

Excess Molar Enthalpies of Binary Mixtures Containing Propylene Carbonate + 23 Alkanoates at 298.15 K

Fabio Comelli,[†] Romolo Francesconi,^{*,‡} and Stefano Ottani[†]

Centro di Studio per la Fisica delle Macromolecole del CNR, via Selmi 2, I-40126 Bologna, Italy, and Dipartimento di Chimica "G. Ciamician", Università degli Studi, via Selmi 2, I-40126 Bologna, Italy

Excess molar enthalpies, H_m^E , of binary mixtures containing propylene carbonate + 23 alkanooates as a function of the mole fraction of propylene carbonate have been determined at 298.15 using a flow microcalorimeter. H_m^E values are positive for all mixtures, increasing as the chain length of the alkanooate is increased with a maximum at a mole fraction of ≈ 0.5 . Maximum values range from 26 J·mol⁻¹ for methyl acetate to 960 J·mol⁻¹ for ethyl octanoate. Binary mixtures containing propylene carbonate + each one of the structural isomers have been considered. Results have been correlated using the Redlich–Kister equation and have been qualitatively explained.

Introduction

Several recent chemical and electrochemical studies have focused on propylene carbonate, an aprotic solvent with a high potential for industrial uses such as in lithium batteries (Gabano, 1983; Tobishima et al., 1988; Pistoia, 1994) because it does not react with lithium to evolve hydrogen.

Following our systematic studies on the physical properties of binary organic liquid mixtures with one or both components as dipolar-protic solvents, we report in this paper the excess molar enthalpies, H_m^E , of binary mixtures containing propylene carbonate + 23 alkanooates at 298.15 K.

We have not considered mixtures containing alkanooates with a number of carbon atoms $n > 10$ as they are only partially miscible in propylene carbonate.

To our knowledge, no literature results are available for the mixtures studied in this paper.

Experimental Section

Chemicals. Chemicals were purchased from Aldrich Chemical Co. with the exception of methyl and ethyl acetate and butyl butyrate, which were Fluka products.

Liquids were used without further purification after gas chromatography failed to show any significant impurities.

Purities of components were also checked by comparing their densities, ρ , at (293.15 or 298.15) K with those reported in the literature. Both ours and literature values are listed in Table 1.

Before measurements, liquids were kept in dark bottles, dried over molecular sieves (Union Carbide, type 4A, $1/16$ in. pellets), and degassed by ultrasound (Ultrasonic bath, Hellma, type 460, Milan, Italy).

Apparatus and Procedure. Densities, ρ , of pure components were determined using an Anton Paar vibrating-tube digital densimeter (DMA 60) equipped with a measuring cell (type 602). Procedural details have been described elsewhere (Fermeglia and Lapasin, 1988). The

Table 1. Mole Percent Purities of Pure Components and Densities, ρ , Compared with Literature Values

component (purity mol %)	T/K	$\rho/\text{g}\cdot\text{cm}^{-3}$	
		this paper	lit.
propylene carbonate (99.7)	298.15	1.199 45	1.199 5 ^a
methyl acetate (>99)	298.15	0.926 63	0.927 0 ^b
ethyl acetate (99.5)	298.15	0.894 38	0.894 55 ^c
vinyl acetate (>99)	298.15	0.925 77	0.925 5 ^d
propyl acetate (99)	298.15	0.883 33	0.883 03 ^c
butyl acetate (99.7)	298.15	0.876 19	0.876 34 ^c
pentyl acetate (99)	298.15	0.872 58	0.871 9 ^c
hexyl acetate (99)	298.15	0.868 55	0.868 42 ^e
methyl propanoate (99)	293.15	0.914 89	0.915 0 ^f
ethyl propanoate (99)	298.15	0.883 33	0.883 1 ^c
propyl propanoate (99)	293.15	0.881 11	0.880 9 ^f
butyl propanoate (99)	293.15	0.875 43	0.875 4 ^f
methyl butyrate (99)	293.15	0.898 50	0.898 4 ^f
ethyl butyrate (99)	298.15	0.873 56	0.873 94 ^c
propyl butyrate (99)	293.15	0.872 93	0.873 0 ^f
butyl butyrate (>99)	293.15	0.869 60	0.870 0 ^f
ethyl pentanoate (99)	298.15	0.869 38	0.869 0 ^f
ethyl hexanoate (>99)	293.15	0.873 01	0.873 0 ^f
ethyl heptanoate (99)	293.15	0.881 51	0.881 5 ^f
ethyl octanoate (99)	298.15	0.862 32	0.862 4 ^f
<i>tert</i> -butyl acetate (>99)	293.15	0.866 30	0.866 5 ^f
ethyl isobutyrate (99)	293.15	0.868 31	0.868 0 ^f
isobutyl acetate (99)	293.15	0.871 5	0.871 2 ^f
methyl pentanoate (99)	298.15	0.884 85	0.884 50 ^g

