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A calorimetric study of propylene carbonate + acetic or propionic acid at (288.15, 298.15 and 313.15) K

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Abstract

Determinations of heat capacities, C_p, and excess molar enthalpies, H_m^E, of the binary mixtures propylene carbonate + acetic or propionic acid were carried out at (285.15, 298.15 and 313.15) K using a Perkin-Elmer DSC differential scanning calorimeter and an LKB flow microcalorimeter. All experimental values are positive and increase with the increase of temperature. The data have been fitted to a simple cubic polynomial (for C_p) and the Redlich–Kister equation (for H_m^E) to estimate the adjustable parameters and standard deviations of these systems. Results have been discussed in terms of molecular interactions and have been interpretated by an extended cell model. © 1997 Elsevier Science B.V.

Keywords: Calorimeter; Enthalpies; Extended cell model; Heat capacity

1. Introduction

This paper reports determinations of excess molar enthalpies, H_m^E, and heat capacities, C_p, of binary mixtures containing propylene carbonate with acetic or propionic acid at (288.15, 298.15 and 313.15) K and atmospheric pressure.

The importance of propylene carbonate as a solvent for a variety of industrial applications particularly in lithium high-batteries has been widely stressed [1–3] and the employment of this substance has been the subject of several of our previous papers to provide information about the thermodynamic properties of binary mixtures containing an aprotic polar solvent (propylene carbonate) and some series of chemicals having different functional groups [4–6]. A further aim of the present investigation is to study the effect of the temperature on the physical properties of such binary mixtures.

We are not aware of any previous investigations on heat capacities C_p or excess molar enthalpy H_m^E for the present systems.

2. Experimental

2.1. Chemicals

Propylene carbonate was purchased from Aldrich, acetic and propionic acids were Fluka and Merck products. Their purities are 99.7, 99.8 and 99.5 mol%, respectively, and were used without further purification since a GLC analysis revealed the presence of no major impurities.

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Table 1
Densities, ρ, and refractive indices, n_D, of pure chemicals and comparison with literature values at 298.15 K

Component	ρ/ (g cm^{-3})		n_D	
	expt.	lit.	expt.	lit.
Propylene carbonate	1.19957	1.1995 [7] 1.1992 [8] 1.1993 [9]	1.4195	1.4194 [7]
Acetic acid	1.04378	1.04392 [10] 1.0437 [11]	1.3699	1.3698 [10]
Propionic acid	0.98796	0.98808 [10] 0.9869 [12]	1.3842	1.3843 [10]

Purities of components were also checked by comparing their measured densities, ρ, and refractive indices, n_D^{25}, with those reported in literature [7–12], as shown in Table 1.

Densities ρ were determined with an accuracy of $\pm 1 \times 10^{-5}$ g cm^{-3} using a digital vibrating tube densimeter (Anton Paar, model DMA 60/602, Graz, Austria) and refractive indices, n_D, were measured at 298.15 K using an Abbe refractometer (Carl Zeiss, Jena, D) with a precision of ± 0.0001.

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

2.2. *Calorimetric measurements*

Excess molar enthalpies, H_m^E, were performed using an LKB flow microcalorimeter (LKB, model 2107, Produkter AB, Bromma, Sweden) equipped with two automatic burettes (ABU, Radiometer, Cophenagen, Denmark) to pump pure liquids into the mixing cell of the calorimeter. Details of the equipment and its operating procedure have been described elsewhere [13,14].

Mole fractions x_1 of propylene carbonate (component 1) were obtained from fluxes and the observed standard error was $\delta x_1 \approx 0.0003$.

Calibration of the calorimeter was carried out by comparing the excess molar enthalpies at 298.15 K for the test mixture hexane + cyclohexane, leading to a discrepancy of < 0.5 in H_m^E between our values and those reported in literature [15].

The heat capacities, C_p, were determined using a Perkin–Elmer differential scanning calorimeter DSC 7, interfaced to a Unix computer.

The external block temperature control was set at 238.15 K, so that operation down to 273.15 K were easily performed. The instrument was equipped with dry box assembly and dry nitrogen was used as purge gas. The calibration of the apparatus and operating procedure have been already described in a previous paper [16].

