672	65.7
0.2907	423.7	0.7868	334.1		
Dimethylcarbonate(1) + 2-methylcyclohexanone(2)					
0.0565	89.1	0.4181	556.7	0.8518	314.6
0.1069	168.6	0.4893	574.8	0.8961	242.0
0.1523	250.6	0.5897	570.0	0.9200	194.4
0.1932	313.2	0.6832	519.8	0.9452	139.6
0.2643	414.0	0.7419	467.0	0.9718	75.5
0.3239	484.0	0.8117	379.7		
Dimethylcarbonate(1) + 2,6-dimethylcyclohexanone(2)					
0.0637	131.4	0.4496	675.2	0.8673	348.7
0.1198	242.3	0.5213	697.7	0.9074	255.1
0.1695	336.2	0.6203	676.4	0.9289	200.3
0.2139	410.8	0.7102	603.8	0.9515	136.8
0.2899	528.9	0.7656	531.3	0.9751	72.5
0.3525	605.5	0.8305	425.3		
Diethylcarbonate(1) + cyclohexanone(2)					
0.0344	38.6	0.2994	214.8	0.7737	170.0
0.0665	69.4	0.3630	232.2	0.8368	131.9
0.0965	96.4	0.4608	244.2	0.8724	107.0
0.1247	121.7	0.5619	236.5	0.9112	78.0
0.1761	155.2	0.6309	225.0	0.9535	44.2
0.2217	181.7	0.7195	193.4		
Diethylcarbonate(1) + 2-methylcyclohexanone(2)					
0.0399	23.9	0.3330	160.6	0.7999	138.7
0.0768	44.7	0.3997	178.4	0.8570	108.8
0.1110	65.2	0.4997	195.3	0.8880	86.8
0.1427	80.0	0.5998	192.5	0.9230	63.9
0.1998	109.4	0.6664	181.6	0.9600	33.9
0.2497	132.0	0.7498	159.4		
Diethylcarbonate(1) + 2,6-dimethylcyclohexanone(2)					
0.0452	36.7	0.3621	232.4	0.8196	165.4
0.0864	66.6	0.4308	250.0	0.8720	125.0
0.1243	96.9	0.5317	261.7	0.9008	100.9
0.1591	124.6	0.6301	253.4	0.9316	71.1
0.2211	162.1	0.6942	229.8	0.9646	38.5
0.2745	190.9	0.7730	196.8		

Table 3
Experimental excess molar enthalpies H_m^E of dialkylcarbonates + cyclic ketones at 313.15 K