^a Moumouzas et al. (1991). ^b Martin et al. (1994). ^c Riddick et al. (1986). ^d Benito et al. (1994). ^e El-Banna (1997). ^f Beilstein Handbook. ^g Ortega et al. (1991).

temperature measurements were precise to ± 0.01 K, and the accuracy of density was better than $\pm 1 \times 10^{-5}$ g·cm⁻³.

The flow microcalorimeter (LKB Produkter, model 2107, Bromma, Sweden) used for the H_m^E measurements and the experimental procedure have been described previously (Monk and Wadso, 1968; Francesconi and Comelli, 1986).

Chemicals were pumped into the mixing cell of the calorimeter by means of two automatic burets (ABU 80, Radiometer, Copenhagen, Denmark), and the calorimeter cell was thermostated at (298.15 ± 0.01) K and controlled by calibrated thermoresistors inside the apparatus.

Mole fractions, x_1 , of propylene carbonate (component 1) have been determined from calibrated flow rates that were

* To whom correspondence should be sent.

[†] Centro di Studio per la Fisica delle Macromolecole.

[‡] Università degli Studi.

Table 2. Experimental Excess Molar Enthalpies, H_m^E , for Propylene Carbonate (1) + Alkanoate (2) Mixtures at 298.15 K

x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$
Propylene Carbonate + Methyl Acetate											
0.0376	9	0.1353	19	0.3196	24	0.5849	26	0.7898	20	0.9185	8
0.0726	14	0.1902	23	0.3851	25	0.6526	25	0.8493	16	0.9575	5
0.1051	18	0.2384	24	0.4843	25	0.7381	23	0.8826	14		
Propylene Carbonate + Ethyl Acetate											
0.0460	38	0.1617	104	0.3666	164	0.6345	168	0.8224	108	0.9328	43
0.0879	68	0.2244	129	0.4355	175	0.6983	156	0.8741	79	0.9653	22
0.1264	87	0.2787	143	0.5365	178	0.7764	129	0.9025	60		
Propylene Carbonate + Propyl Acetate											
0.0536	64	0.1846	190	0.4045	308	0.6708	300	0.8446	186	0.9422	76
0.1017	114	0.2535	241	0.4752	328	0.7310	265	0.8907	131	0.9702	40
0.1452	157	0.3117	275	0.5760	323	0.8030	220	0.9157	104		
Propylene Carbonate + Vinyl Acetate											
0.0435	65	0.1540	184	0.3533	249	0.6211	214	0.8138	124	0.9291	41
0.0834	119	0.2145	220	0.4214	252	0.6860	190	0.8677	86	0.9633	19
0.1202	155	0.2670	238	0.5221	242	0.7662	151	0.8973	65		
Propylene Carbonate + Butyl Acetate											
0.0609	118	0.2060	322	0.4378	475	0.7002	428	0.8617	269	0.9492	116
0.1148	210	0.2802	399	0.5090	488	0.7570	391	0.9033	205	0.9739	62
0.1629	273	0.3417	432	0.6090	473	0.8105	330	0.9257	162		
Propylene Carbonate + Pentyl Acetate											
0.0680	164	0.2261	436	0.4671	604	0.7245	534	0.8752	325	0.9546	136
0.1274	281	0.3047	517	0.5389	623	0.7781	487	0.9132	245	0.9768	73