Before measurements, the calorimeter was checked using the test mixture (water + methanol) at 308.15 K and the discrepancy of heat capacities between our and literature values [17] was < 0.6% in the central range of mole fraction of water.

3. Correlation of the calorimetric data

The experimental H_m^E of binary mixtures are listed in Table 2 and graphically represented in Fig. 1.

The Redlich–Kister equation

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

was fitted to each set of data by the least-squares method.

Values of the adjustable parameters a_k and the calculated standard deviations $\sigma(H_m^E)$, were obtained following the same procedure used in previous papers [4–6,14] and are reported in Table 3.

The experimental C_p of the mixtures, reported in Table 4 and graphically represented in Fig. 2, show nonlinear behaviour. The polynomial function

$$C_p = A_0 + A_1 x_1 + A_2 x_1^2 \qquad (2)$$

was fitted to each set of results.

Table 2
Excess molar enthalpies, H^E_m, of propylene carbonate + acetic acid or propionic acid at 288.15, 298.15 and 313.15 K

x_1	H^E_m/ (J mol^{-1})	x_1	H^E_m/ (J mol^{-1})
Propylene carbonate(1) + *acetic acid*(2)			
T = 288.15 K			
0.0273	90	0.5031	615
0.0532	166	0.5744	607
0.0778	231	0.6694	563
0.1125	311	0.7297	507
0.1444	372	0.8020	423
0.1837	435	0.8434	366
0.2523	515	0.8901	286
0.3103	565	0.9419	164
0.4030	605		
T = 298.15 K			
0.0533	171	0.5035	635
0.0779	238	0.5748	615
0.1012	296	0.6697	565
0.1446	384	0.7300	515
0.1839	453	0.8022	433
0.2526	530	0.8439	366
0.3106	579	0.8903	284
0.4033	629	0.9419	166
T = 313.15 K			
0.0274	104	0.5042	684
0.0535	191	0.5756	672
0.0781	263	0.6704	612
0.1015	325	0.7306	555
0.1449	426	0.8027	472
0.1843	492	0.8443	415
0.2532	582	0.8906	317
0.3113	633	0.9421	186
0.4041	676		
Propylene carbonate(1) + *propionic acid*(2)			
T = 288.15 K			
0.0353	201	0.5688	932
0.0683	353	0.6375	889
0.0990	480	0.7251	773
0.1278	581	0.7786	671
0.1802	717	0.8407	542
0.2267	813	0.8755	451
0.3054	905	0.9134	326
0.3696	947	0.9548	181
0.4679	969		
T = 298.15 K			
0.0354	214	0.5693	966
0.0684	381	0.6379	912
0.0992	516	0.7255	788
0.1280	613	0.7790	687
0.1805	756	0.8409	534
0.2270	849	0.8757	439
0.3058	944	0.9136	328
0.3700	994	0.9548	176
0.4684	1007		
T = 313.15 K			
0.0355	226	0.5700	1040
0.0686	410	0.6387	985
0.0995	540	0.7261	853
0.1283	643	0.7795	746
0.1809	804	0.8414	588
0.2275	906	0.8761	476
0.3065	1018	0.9138	354
0.3707	1069	0.9550	196
0.4692	1090		

Values of A_k, correlation coefficients $|R|$ and standard deviations $\sigma(C_p)$ are summarized in Table 5.

We evaluated the uncertainties in C_p to be < 1%, which lead to an error of the excess molar heat capacities, C^E_p, of ± 1 J mol^{-1} K^{-1}.

