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Excess molar enthalpies of binary mixtures containing dimethyl carbonate or diethyl carbonate and one of six methyl *n*-alkyl ketones
Application of an extended cell model

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Abstract

Excess molar enthalpies H_m^E of binary mixtures containing dimethyl carbonate or diethyl carbonate and six methyl *n*-alkyl ketones have been determined at 298.15 K and atmospheric pressure using a flow microcalorimeter. The systematic behaviour of H_m^E, increasing with the increase in the number of the carbon atoms in the ketone, is confirmed for all mixtures with the exception of mixtures of diethyl carbonate and 2-propanone. The experimental data have been correlated by means of the Redlich–Kister equation and results are interpreted in terms of molecular interactions, and are examined by an extended cell model.

Keywords: Carbonate–ketone mixtures; Flow microcalorimeter; Molar enthalpies; Molecular interactions

1. Introduction

This paper is part of an extensive study of the physical properties of binary liquid mixtures containing ketones [1–6]; the aim of these investigations is to correlate the experimental data with the interactions between the molecules in such mixtures. For this purpose, the excess molar enthalpies H_m^E of binary mixtures of dimethyl carbonate or diethyl carbonate and six methyl *n*-alkyl ketones namely 2-propanone, 2-butanone,

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2-pentanone, 2-hexanone, 2-octanone or 2-undecanone are reported. The excess enthalpy data for these twelve binary systems have not been reported previously.

2. Experimental

The sources of the liquid components and their purities specified by the manufacturers are summarized in Table 1. These liquids were used without further purification (stated purity $\geq 99\%$) with the exception of 2-octanone, which was distilled following the method of Collerson et al. [7]. The purity of solvents was further ascertained by comparing their densities and refractive indices at 298.15 K with the corresponding literature values [8-12]. Densities were measured with a DMA 60/602 digital density meter with a resolution of $1 \times 10^{-6}\,\mathrm{g\,cm^{-3}}$ (A. Paar, Graz, Austria). Details of the apparatus and procedure are available elsewhere [13]. Each mixture was maintained at constant temperature to within 0.005 K by means of an Hetotherm bath circulator (Model 01 DTB 623) and temperature was measured using a digital thermometer (DT 100-25; A. Paar, Graz, Austria). Refractive indices were obtained by means of an Abbe refractometer (Carl Zeiss-Jena; precision 0.0001) calibrated with standard liquids, of known index-values. A flow microcalorimeter from LKB (model 2107) was used for the measurements of the excess molar enthalpies. The calorimeter consists of two solvent automatic burettes (ABU, Radiometer, Copenhagen, Denmark), a thermostatted flow cell (precision ± 0.01 K) and a control unit (LKB, Bromma, Sweden). Details of the equipment and its operations have been described previously [14, 15]. The microcalorimeter was calibrated before each series of measurements by employing a standard mixture of cyclohexane and hexane [16]. The error in the excess molar enthalpy values is estimated to be less than 0.5% over the entire mole fraction range.

3. Results and conclusions

The results from the twelve binary mixtures are given in Table 2 and graphically represented in Figs. 1 and 2. The results have been fitted to the Redlich-Kister equation

Table 1
Sources, density (ρ) and refractive indices (n_D) of pure compounds at 298.15 K and comparison with literature

Compound	Source, (purity in mass%)	ρ in g cm^{-3}		n_D	
		Expt.	Lit.	Expt.	Lit.
Dimethyl carbonate	Aldrich (99)	1.06349	1.06350 [8]	1.3671	1.3670 [9]
Diethyl carbonate	Aldrich (99+)	0.96930	0.96926 [10]	1.3827	1.38287 [10]
2-Propanone	Aldrich (99,9+)	0.78437	0.78440 [10]	1.3567	1.35596 [10]
2-Butanone	Aldrich (99.5+)	0.79971	0.79970 [10]	1.3767	1.37685 [10]
2-Pentanone	Fluka (99+)	0.80152	0.8015 [10]	1.3885	1.38849 [10]
2-Hexanone	Aldrich (99+)	0.80674	0.8067 [10]	1.3992	1.3987 [10]
2-Octanone	Aldrich (98)	0.81434	0.8143 [10]	1.4139	1.4133 [10]
2-Undecanone	Aldrich (99)	0.82231	0.82216 [11] [a]	1.4289	1.42899 [12] [a]

