ELSEVIER

Thermochimica Acta 354 (2000) 89–97

thermochimica acta

www.elsevier.com/locate/tca

Excess molar enthalpies of binary mixtures containing propylene carbonate + some *n*-alkoxy- and *n*-alkoxyethoxy-ethanols at 288.15, 298.15, and 313.15 K

Fabio Comelli[a], Romolo Francesconi[b,*], Carlo Castellari[b]

[a]*Centro di Studio per la Fisica delle Macromolecole del CNR, via Selmi 2, I-40126 Bologna, Italy*
[b]*Dipartimento di Chimica 'G. Ciamician', Università degli Studi, via Selmi 2, I-40126 Bologna, Italy*

Received 20 September 1999; accepted 8 February 2000

Abstract

Excess molar enthalpies, H_m^E, of binary mixtures containing propylene carbonate + six *n*-alkoxyethanols have been determined using an LKB flow microcalorimeter at 288.15, 298.15, and 313.15 K and at atmospheric pressure. The alkoxyethanols were 2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, and 2-(2-butoxyethoxy)ethanol. From the experimental data, deviations in H_m^E have been determined and fitted to the Redlich–Kister polynomial to estimate the binary interactions parameters. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Calorimeter; Enthalpies; Correlation

1. Introduction

This paper is part of our systematic program of research on the measurements of excess properties of binary mixtures containing propylene carbonate [1–4], an aprotic solvent used for a variety of industrial applications, particularly in lithium high-batteries [5–7], being its property to not react with lithium to involve hydrogen. A careful pursuit in the literature reveals that measurements of excess molar volumes, viscosities, relative permittivity and vapor–liquid equilibria of binary mixtures containing propylene carbonate with either higher alkanols, alkoxyethanols or hydrocarbons have been made [8–10].

Experimental results in these binary mixtures suggest the relative importance of hydrogen bonding interactions between the oxy (–O–) and hydroxy (–OH–) groups and the propylene carbonate molecules, giving important information in many practical problems concerning heat transport, mass transport, etc.. . .

The aim of this paper is to provide a set of values of excess molar enthalpies, H_m^E, for a qualitatively characterisation of the molecular interactions in mixtures containing propylene carbonate +2-methoxyethanol, +2-ethoxyethanol, +2-butoxyethanol, +2-(2-methoxyethoxy)ethanol, +2-(2-ethoxyethoxy)ethanol, and +2-(2-butoxyethoxy)ethanol at 288.15, 298.15, and 313.15 K and at atmospheric pressure over the whole concentration range.

* Corresponding author. Tel.: +33-051-2094325; fax: +33-051-2094325.
E-mail address: romolo@ciam.unibo.it (R. Francesconi)

PII: S0040-6031(00)00457-3

No H_m^E data have been found in literature for these systems.

2. Experimental

2.1. Chemicals

Chemicals were Aldrich and Fluka products. Propylene carbonate (purity, 99.8 mol%), 2-methoxyethanol (better than 99.9 mol%), 2-ethoxyethanol (better than 99.5 mol%), and 2-butoxyethanol (better than 99.8 mol%) were used as received owing to their purity grade from purchaser. 2-(2-Methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, and 2-(2-butoxyethoxy)ethanol, all showing a stated purity better than 99 mol% (from purchaser) have been fractionally distilled on an 80-theoretical plate column and the fraction distilling within ±0.01 K interval has been used for the measurements. Obtained new purities were 99.8 mol% and were checked on a Hewlett-Packard gas chromatograph model 5890 by using an HP (cross linked 5% Me siloxane capillary column).

Purities of components have also been checked by comparing their measured densities, ρ, and refractive indices, n_D^{25}, at 298.15 K with those reported in literature [11–21], as shown in Table 1. Densities have been determined with an accuracy of $\pm 1\times10^{-5}$ g cm^{-3} using a vibrating density meter (Anton Paar, model DMA 60/602, Graz, Austria) and refractive indices using an Abbe refractometer (Carl Zeiss, Jena, D) with a precision of ±0.0001.