x_1	H_m^E/J mol^{-1}	x_1	H_m^E/J mol^{-1}	x_1	H_m^E/J mol^{-1}
Dimethylcarbonate(1) + cyclohexanone(2)					
0.0487	78.2	0.3807	451.0	0.8310	264.6
0.0929	147.7	0.4504	473.1	0.8806	201.6
0.1332	205.8	0.5514	465.4	0.9077	161.6
0.1700	259.3	0.6485	428.8	0.9365	109.4
0.2351	339.2	0.7109	386.4	0.9672	62.9
0.2907	393.5	0.7867	314.2		
Dimethylcarbonate + 2-methylcyclohexanone(2)					
0.0562	104.8	0.4168	520.4	0.8512	296.7
0.1064	185.4	0.4880	548.1	0.8956	219.3
0.1516	254.5	0.5884	540.4	0.9196	173.9
0.1924	312.1	0.6820	486.7	0.9449	120.2
0.2633	401.8	0.7409	440.4	0.9717	62.9
0.3227	456.0	0.8109	357.1		
Dimethylcarbonate(1) + 2,6-dimethylcyclohexanone(2)					
0.0633	111.0	0.4480	641.4	0.8665	346.9
0.1191	215.5	0.5197	673.7	0.9069	249.4
0.1687	301.8	0.6188	655.7	0.9285	196.8
0.2129	374.1	0.7088	591.9	0.9512	138.9
0.2886	489.4	0.7645	522.3	0.9750	70.0
0.3511	565.5	0.8296	416.1		
Diethylcarbonate(1) + cyclohexanone(2)					
0.0344	37.1	0.2996	199.9	0.7739	162.4
0.0665	64.3	0.3632	218.6	0.8369	128.0
0.0966	90.0	0.4611	230.6	0.8725	105.7
0.1248	113.1	0.5621	223.7	0.9112	76.5
0.1762	146.6	0.6311	211.9	0.9536	42.6
0.2219	172.5	0.7196	185.6		
Diethylcarbonate(1) + 2-methylcyclohexanone(2)					
0.0398	23.0	0.3322	142.0	0.7992	131.4
0.0765	42.3	0.3988	171.2	0.8565	102.6
0.1106	59.9	0.4987	186.0	0.8884	86.6
0.1422	76.8	0.5989	186.8	0.9227	59.3
0.1992	102.4	0.6655	174.3	0.9598	33.1
0.2490	125.9	0.7490	151.1		
Diethylcarbonate(1) + 2,6-dimethylcyclohexanone(2)					
0.0449	35.0	0.3609	223.2	0.8188	159.6
0.0860	66.5	0.4295	240.7	0.8714	121.5
0.1237	93.1	0.5304	252.7	0.9004	99.3
0.1584	117.3	0.6289	240.5	0.9313	69.3
0.2169	153.9	0.6932	220.9	0.9644	38.5
0.2735	184.4	0.7721	189.1		

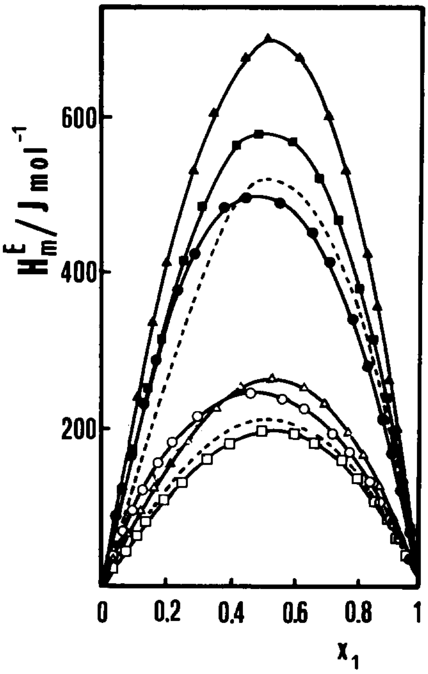

Fig. 1. Excess molar enthalpies H_m^E at 298.15 K for the binary mixtures containing dialkylcarbonates + cyclic ketones: ●, dimethylcarbonate + cyclohexanone; ■, + 2-methylcyclohexanone; and ▲, + 2,6-dimethylcyclohexanone; ○, diethylcarbonate + cyclohexanone; □, + 2-methylcyclohexanone; and △, + 2,6-dimethylcyclohexanone, respectively. (——), Redlich–Kister fit; (– – –), dialkylcarbonates + hexanone, Ref. [4].

The Redlich–Kister polynomial equation

$$H_m^E/x_1x_2 = \sum_{k \geqslant 0} a_k(x_1 - x_2)^k \tag{1}$$

was fitted by the method of least-squares. The parameters a_k are given in Table 4 together with the standard deviation $\sigma(H_m^E)$ defined as

$$\sigma(H_m^E) = [\phi/(N - n)]^{0.5} \tag{2}$$

where N is the number of experimental values and n the number of adjustable parameters a_k; ϕ is the objective function defined as

$$\phi = \sum_{k=1}^{N} \eta_k^2 \tag{3}$$

where $\eta_k = H_{m,\mathrm{calcd}}^E - H_m^E$; H_m^E is the experimental value and $H_{m,\mathrm{calcd}}^E$ is evaluated through Eq. (1).