[a] at 293.15 K.

$$H_m^E = x_1 x_2 \sum_{k \geq 0} A_k (x_1 - x_2)^k \tag{1}$$

where x_1, x_2 refer to the mole fractions of dimethyl carbonate or diethyl carbonate and ketones, respectively. The adjustable parameters A_k, which were used to calculate the

Table 2
Values of excess molar enthalpies at 298.15 K, observed and calculated using Eq. (1)

x_1	H_m^E in J mol^{-1}		x_1	H_m^E in J mol^{-1}	
	Expt.	Calc.		Expt.	Calc.
Dimethyl carbonate + 2-propanone					
0.0351	15.8	16.6	0.5674	188.7	189.8
0.0679	31.7	32.6	0.6362	181.5	183.0
0.0985	45.7	47.8	0.7240	159.3	161.2
0.1271	62.8	61.9	0.7776	138.9	140.6
0.1793	90.8	87.2	0.8399	109.2	109.9
0.2256	109.1	108.6	0.8749	89.4	89.5
0.3041	144.5	140.9	0.9130	66.7	64.9
0.3682	161.3	162.3	0.9545	36.7	35.4
0.4664	183.5	184.0			
Dimethyl carbonate + 2-butanone					
0.0425	29.3	28.5	0.6150	263.5	266.5
0.0815	56.2	57.2	0.6408	247.8	245.9
0.1174	82.3	84.7	0.7615	208.4	205.9
0.1507	109.2	110.3	0.8098	175.8	174.9
0.2102	155.5	154.4	0.8647	133.9	133.1
0.2619	192.8	189.2	0.8949	108.0	107.2
0.3474	237.4	236.0	0.9274	73.1	76.9
0.4151	259.5	261.2	0.9623	41.7	41.6
0.5156	274.6	277.0			
Dimethyl carbonate + 2-pentanone					
0.0502	42.8	42.5	0.6556	350.5	352.8
0.0956	83.8	86.8	0.7173	320.6	318.1
0.1369	125.8	129.3	0.7919	261.4	259.0
0.1745	171.3	168.3	0.8354	219.6	216.3
0.2408	239.2	233.8	0.8839	163.5	161.6
0.2972	284.8	283.0	0.9103	126.7	128.7
0.3881	341.6	343.7	0.9384	91.4	91.3
0.4582	369.4	371.6	0.9682	47.1	48.7
0.5592	375.7	380.0			
Dimethyl carbonate + 2-hexanone					
0.0575	49.8	53.1	0.6874	463.1	463.0
0.1088	120.8	118.6	0.7456	417.5	410.7
0.1548	190.6	184.5	0.8147	331.6	329.5
0.1963	250.1	245.4	0.8543	276.2	273.6
0.2681	342.6	344.9	0.8979	208.1	203.7
0.3282	417.1	415.7	0.9214	161.5	162.1
0.4229	489.2	493.8	0.9462	111.5	115.0

Table 2 (*continued*)