C^E_p have been determined using the following formula

$$C^E_p = C_p - x_1 C_{p1} - x_2 C_{p2} \tag{3}$$

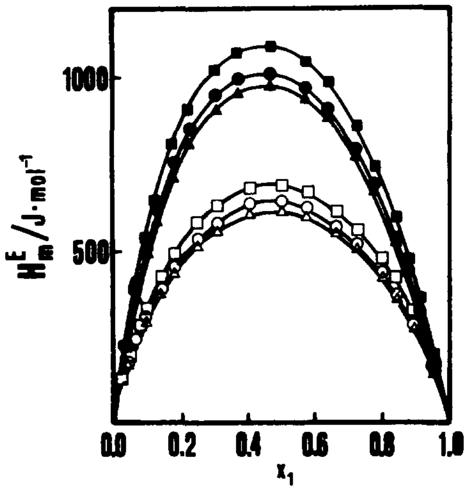


Fig. 1. Excess molar enthalpies, H^E_m, of propylene carbonate + acetic acid or propionic acid. Open symbols (△), (○), (□) refer to propylene carbonate + acetic acid at 288.15, 298.15 and 313.15 K, respectively; closed symbols (▲), (●), (■) refer to propylene carbonate + propionic acid at 288.15, 298.15 and 313.15 K, respectively. Solid curves represent plot of Redlich–Kister equation.

Table 3
Least-squares parameters, a_k, and standard deviation, $\sigma(H_m^E)$, of propylene carbonate + acetic or propionic acid at (288.15, 298.15 and 313.15) K

Mixture	a_0	a_1	a_2	a_3	$\sigma(H_m^E)$
T = 288.15 K					
Propylene carbonate + acetic acid	2467.0	−138.9	867.1		3.0
Propylene carbonate + propionic acid	3850.8	−473.7	1414.7	−482.7	4.3
T = 298.15 K					
Propylene carbonate + acetic acid	2528.3	−199.4	857.7		2.7
Propylene carbonate + propionic acid	4000.8	−557.7	1385.9	−744.0	3.3
T = 313.15 K					
Propylene carbonate + acetic acid	2729.4	−200.9	1074.1		4.1
Propylene carbonate + propionic acid	4320.9	−573.1	1429.4	−673.1	3.8

where C_{p1} and C_{p2} are the heat capacities of the pure components.

The graphical representation of C_p^E values at 298.15 K for propylene carbonate + acetic or propionic acid mixtures is shown in Fig. 3.

4. The cell model

An attempt to describe the systems in this paper by means of the cell model, elaborated by Prigogine et al. [18–20], Salsburg and Kirkwood [21] and Rowlinson [22,23] was carried out, starting from the theoretical expression for H_m^E

$$H_m^E = x_1x_2E_{11}z[-1.44\theta + 10.76(RT/zE_{11})^2 \times (-2\theta - \delta^2 + 4\delta\theta x_2 + 4x_1x_2\theta^2)] \quad (4)$$

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

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

$$E = E_{11} + E_{22} - 2E_{12} \quad (7)$$

where z is the number of nearest neighbors in the quasi-lattice model, E_{ij} the interaction energy

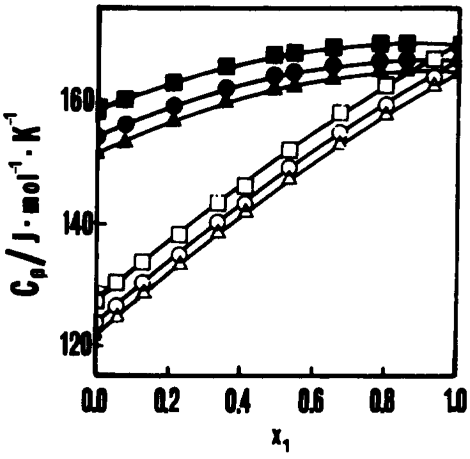


Fig. 2. Heat capacities of mixtures, C_p, as a function of mole fraction x_1 of propylene carbonate for the propylene carbonate + acetic or propionic acid mixtures. Open symbols (△), (○), (□) refer to PC + acetic acid at 288.15, 298.15 and 313.15 K, respectively; closed symbols (▲), (●), (■) refer to propylene carbonate + propionic acid at 288.15, 298.15 and 313.15 K, respectively. Solid curves are plots of Eq. (2).

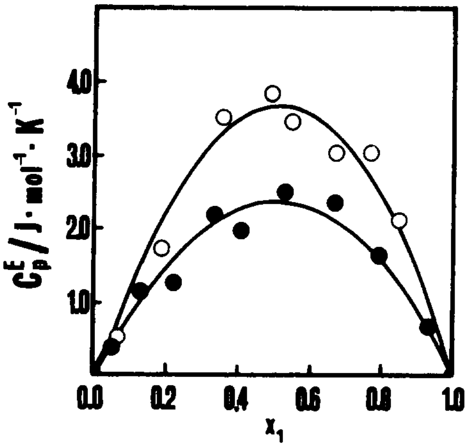


Fig. 3. Excess molar heat capacities, C_p^E, of propylene carbonate + acetic acid (○) or + propionic acid (●) at 298.15 K. Solid curves represent Eq. (2).