0.1797	366	0.3688	559	0.6367	602	0.8402	399	0.9334	194		
Propylene Carbonate + Hexyl Acetate											
0.0752	216	0.2453	547	0.4938	723	0.7453	638	0.8864	419	0.9590	177
0.1398	371	0.3278	636	0.5653	725	0.7960	579	0.9213	298	0.9791	97
0.1960	477	0.3940	684	0.6611	704	0.8541	480	0.9398	249		
Propylene Carbonate + Methyl Propanoate											
0.0450	38	0.1585	106	0.3611	174	0.6293	173	0.8716	80	0.9314	41
0.0861	68	0.2204	135	0.4298	181	0.6935	158	0.9005	57	0.9645	21
0.1238	89	0.2737	150	0.5309	183	0.7724	129				
Propylene Carbonate + Ethyl Propanoate											
0.0535	90	0.1844	236	0.4042	363	0.6706	340	0.8906	145	0.9421	76
0.1016	154	0.2533	290	0.4749	376	0.7307	307	0.9156	110	0.9702	39
0.1450	199	0.3114	325	0.5757	374	0.8028	248				
Propylene Carbonate + Propyl Propanoate											
0.0606	137	0.2052	360	0.4364	527	0.6991	474	0.9029	199	0.9489	104
0.1143	237	0.2791	431	0.5080	545	0.7560	426	0.9253	149	0.9738	55
0.1622	305	0.3405	483	0.6077	532	0.8229	331				
Propylene Carbonate + Butyl Propanoate											
0.0678	183	0.2255	467	0.4663	666	0.7239	592	0.9129	252	0.9545	137
0.1271	310	0.3040	561	0.5381	684	0.7775	523	0.9332	196	0.9767	71
0.1792	396	0.3680	624	0.6361	652	0.8398	412				
Propylene Carbonate + Methyl Butyrate											
0.0527	79	0.1820	212	0.4004	320	0.6670	299	0.8891	136	0.9413	71
0.1001	137	0.2503	258	0.4710	333	0.7276	272	0.9144	101	0.9697	37
0.1430	177	0.3080	288	0.5718	329	0.8003	221				
Propylene Carbonate + Ethyl Butyrate											
0.0611	141	0.2066	364	0.4386	536	0.7010	476	0.9036	198	0.9494	109
0.1152	242	0.2809	438	0.5102	541	0.7576	427	0.9259	153	0.9740	56
0.1634	308	0.3424	486	0.6098	529	0.8242	336				
Propylene Carbonate + Propyl Butyrate											
0.0680	188	0.2260	485	0.4670	692	0.7244	591	0.9132	258	0.9546	141
0.1274	319	0.3046	579	0.5388	692	0.7780	528	0.9334	193	0.9768	74
0.1797	415	0.3687	638	0.6367	663	0.8402	416				
Propylene Carbonate + Butyl Butyrate											
0.0751	234	0.2451	610	0.4935	826	0.7451	685	0.9212	315	0.9590	175
0.1397	402	0.3276	712	0.5650	816	0.7958	607	0.9397	237	0.9791	94
0.1959	524	0.3937	773	0.6608	769	0.8539	493				
Propylene Carbonate + Ethyl Pentanoate											
0.0683	189	0.2267	493	0.4680	683	0.7252	586	0.9135	269	0.9548	147
0.1278	323	0.3055	585	0.5398	687	0.7787	526	0.9337	208	0.9769	78
0.1803	416	0.3697	635	0.6376	665	0.8407	422				
Propylene Carbonate + Ethyl Hexanoate											
0.0753	237	0.2451	606	0.4944	810	0.7458	683	0.9215	307	0.9591	176
0.1401	404	0.3283	710	0.5659	811	0.7964	608	0.9399	243	0.9791	94
0.1964	523	0.3946	775	0.6617	767	0.8544	493				