x_1	H_m^E in J mol^{-1}		x_1	H_m^E in J mol^{-1}	
	Expt.	Calc.		Expt.	Calc.
0.4942	517.6	521.5	0.9724	59.6	61.3
0.5944	507.6	514.4			
Dimethyl carbonate + 2-octanone					
0.0719	130.2	127.6	0.7360	655.7	652.3
0.1341	242.9	247.5	0.7880	571.6	577.2
0.1885	348.8	351.6	0.8479	462.3	461.7
0.2365	437.0	438.7	0.8814	379.8	382.2
0.3172	574.6	567.8	0.9177	283.7	282.9
0.3825	645.3	650.8	0.9370	228.1	224.1
0.4817	734.0	732.6	0.9571	160.8	158.1
0.5534	757.9	754.4	0.9781	82.1	83.8
0.6502	728.0	730.0			
Dimethyl carbonate + 2-undecanone					
0.0924	248.5	249.9	0.7858	874.1	883.0
0.1692	440.1	442.2	0.8302	768.0	768.2
0.2341	588.1	592.2	0.8800	599.8	600.5
0.2895	710.5	709.5	0.9072	490.3	489.9
0.3794	882.9	873.5	0.9362	362.3	356.2
0.4491	977.3	972.7	0.9514	282.5	279.3
0.5501	1060.5	1060.1	0.9670	195.4	195.3
0.6198	1072.7	1071.6	0.9832	102.9	102.5
0.7097	1002.1	1012.3			
Diethyl carbonate + 2-propanone					
0.0247	10.4	9.3	0.4769	230.2	232.5
0.0482	20.3	21.7	0.5486	232.5	230.9
0.0706	34.8	35.9	0.6457	218.5	214.8
0.0919	51.5	50.8	0.7085	199.5	196.2
0.1319	80.5	80.6	0.7848	165.5	163.7
0.1684	107.2	108.0	0.8294	139.4	139.0
0.2330	152.1	152.6	0.8794	104.1	105.6
0.2883	183.3	183.7	0.9358	60.3	60.6
0.3779	214.4	217.7			
Diethyl carbonate + 2-butanone					
0.0299	7.0	5.7	0.5261	145.2	146.0
0.0581	13.7	14.0	0.5967	145.5	145.2
0.0846	21.8	23.6	0.6894	135.2	134.5
0.1097	32.3	33.7	0.7474	120.4	121.4
0.1561	53.8	53.6	0.8162	99.5	98.4
0.1978	71.5	71.2	0.8555	81.5	81.5
0.2700	99.9	98.7	0.8988	58.6	59.8
0.3303	117.3	117.1	0.9467	32.8	32.6
0.4252	136.7	136.9			

Table 2 (*continued*)

x_1	H_m^E in J mol^{-1}		x_1	H_m^E in J mol^{-1}	
	Expt.	Calc.		Expt.	Calc.
Diethyl carbonate + 2-pentanone					
0.0354	8.9	7.3	0.5696	151.2	151.7
0.0684	17.3	18.5	0.6381	146.6	146.3
0.0993	28.9	31.3	0.7337	128.5	127.0
0.1281	43.1	44.3	0.7791	109.7	112.4
0.1806	68.8	68.4	0.8411	87.8	86.5
0.2271	89.3	88.5	0.8758	69.3	69.3
0.3060	117.5	116.9	0.9137	46.7	48.7
0.3702	133.0	133.7	0.9549	25.7	25.2
0.4686	150.0	148.7			
Diethyl carbonate + 2-hexanone					
0.0407	17.8	16.5	0.6044	205.3	206.3
0.0782	36.8	37.3	0.6708	194.5	193.6
0.1129	55.7	59.0	0.7535	164.1	165.6
0.1451	79.9	79.8	0.8030	140.6	141.7
0.2030	114.9	115.9	0.8594	109.6	107.7
0.2535	145.4	143.8	0.8907	86.1	86.0
0.3375	180.1	179.7	0.9244	59.6	60.7
0.4044	198.9	198.3	0.9607	32.0	31.9
0.5046	212.1	210.8			
Diethyl carbonate + 2-octanone					
0.0511	42.9	46.0	0.6596	331.8	330.8
0.0852	78.8	78.4	0.7210	303.0	300.3
0.1227	114.1	114.4	0.7949	248.3	247.0
0.1571	149.2	147.1	0.8379	207.8	207.5
0.2197	208.1	203.7	0.8857	158.8	156.2
0.2716	248.8	246.0	0.9118	123.9	124.8
0.3587	300.5	303.5	0.9394	87.0	88.9
0.4271	331.3	334.5	0.9688	46.1	47.6
0.5280	351.4	354.3			
Diethyl carbonate + 2-undecanone					
0.0661	98.9	99.5	0.7182	507.1	503.7
0.1240	185.6	190.6	0.7727	451.4	448.4
0.1752	272.9	269.3	0.8360	365.4	362.1
0.2207	337.7	334.9	0.8717	301.7	301.8
0.2892	436.1	432.3	0.9107	222.0	225.2
0.3616	494.0	495.2	0.9315	181.4	179.3
0.4593	557.3	557.8	0.9533	124.2	127.1
0.5311	568.2	575.6	0.9761	67.7	67.8
0.6295	558.3	559.6			