Before use, all compounds have been degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy) and than dried in darkness over molecular sieves (Union Carbide, type 4A, 1/16 in. pellets) to reduce water content.

2.2. Calorimetric measurements

The flow microcalorimeter (LKB, model 2107, Produkter AB, Bromma, Sweden) used to determine the excess molar enthalpies of binary mixtures is

Table 1
Densities, ρ, and refractive indices, n_D^{25}, of pure chemicals with comparison with literature data at 298.15 K

Component	ρ (g cm^{-3})		n_D^{25}	
	Expt.	Lit.	Expt.	Lit.
Propylene carbonate	1.19952	1.1995 [11] 1.1993 [12] 1.1992 [13] 1.1951 [14] 1.1988 [15]	1.4195	1.4194 [11] 1.4199 [14] 1.4210 [15]
2-Methoxyethanol	0.96924	0.96024 [14] 0.96015 [16] 0.9600 [17] 0.9602 [18]	1.4003	1.4002 [14] 1.4004 [16]
2-Ethoxyethanol	0.92505	0.92520 [14] 0.9251 [18] 0.92572 [16]	1.4055	1.4057 [14] 1.4050 [18]
2-Butoxyethanol	0.89631	0.89625 [14] 0.89623 [19]	1.4175	1.4176 [14]
2-(2-Methoxyethoxy)ethanol	1.01591	1.0167 [14] 1.0164 [20]	1.4243	1.4245 [14]
2-(2-Ethoxyethoxy)ethanol	0.98429	0.9841 [14] 0.9839 [20]	1.4255	1.4254 [14]
2-(2-Butoxyethoxy)ethanol	0.95688[a]	0.9579[a] [21]	1.4346[a]	1.4341[a] [21]

[a] At 293.15 K.

basically of the type employed by early workers [22] and the description of the apparatus is given previously [23].

The temperature was accurate to ±0.01 K and monitored by a calibrated quartz thermometer fixed into the cell compartment.

Two automatic burets (ABU, Radiometer, Copenhagen, Denmark) have been used to pump pure liquids into the mixing cell of the calorimeter and mole fractions x_1 of propylene carbonate have been determined from fluxes, with observed standard errors $\delta x_1 \approx 0.0002$.

The performance of the apparatus and its reliability for the H_m^E measurements have been checked by determining the excess molar enthalpies of the test mixtures hexane + cyclohexane [24]. The data obtained in the present paper lead to a discrepancy of <0.5 J mol^{-1} in H_m^E.

3. Correlation of the calorimetric data

The measured excess molar enthalpies, H_m^E, are given in Table 2. To each of the 18 sets of experimental values, a Redlich–Kister polynomial of the type

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

has been fitted by a method of unweighted least-squares, where x_1, x_2 are the molar fractions of propylene carbonate and alkoxyethanols, and a_k are the adjustable parameters. The a_k values are given in Table 3 together with the standard deviation $\sigma(H_m^E)$ defined as

$$\sigma(H_m^E) = \left| \frac{\phi_{min}}{(N-n)} \right|^{0.5} \quad (2)$$

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

$$\phi = \sum_{k=1}^{N} \eta_k^2 \quad (3)$$

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

Figs. 1 and 2 report the experimental points of six mixtures at 298.15 K while Fig. 3 shows $H_m^E(x_1 = 0.5)$, the equimolar excess enthalpies H_m^E, plotted against the temperature T (K).