Table 4
Heat capacities, C_p, of propylene carbonate + acetic or propionic acid mixtures at 288.15, 298.15 and 313.15 K

x_1	C_p/ (J mol^{-1} K^{-1})	x_1	C_p/ (J mol^{-1} K^{-1})
Propylene carbonate(1) + acetic acid(2)			
$T = 288.15$ K			
0.0000	121.4	0.5353	147.5
0.0554	124.1	0.6737	152.6
0.1282	128.4	0.7985	157.6
0.2292	132.6	0.9322	162.3
0.3359	138.4	1.0000	164.6
0.4121	141.5		
$T = 298.15$ K			
0.0000	123.8	0.5353	149.1
0.0554	126.5	0.6737	154.9
0.1282	130.4	0.7985	159.4
0.2292	134.7	0.9322	164.2
0.3359	140.3	1.0000	166.4
0.4121	143.1		
$T = 313.15$ K			
0.0000	127.2	0.5353	151.8
0.0554	130.0	0.6737	158.0
0.1282	133.4	0.7985	162.4
0.2292	137.7	0.9322	166.8
0.3359	143.3	1.0000	169.1
0.4121	145.9		
Propylene carbonate(1) + propionic acid(2)			
$T = 288.15$ K			
0.0000	151.3	0.5480	162.1
0.0776	152.8	0.6528	163.1
0.2105	156.0	0.7818	165.0
0.3544	159.8	0.8553	165.3
0.4917	161.6	1.0000	164.6
$T = 298.15$ K			
0.0000	154.1	0.5480	164.2
0.0776	155.5	0.6528	165.1
0.2105	158.3	0.7818	166.8
0.3544	162.0	0.8553	166.7
0.4917	164.0	1.0000	166.4
$T = 313.15$ K			
0.0000	158.2	0.5480	167.6
0.0776	159.7	0.6528	168.2
0.2105	162.4	0.7818	169.3
0.3544	165.3	0.8553	169.1
0.4917	167.3	1.0000	169.1

between molecules i and j, δ and θ the normalized parameters.

Values of z in the 8–12 range lead practically to the same results.

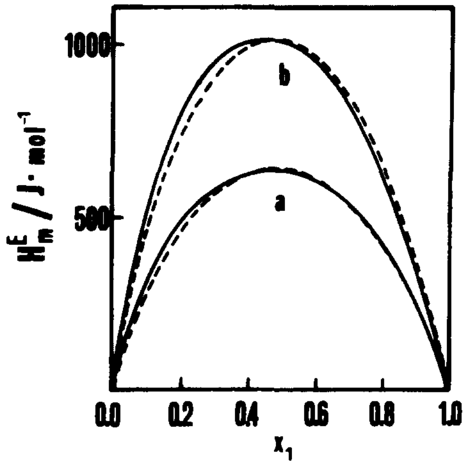


Fig. 4. Comparison between the Redlich–Kister fit (solid curve), Eq. (1), and the cell model (dashed curve) Eq. (4), for H^E_m of propylene carbonate + acetic acid (a) or + propionic acid (b) at 298.15 K.

Values of δ have been calculated from Eq. (5) with E_{11} and E_{22} evaluated as the heats of vaporization reported in the literature [10].

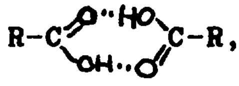
Table 6 shows the interaction energy values, E_{ij}, between the molecules for the mixtures studied in this paper.

An example of comparison between Redlich–Kister and cell model fits is shown in Fig. 4 for propylene carbonate + acetic or propionic acid at 298.15 K.

5. Conclusions

Values of H^E_m are positive for all mixtures, as can be seen from Fig. 1. In fact, hydrogen bondings of pure organic acids are broken during mixing with the ester propylene carbonate and the energy intake is needed.