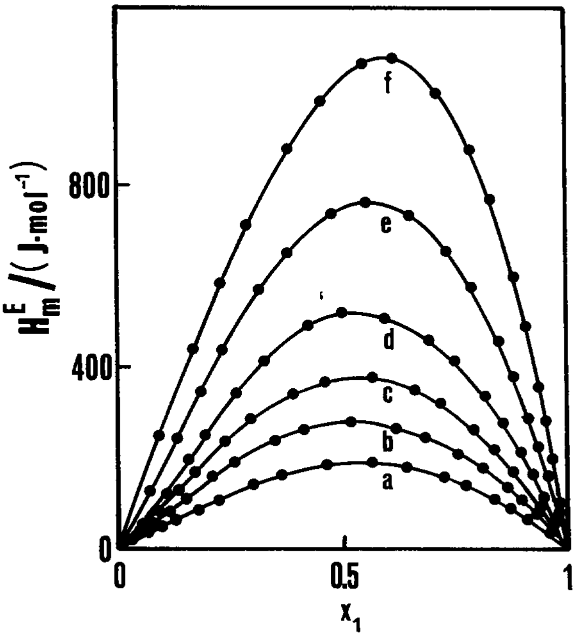

Fig. 1. Excess molar enthalpies of dimethyl carbonate + 2-propanone (a), + 2-butanone (b), + 2-pentanone (c), + 2-hexanone (d), + 2-octanone (e) or + 2-undecanone (f) at 298.15 K. Solid curves are least-squares representation of results of Eq. (1).

solid curves in Figs. 1 and 2, and the standard deviation $\sigma(H_m^E)$ are reported in Table 3. The values of $\sigma(H_m^E)$ were obtained using the formula

$$\sigma(H_m^E) = (\phi_{min}/(N - n))^{0.5} \tag{2}$$

where ϕ_{min} is the minimum value of the objective function ϕ defined as

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

with N the number of experimental points, $\eta_k = H_{m,calc}^E - H_m^E$, $H_{m,calc}^E$ being determined from the right-hand side of Eq. (1), and n the number of adjustable parameters. Fig. 3 shows $H_m^E(x_1 = 0.5)$, the equimolar excess enthalpy, plotted vs. n_c, the number of carbon atoms of the methyl n-alkyl ketones. The same figure reports also values of $H_m^E(x_1 = 0.5)$ for the mixtures dimethyl carbonate or diethyl carbonate + some n-alkanes, as a comparison [17, 18]. A thermodynamic description of the curves in Figs. 1 and 3 has been attempted on the basis of an extended cell model worked out by Prigogine et al. [19–21], Salsburg and Kirkwood [22] and Rowlinson [23, 24]. The theoretical expression for H_m^E given by this model and reported in Ref. [21] is

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

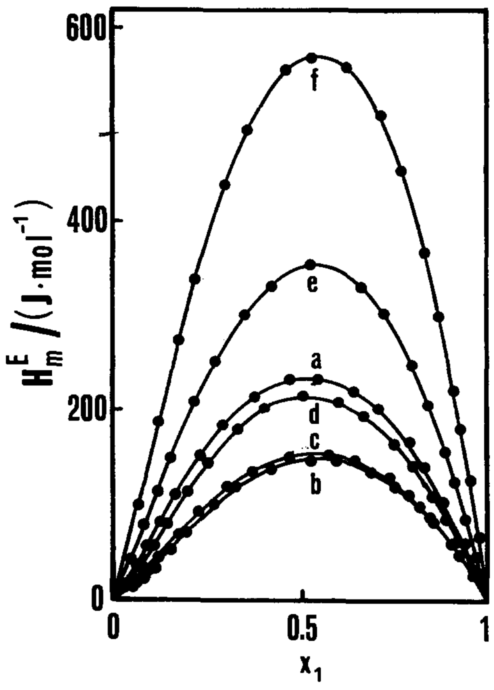

Fig. 2. Excess molar enthalpies of diethyl carbonate + 2-propanone (a), + 2-butanone (b), + 2-pentanone (c), + 2-hexanone (d), + 2-octanone (e) or + 2-undecanone (f) at 298.15 K. Solid curves are least-squares representation of results by Eq. (1).