Table 2
Excess molar enthalpies, H_m^E, of propylene carbonate + *n*-alkoxy- and *n*-alkoxyethoxy-ethanols

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
Propylene carbonate(1) + 2-methoxyethanol(2)					
T=288.15 K					
0.0373	67	0.3175	577	0.7882	694
0.0719	134	0.3827	663	0.8481	576
0.1042	198	0.4819	762	0.8816	490
0.1342	263	0.5826	809	0.9178	372
0.1887	368	0.6504	802	0.9571	216
0.2367	442	0.7362	744		
T=298.15 K					
0.0373	69	0.3177	608	0.7884	675
0.0720	139	0.3829	698	0.8482	568
0.1043	200	0.4822	788	0.8817	470
0.1343	273	0.5829	817	0.9179	353
0.1888	381	0.6507	814	0.9563	209
0.2369	478	0.7364	757		
T=313.15 K					
0.0374	83	0.3180	709	0.7886	747
0.0721	167	0.3833	815	0.8484	610
0.1044	248	0.4826	900	0.8818	515
0.1345	313	0.5832	931	0.9180	388
0.1890	455	0.6508	916	0.9572	221
0.2371	563	0.7367	828		

Table 2 (*Continued*)

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
Propylene carbonate(1) + 2-ethoxyethanol(2)					
T=288.15 K					
0.0454	130	0.3637	872	0.8205	761
0.0869	254	0.4324	956	0.8739	609
0.1250	363	0.5333	1007	0.9024	497
0.1600	464	0.6317	999	0.9327	373
0.2222	619	0.6957	950	0.9652	213
0.2759	742	0.7742	845		
T=298.15 K					
0.0455	134	0.3640	892	0.8207	753
0.0871	259	0.4327	981	0.8729	600
0.1252	366	0.5337	1039	0.9016	494
0.1602	467	0.6320	1021	0.9321	358
0.2225	630	0.6960	970	0.96421	207
T=313.15 K					
0.0456	158	0.3644	1032	0.8210	834
0.0872	303	0.4332	1111	0.8731	668
0.1253	435	0.5342	1175	0.9017	535
0.1604	544	0.6324	1153	0.9322	396
0.2228	731	0.6963	1086	0.9572	268
0.2765	869	0.7747	944		
Propylene carbonate(1) + 2-butoxyethanol(2)					
T=288.15 K					
0.0606	305	0.4362	1207	0.8609	848
0.1142	535	0.5077	1238	0.9028	662
0.1621	705	0.6075	1238	0.9253	533
0.2050	834	0.6990	1183	0.9489	396
0.2789	1003	0.7558	1110	0.9738	219
0.3403	1107	0.8228	967		
T=298.15 K					
0.0606	303	0.4365	1275	0.8610	815
0.1143	526	0.5080	1328	0.9029	632
0.1622	724	0.6077	1320	0.9253	513
0.2052	853	0.6992	1235	0.9490	360
0.2792	1052	0.7560	1144	0.9733	205
0.3405	1173	0.8229	969		
T=313.15 K					
0.0607	325	0.4367	1476	0.8612	914
0.1144	578	0.5083	1535	0.9030	683
0.1623	792	0.6080	1515	0.9254	554
0.2053	956	0.6994	1404	0.9490	399
0.2872	1217	0.7562	1279	0.9738	218
0.3407	1343	0.8231	1067		
Propylene carbonate(1) + 2-(2-methoxyethoxy)ethanol(2)					
T=288.15 K					
0.0250	−19	0.3165	79	0.8065	345
0.0547	−32	0.4099	147	0.8475	333
0.1037	−31	0.4807	186	0.8929	287
0.1479	−18	0.5814	248	0.9174	248
0.1880	2	0.6758	305	0.9434	194
0.2576	39	0.7353	334	0.9709	110

Table 2 (*Continued*)