Table 2. (Continued)

x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$
Propylene Carbonate + Ethyl Heptanoate											
0.0822	275	0.2639	709	0.5182	898	0.7634	753	0.9281	356	0.9627	204
0.1520	477	0.3497	830	0.5891	889	0.8114	669	0.9451	293	0.9810	110
0.2119	618	0.4176	871	0.6826	849	0.8658	555				
Propylene Carbonate + Ethyl Octanoate											
0.0891	335	0.2812	845	0.5399	957	0.7789	777	0.9337	385	0.9657	228
0.1636	582	0.3698	941	0.6101	920	0.8244	699	0.9494	319	0.9826	121
0.2268	743	0.4389	954	0.7013	854	0.8756	601				
Propylene Carbonate + <i>tert</i> -Butyl Acetate											
0.0610	141	0.2090	403	0.4423	588	0.7040	513	0.8638	300	0.9501	123
0.1167	255	0.2839	485	0.5139	607	0.7603	454	0.9049	225	0.9744	66
0.1654	339	0.3458	544	0.6133	576	0.8236	368	0.9269	175		
Propylene Carbonate + Ethyl Isobutyrate											
0.0615	131	0.2076	351	0.4401	531	0.7022	495	0.9041	207	0.9497	109
0.1158	224	0.2821	428	0.5117	554	0.7585	434	0.9263	158	0.9742	56
0.1642	290	0.3438	483	0.6112	535	0.8250	340				
Propylene Carbonate + Isobutyl Acetate											
0.0616	124	0.2081	336	0.4408	480	0.7029	429	0.9044	198	0.9498	110
0.1161	218	0.2828	408	0.5125	493	0.7593	384	0.9266	150	0.9743	61
0.1646	286	0.3445	443	0.6119	474	0.8255	311				
Propylene Carbonate + Methyl Pentanoate											
0.0604	119	0.2045	328	0.4354	490	0.6982	438	0.9025	187	0.9487	111
0.1139	206	0.2783	403	0.5096	500	0.7552	396	0.9140	175	0.9737	58
0.1616	272	0.3395	447	0.6067	486	0.8223	315				

Table 3. Adjustable Parameters, a_k , Eq 1, and Standard Deviations, $\sigma(H_m^E)$, of Binary Mixtures of Propylene Carbonate + 23 Alkanoates at 298.15 K

mixture	a_0	a_1	a_2	a_3	a_4	$\sigma(H_m^E)/\text{J}\cdot\text{mol}^{-1}$
propylene carbonate						
+ methyl acetate	101.5	12.1	88.7	-83.9		0.4
+ ethyl acetate	713.9	67.6	77.5	-217.4		1.1
+ vinyl acetate	973.2	-307.5	377.3	-316.1	-280.6	1.4
+ propyl acetate	1315.5	92.0				2.8
+ butyl acetate	1939.5	144.0	380.6			3.1
+ pentyl acetate	2462.6	307.6	548.9			4.0
+ hexyl acetate	2889.1	323.9	1144.8	472.5		4.8
+ methyl propanoate	741.8	12.2	25.9	-186.9		1.8
+ ethyl propanoate	1517.4	112.6	94.1	-376.5		2.2
+ propyl propanoate	2176.2	240.8	188.7	-495.1		2.6
+ butyl propanoate	2718.1	374.7	410.6	-269.2		3.9
+ methyl butyrate	1335.4	57.8	142.6	-254.5		2.2
+ ethyl butyrate	2179.9	210.6	244.0	-411.4		3.0
+ propyl butyrate	2776.1	269.7	416.7	-150.7		3.6
+ butyl butyrate	3272.3	248.9	741.6	363.6		4.7
+ ethyl pentanoate	2751.8	225.5	561.8			3.1
+ ethyl hexanoate	3247.5	261.3	801.0	339.0		2.2
+ ethyl heptanoate	3596.1	158.7	1204.0	1117.4		5.4
+ ethyl octanoate	3837.6	-455.0	1751.9	2280.8		6.2
+ <i>tert</i> -butyl acetate	2405.5	74.1	184.5			2.8
+ ethyl isobutyrate	2204.7	341.1	117.6	-386.4		3.7
+ isobutyl acetate	1962.3	72.5	363.7			2.5
+ methyl pentanoate	2006.4	105.2	191.5			2.8

selected to cover the whole mole fraction range. In the extreme points, the measurements were carried out at a flow speed of 0.125 mL/min. The average uncertainty in H_m^E was estimated to be 1%, and that in mole fraction was $\pm 1 \times 10^{-4}$. Two replicate measurements were made for each point.