Also the C=O group of ester may give rise to hydrogen bonding with acids, but the energy involved must be smaller since acids associate in the stable form



with two hydrogen bonds.

Values of H^E_m for mixtures containing acetic acid are smaller than the ones containing propionic acid. It is

Table 5
Parameters, A_k, correlation coefficients, $|R|$, and standard deviations, $\sigma(C_p)$, $\sigma(C_p^E)$, of heat capacities C_p and excess heat capacities, C_p^E, for propylene carbonate + acetic or propionic acid mixtures at (288.15, 298.15 and 313.15) K

Mixture	Function/ ($J\ mol^{-1}\ K^{-1}$)	A_0	A_1	A_2	$\|R\|$	$\sigma(C_p)$, $\sigma(C_p^E)$ ($J\ mol^{-1}\ K^{-1}$)
$T = 288.15$ K						
Propylene carbonate + acetic acid	C_p	121.36	53.586	−10.320	0.99979	0.24
	C_p^E	−0.0589	10.375	−10.320	0.94995	0.24
Propylene carbonate + propionic acid	C_p	151.02	29.099	−15.220	0.99503	0.39
	C_p^E	−0.2567	15.746	−15.220	0.94577	0.39
$T = 298.15$ K						
Propylene carbonate + acetic acid	C_p	123.68	52.146	−9.3632	0.99982	0.22
	C_p^E	−0.0876	9.5401	−9.3632	0.94864	0.22
Propylene carbonate + propionic acid	C_p	153.80	27.509	−14.765	0.99543	0.34
	C_p^E	−0.2550	15.188	−14.765	0.95403	0.34
$T = 313.15$ K						
Propylene carbonate + acetic acid	C_p	127.10	50.487	−8.3431	0.99958	0.33
	C_p^E	−0.1289	8.6054	−8.3431	0.96979	0.33
Propylene carbonate + propionic acid	C_p	158.05	25.115	−14.043	0.99800	0.20
	C_p^E	−0.0118	13.755	−13.742	0.99060	0.20

interesting to remark that this result agrees with the conclusions of the study of Davies [24] on the binding energies of hydrogen bonds for organic acids in the gas phase.

Values of E_{ij} obtained through the cell model are reported in Table 6 and indicate a direct relationship between H_m^E and $E_{11} + E_{22} - 2E_{12}$, as stated by the approximated model of regular solutions.

Furthermore, H_m^E increases with the increase of temperature and the amount is nearly the same for acetic and propionic acids.

If we remember the definition of H_m^E as a function of the enthalpy of the mixture, H, and of the pure components, H_i,

$$H_m^E = H - x_1 H_1 - x_2 H_2 \tag{8}$$

Table 6
Interaction energies, E_{ij}, between molecules for propylene carbonate + acetic or propionic acid, Eqs. (4)–(7), with $z = 8$, Eq. (4) at (288.15, 298.15 and 313.15) K

Mixture	E_{11} [a]	E_{22} [a]	E_{12} [a]	$E_{11} + E_{22} - 2E_{12}$
$T = 288.15$ K				
Propylene carbonate				
+acetic acid	55.25	23.26	39.03	0.45
+propionic acid	55.25	31.05	42.81	0.68
$T = 298.15$ K				
Propylene carbonate				
+acetic acid	55.25	23.37	39.08	0.46
+propionic acid	55.25	31.15	42.84	0.72
$T = 313.15$ K				
Propylene carbonate				
+acetic acid	55.25	23.53	39.15	0.48
+propionic acid	55.25	31.30	42.89	0.77

[a] E_{ij} in kJ mol^{-1}.

and its derivative with respect to the temperature

$$\partial H_m^E/\partial T \equiv C_p^E = C_p - x_1 C_{p1} - x_2 C_{p2} \qquad (9)$$

we see that a positive value for $\partial H_m^E/\partial T$ matches with the positive excess heat capacities C_p^E as shown in Fig. 3.

As can be seen from comparison of Figs. 1 and 2, the C_p curves show a behavior similar to the ones of H_m^E, with larger values for propylene carbonate + propionic mixtures and almost the same positive temperature increase for both the acids. As a consequence, the A_i parameters in Eq. (2) are temperature dependent.

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