Table 3

Redlich–Kister parameters A_k and standard deviations $\sigma(H^E_m)$ in J mol^{-1} of the excess molar enthalpy according to Eq. (1)

Mixture	A_0	A_1	A_2	A_3	A_4	$\sigma(H^E_m)$
Dimethyl carbonate						
+ 2-propanone	751.7	174.1	−114.3			1.9
+ 2-butanone	1105.3	131.5	−217.0	133.8		2.3
+ 2-pentanone	1518.8	213.3	−350.1	187.4		3.1
+ 2-hexanone	2090.0	328.2	−603.4	502.5		4.4
+ 2-octanone	2964.9	832.9	−166.2	344.1		4.0
+ 2-undecanone	4104.3	1743.2	445.3			5.1
Diethyl carbonate						
+ 2-propanone	932.1	0	0	363.0	−285.3	2.0
+ 2-butanone	579.0	123.0	0	127.0	−207.9	1.0
+ 2-pentanone	603.8	105.7	0	103.0	−281.7	1.5
+ 2-hexanone	842.5	92.8	0	163.6	−293.6	1.5
+ 2-octanone	1408.2	251.8	−187.1	23.9		2.7
+ 2-undecanone	2283.6	449.0	−93.9	324.0		3.7

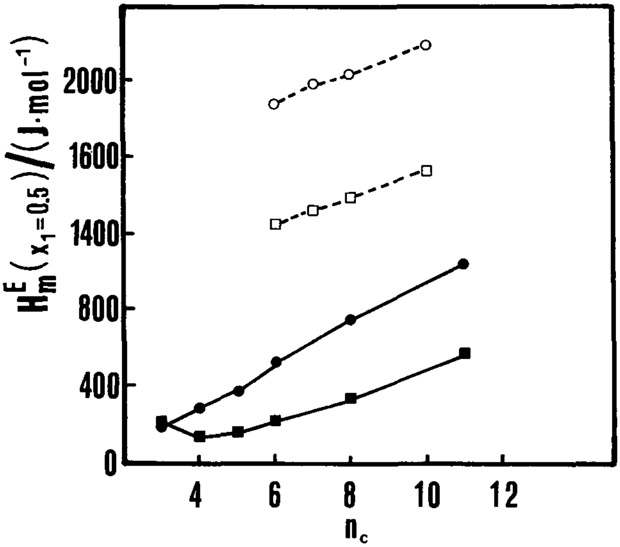

Fig. 3. Values of equimolar enthalpies $H_m^E(x_1 = 0.5)$ at 298.15 K and atmospheric pressure as a function of carbon atoms of ketones, n_c, for binary mixtures of dimethyl carbonate (●) or diethyl carbonate (■) + ketones. (○): dimethyl carbonate + alkanes. Ref. [17]; (□): diethyl carbonate + alkanes, Ref. [18].

where z is the number of the nearest neighbours in the quasi lattice model ($z = 8$ in our case)

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

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

$E_{k,k}$ = intermolecular energy between identical molecules kk, $E_{1,2}$ = intermolecular energy between dissimilar molecules.

Calculation of H_m^E by Eq. (4) for each mixture was carried out following the procedure outlined in Ref. [25], in which the lattice model has been applied with good results. Essentially, H_m^E is adjusted so that the experimental $H_m^E(x = 0.5)$ equals the value calculated by the right-hand side of Eq. (4). E_{11} and E_{22} are evaluated from the heats of vapourization of the pure components (see Table 4). Fig. 4 shows an example of the application of this theory which gave a good representation of the experimental data particularly when the curves are symmetric. Figs. 1 and 3 stress the different behaviour of dimethyl carbonate and diethyl carbonate in H_m^E vs. x_1 curves for mixtures of alkyl ketones. In fact, dimethyl carbonate shows a regular increase of enthalpy as a function of the number n_c of ketone carbon atoms whereas the corresponding curves for diethyl carbonate exhibit a marked decrease of enthalpy for $n \leq 4$. This anomaly, occurring for low values of n_c, is not explained, however, by the Patterson effect which is due to interactions between long-chain molecules and should appear therefore for large n_c. Table 4 reports the interaction energies between molecules for the twelve mixtures obtained from theory [21]. The last column of this table reports values of