Before measurements, the calorimeter was checked using the test mixture cyclohexane + hexane for which literature values are well-known (Gmehling, 1993), and the agreement between ours and literature data was better than 0.5% over the central range of mole fraction of cyclohexane.

Results and Discussion

The H_m^E data are given in Table 2, and their graphical representation is shown in Figure 1. H_m^E values were

fitted to the Redlich–Kister equation

$$H_m^E/\text{J}\cdot\text{mol}^{-1} = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \quad (1)$$

where a_k are the adjustable parameters obtained by unweighted least-squares regression and x_1 , x_2 are the molar fractions of propylene carbonate and alkanoates, respectively. The parameters a_k and the standard deviations, $\sigma(H_m^E)$, are listed in Table 3.

Figure 1 reports all 23 mixtures. For sake of clarity, only the Redlich–Kister curves are represented and not the experimental points, which in many cases overlap within the limits of the experimental uncertainty.

Mixtures show endothermic mixing in all cases, and H_m^E values exhibit a maximum at a mole fraction close to

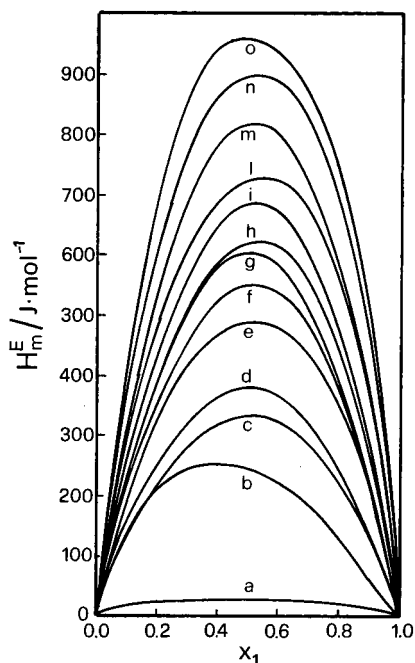


Figure 1. Excess molar enthalpies, H_m^E , of propylene carbonate + 23 alkanooates at 298.15 K, according to their increasing number of C-atoms. Solid lines, Redlich–Kister equation. (a) methyl acetate (3 C-atoms, C_3); (b) vinyl acetate (C_4); (c) propyl acetate, methyl butyrate (C_5); (d) ethyl propionate (C_5); (e) methyl pentanoate, isobutyl acetate, butyl acetate (C_6); (f) ethyl isobutyrate, propyl propanoate, ethyl butyrate (C_6); (g) *tert*-butyl acetate (C_6); (h) pentyl acetate (C_7); (i) butyl propanoate, ethyl pentanoate (C_7); (l) hexyl acetate (C_8); (m) ethyl hexanoate, butyl butyrate (C_8); (n) ethyl heptanoate (C_9); (o) ethyl octanoate (C_{10}).

0.5 increasing as the chain length of the alkanooates is increased. Maximum values range from 26 to 960 $J \cdot mol^{-1}$.

Figure 1 shows also the grouping of 19 of the 23 mixtures into four sets of structural isomers with 5 to 8 C atoms, respectively. For example, curves c and d refer to the structural isomers with five atoms of carbon. Moreover, curve c refers to H_m^E data of propylene carbonate + propyl acetate and + methyl butyrate, which overlap (see Table 2).