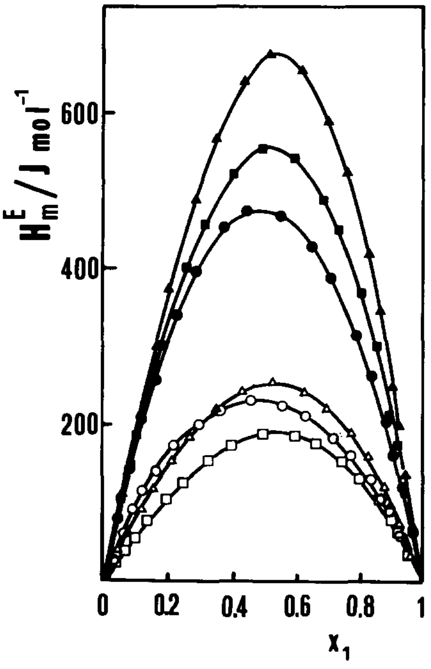

Fig. 2. Excess molar enthalpies H_m^E at 313.15 K for the binary mixtures containing dialkylcarbonates + cyclic ketones. The symbols are the same as in Fig. 1.

The number of parameters of Table 4 corresponds to values of $\sigma(H_m^E)$ compared with the mean uncertainty in the experimental H_m^E calculated following the procedure given in Ref. [13].

4. The cell model

An attempt to describe the mixtures of this paper by means of an extended cell model (described by Prigogine [15]) was carried out, starting from the theoretical expression

$$H_m^E = x_1 x_2 E_{11} z[-1.44\theta + 10.76(RT/zE_{11})^2(-2\theta - \delta^2 + 4\delta\theta x_2 + 4x_1x_2\theta^2)] \tag{4}$$

where z is the number of nearest neighbors in the cell model

$$\delta = (E_{22} - E_{11})/E_{11} \tag{5}$$

$$\theta = [E_{12} - (E_{11} + E_{22})/2]E_{11} \tag{6}$$

where E_{kk} is the intermolecular energy between identical molecules kk and E_{12} the intermolecular energy between dissimilar molecules.

Table 4
Redlich–Kister parameter a_k and standard deviations $\sigma(H_m^E)$ of the excess molar enthalpy H_m^E according to Eq. (1)

Mixture	T/K	a_0	a_1	a_2	a_3	$\sigma(H_m^E)$
Dimethylcarbonate(1)						
+ cyclohexanone(2)	298.15	2003.9	−129.6	0	263.3	2.3
	313.15	1906.0	−81.9	−112.0	270.2	2.2
+ 2-methylcyclohexanone(2)	298.15	2321.2	201.3	−200.1	475.0	2.5
	313.15	2187.8	238.0	−61.3		2.4
+ 2,6-dimethylcyclohexanone(2)	298.15	2784.1	460.6	−210.7		2.6
	313.15	2673.4	598.4	−302.8		2.8
Diethylcarbonate(1)						
+ cyclohexanone(2)	298.15	974.6	−84.3	108.3		1.0
	313.15	918.4	−58.3	125.2		1.1
+ 2-methylcyclohexanone(2)	298.15	773.4	149.0			1.0
	313.15	737.4	146.6			1.5
+ 2,6-dimethylcyclohexanone(2)	298.15	1046.4	152.8	−69.0		1.6
	313.15	1003.0	148.6	−47.4		1.3