Table 4
Interaction energies E_{ij} in J mol^{-1} between molecules for the twelve mixtures

Mixture	E_{11}	E_{22}	E_{12}	$E_{11}+E_{22}-2E_{12}$[a]
Dimethyl carbonate				
+ 2-propanone	2094.1[b]	1787.1	1936.8	7.6
+ 2-butanone	2094.1[b]	1970.6	2026.8	11.1
+ 2-pentanone	2094.1[b]	2193.3	2136.2	15.0
+ 2-hexanone	2094.1[b]	2460.9	2267.2	20.6
+ 2-octanone	2094.1[b]	2962.6	2512.9	30.9
+ 2-undecanone	2094.1[b]	3798.8[c]	2923.5	45.9
Diethyl carbonate				
+ 2-propanone	2489.5	1787.1	2133.7	9.2
+ 2-butanone	2489.5	1970.6	2227.1	5.9
+ 2-pentanone	2489.5	2193.3	2338.4	6.0
+ 2-hexanone	2489.5	2460.9	2470.9	8.6
+ 2-octanone	2489.5	2962.6	2719.1	13.9
+ 2-undecanone	2489.5	3798.8	3132.6	23.1

[a] E_{11}, E_{22}, Ref. [10]; E_{12}, Ref. [21]. [b] obtained from Clausius–Clapeyron. [c] extrapolated, Ref. [11].

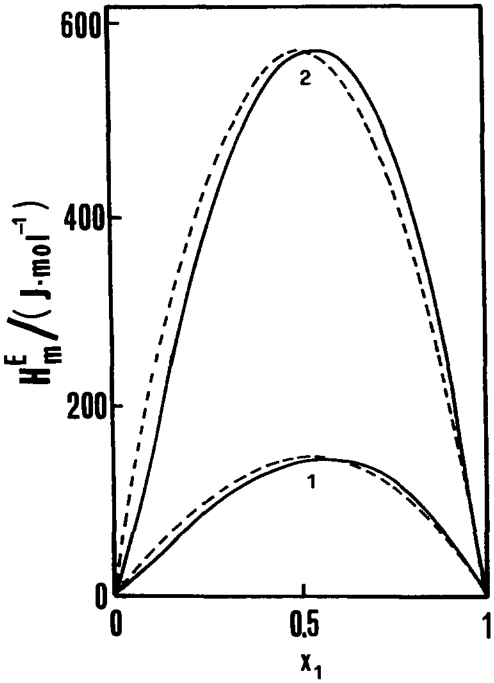

Fig. 4. Example of application of the cell model theory on the diethyl carbonate + 2-propanone (1) or + 2-undecanone (2) mixture. (———), calculated by use of Eq. (1) with the parameters of Table 3; (– – – –), calculated from theory, Ref. [21].

$E_{11} + E_{22} - 0.5\ E_{12}$, whose trend is in agreement with graphs of Fig. 3 and may be considered a confirmation of the validity of the theory used in this paper.

Finally, the curves $H_m^E(x_1 = 0.5)$ vs. n_c for the mixtures dimethyl carbonate or diethyl carbonate + some alkanes, shown in Fig. 3 for comparison, may be explained considering that the E_{12} interactions between the C=O group of the carbonate and the CH_2 chain of alkanes are small when compared with the hydrogen bonding between C=O groups of carbonate or ketone and H atoms. As a consequence, the prevalent contribution to the heat of mixing for the mixtures carbonate + alkanes is given by the E_{11} and E_{22} terms, that is breaking of bonds between similar molecules, leading to larger values of H_m^E.

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