We see that (1) isoalkanoates show the same H_m^E of the corresponding alkanooates; (2) within each set of isomers, alkyl acetates have the smallest values of H_m^E ; (3) the H_m^E values of vinyl acetate (four C atoms) follow the same trend of the other compounds as the number of C atoms is increased. However, the double bond leads to a significant

increase of H_m^E in comparison to methyl acetate (three C atoms) in mixtures with propylene carbonate.

Also asymmetry of the H_m^E vs x_1 curve is evident, in contrast to the nearly symmetrical curves of saturated alkanooates.

It must be pointed out that vinyl acetate and methyl acetate, in mixtures with dimethyl carbonate, show a calorimetric behavior quite different from that in propylene carbonate (Comelli et al., 1997), with negative H_m^E 's for mixtures containing vinyl acetate and very low positive values for mixtures with methyl acetate.

Literature Cited

- Benito, G. C.; Cartom, A.; Uruena, M. A. Vapor–Liquid Equilibria for the Mixtures Ether + 2-Butanol and Propyl Acetate at 101.3 kPa. *J. Chem. Eng. Data* **1994**, *39*, 249–250.
- Comelli, F.; Francesconi, R.; Ottani, S. Excess Molar Enthalpies and Excess Molar Volumes of Dimethyl Carbonate + Seven Alkyl Acetates at 298.15 K. *J. Chem. Eng. Data* **1997**, *42*, 1208–1211.
- El-Banna, M. Densities and Viscosities for Mixtures of Pentyl Acetate and Hexyl Acetate with Normal Alkanols at 298.15 K. *J. Chem. Eng. Data* **1997**, *42*, 31–34.
- Fermeglia, M.; Lapasin, J. Excess Volumes and Viscosities of Binary Mixtures of Organics. *J. Chem. Eng. Data* **1988**, *33*, 415–417.
- Francesconi, R.; Comelli, F. Liquid-Phase Enthalpy of Mixing for the System 1,3-Dioxolane–Chlorobenzene in the Temperature Range 288.15–313.15 K. *J. Chem. Eng. Data* **1986**, *31*, 250–253.
- Francesconi, R.; Castellari, C.; Comelli, F. Excess Molar Enthalpies of Diethyl Carbonate + Fourteen *n*-Alkyl Alkanooates at 298.15 K. *Thermochim. Acta* **1997**, *306*, 99–103.
- Gabano, J.-P., Ed. *Lithium Batteries*; Academic Press: New York, 1983.
- Gmehling, I. Excess Enthalpies for 1,1,1-Trichloroethane with Alkanes, Ketones, and Esters. *J. Chem. Eng. Data* **1993**, *38*, 143–146.
- Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, FL, 1996.
- Luckenbach, R. *Beilstein Handbook of Organic Chemistry*; Springer-Verlag: Heidelberg, Germany.
- Martin, M. C.; Cocero, M. J.; Mato, R. B. Vapor–Liquid Equilibrium Data at 298.15 K for Binary Systems Containing Methyl Acetone or Methanol with 2-Methoxyethanol or 2-Ethoxyethanol. *J. Chem. Eng. Data* **1994**, *39*, 535–537.
- Monk, P.; Wadso, I. A Flow Micro Reaction Calorimeter. *Acta Chem. Scand.* **1968**, *22*, 1842–1852.
- Moumouzias, G.; Ponopoulos, D.; Ritzoulis, G. Excess Properties of the Binary Liquid System Propylene Carbonate + Acetonitrile. *J. Chem. Eng. Data* **1991**, *36*, 20–23.
- Ortega, I.; Matos, J. S.; Pena, J. A. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1991**, (3), 180.
- Pistoia, G. *Lithium Batteries*. In *Industrial Chemical Library*; Elsevier: Amsterdam, 1994; Vol. 5.
- Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986.
- Tobishima, S.; Arakawa, M.; Yamaki, E. Electrolytic Properties of $LiClO_4$ –Propylene Carbonate Mixed with Amieie–Solvents for Lithium Batteries. *Electrochim. Acta* **1988**, *33*, 239–244.

Received for review October 17, 1997. Accepted January 28, 1998.

JE9702504