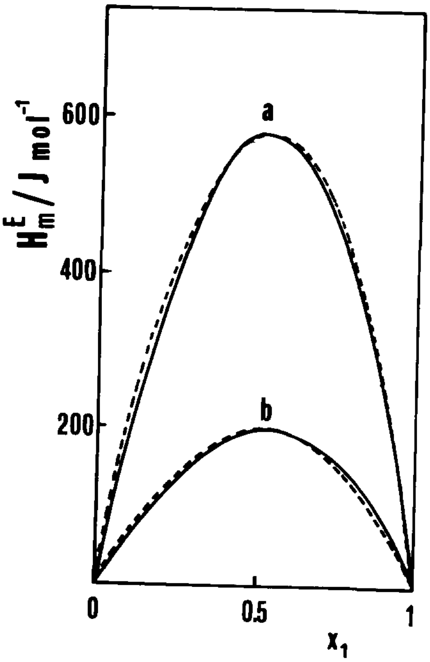

Fig. 3. Excess molar enthalpies H_m^E at 298.15 K of binary mixtures containing dialkylcarbonates + 2-methylcyclohexanone: (a), dimethylcarbonate; (b), diethylcarbonate. Comparison between Redlich–Kister fit (——) and cell model (---) at 298.15 K.

Eq. (4) has been applied to all our systems and Fig. 3 represents an example of the application of this theory.

A value of $z = 8$ was chosen and δ calculated from Eq. (5), with E_{11} and E_{22} evaluated by the heats of vaporization. The heat of vaporization of diethylcarbonate and cyclohexanone were taken from Ref. [7] while those of dimethylcarbonate, 2-methylcyclohexanone and 2,6-dimethylcyclohexanone, not quoted in the literature, were calculated from vapor liquid data [16] using the Clausius–Clapeyron expression. The calculated values of heats of vaporization are $H_v = 8765$, 10651 and 10303 cal mol^{-1} for dimethylcarbonate, 2-methylcyclohexanone and 2,6-dimethylcyclohexanone, respectively. E_{12} is taken from Eq. (4) with the parameter θ adjusted so that the experimental H_m^E at its maximum equals the value calculated by the right-hand side of Eq. (4). Table 4 collects the interaction energies between molecules.

5. Conclusions

The curves of H_m^E versus x_1 in Figs. 1 and 2, for the systems containing dimethylcarbonate or diethylcarbonate + cyclic ketones, show positive values for all mixtures at the two temperatures 298.15 and 313.15 K.

The temperature dependence of H_m^E is always negative.

The systems containing dimethylcarbonate give values of H_m^E nearly three times the corresponding values for diethylcarbonates.

An increased number of methyl groups in the cyclic ketones leads to increased values of H_m^E. This effect is marked for the mixtures containing dimethylcarbonate and less clear for diethylcarbonate, probably due to the lower values of H_m^E, not exceeding 50 J mol^{-1}.

Fig. 3 compares the Redlich–Kister smoothing fits, Eq. (1), with the curves calculated by the cell model expression, Eq. (4). Only the graph for the systems dialkylcarbonates + 2-methylcyclohexanone are given in this figure, the other mixtures showing a similar behavior.

Table 5, recording interaction energies between molecules, may explain, at least qualitatively, the trends of Figs. 1 and 2. In fact, when going from cyclohexanone to

Table 5
Interaction energies between molecules for dialkylcarbonates + cyclic ketones

Mixture	E_{11}	E_{22}	E_{12}
Dimethylcarbonate(1)			
+ cyclohexanone(2)	8765	10730	9706
+ 2-methylcyclohexanone(2)	8765	10651	9660
+ 2,6-dimethylcyclohexanone(2)	8765	10303	9476
Diethylcarbonate(1)			
+ cyclohexanone(2)	10420	10730	10555
+ 2-methylcyclohexanone(2)	10420	10651	10519
+ 2,6-dimethylcyclohexanone(2)	10420	10303	10340

dimethylcyclohexanone, the interaction energy E_{22} of ketone decreases less than the interaction energy between dissimilar molecules, $2E_{12}$, and thus the H_m^E values, approximately proportional to $E_{11} + E_{22} - 2E_{12}$, increase. This effect is probably due to the steric hindrance of CH_3 groups moving away from ketone molecules whose interaction is carried out through C=O groups. For diethylcarbonate, this trend is not regular.

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