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
T=298.15 K					
0.0201	−15	0.3166	120	0.8065	358
0.0547	−27	0.4100	189	0.8475	336
0.1038	−23	0.4808	242	0.8929	292
0.1480	−2	0.5815	300	0.9175	247
0.1880	22	0.6759	350	0.9434	187
0.2578	69	0.7354	365	0.9703	109
T=333.15 K					
0.0201	−3	0.3165	214	0.8065	444
0.0547	−4	0.4099	301	0.8475	399
0.1037	17	0.4808	365	0.8929	329
0.1479	49	0.5816	441	0.9175	273
0.1880	89	0.6758	479	0.9434	206
0.2578	152	0.7353	473	0.9709	116
Propylene carbonate(1) + 2-(2-ethoxyethoxy)ethanol(2)					
T=288.15 K					
0.0625	18	0.4445	375	0.8649	415
0.1177	68	0.5161	412	0.9057	355
0.1667	121	0.6155	458	0.9276	300
0.2106	173	0.7060	476	0.9505	220
0.2858	247	0.7620	487	0.9746	126
0.3479	305	0.8276	467		
T=298.15 K					
0.0626	24	0.4447	430	0.8650	434
0.1177	81	0.5163	469	0.9058	354
0.1668	141	0.6156	507	0.9276	305
0.2107	194	0.7062	524	0.9506	222
0.2859	286	0.7621	513	0.9741	127
0.3481	351	0.8277	473		
T=313.15 K					
0.0626	39	0.4448	556	0.8650	487
0.1178	109	0.5165	623	0.9058	387
0.1668	176	0.6158	667	0.9276	319
0.2107	249	0.7062	661	0.9506	236
0.2860	365	0.7621	626	0.9747	136
0.3481	456	0.8278	559		
Propylene carbonate(1) + 2-(2-butoxyethoxy)ethanol(2)					
T=288.15 K					
0.0772	117	0.5012	626	0.8893	470
0.1434	241	0.5725	635	0.9234	379
0.2008	338	0.6677	645	0.9414	310
0.2509	421	0.7510	635	0.9602	228
0.3344	515	0.8008	612	0.9797	124
0.4011	574	0.8577	536		
T=298.15 K					
0.0773	121	0.5013	707	0.8894	531
0.1435	259	0.5726	729	0.9235	419
0.2008	371	0.6678	742	0.9415	342
0.2510	458	0.7511	724	0.9602	252
0.3345	584	0.8008	689	0.9793	140
0.4012	639	0.8578	620		

Table 2 (*Continued*)

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
T=313.15 K					
0.0773	141	0.5013	896	0.8894	589
0.1435	295	0.5727	939	0.9235	451
0.2008	437	0.6679	944	0.9415	363
0.2509	553	0.7510	875	0.9602	262
0.3345	720	0.8008	807	0.9797	142
0.4012	807	0.8578	682		

H_m^E values are positive for all mixtures with the exception of the mixtures containing 2-(2-methoxyethoxy)ethanol showing negative values when the mole fraction x_1<0.2.

In Figs. 1 and 2 we see that H_m^E values of mixtures containing 2-alkoxyethanols are higher than those containing 2-(2-alkoxyethoxy)ethanols, increase as the molecular weight of the ethanol increases, showing maxima values of $H_m^E \cong 1570$ J mol^{-1} in the mixtures containing 2-butoxyethanol and $H_m^E \cong 950$ J mol^{-1} for 2-(2-butoxyethoxy)ethanol.

Quasi symmetrical curves are shown by mixtures containing 2-alkoxyethanols, while asymmetrical trends were found for mixtures with 2-(2-alkoxyethoxy)ethanols.

Finally, Fig. 3 shows the influence of temperature on H_m^E's, which increase with the same trend for all mixtures as the temperature increases.

An interesting comparison may be done between the H_m^E values of mixtures of present paper, propylene carbonate + *n*-alkoxy or *n*-alkoxyethoxy-ethanols, and those obtained from diethyl carbonate + same ethanols [25].

The more remarkable features are:

1. The H_m^E's of mixtures containing propylene carbonate show a larger dependence both on

Table 3
Least-squares parameters, a_k, Eq. (1), and standard deviations, $\sigma(H_m^E)$, Eq. (2), of experimental excess molar enthalpies, H_m^E, of propylene carbonate + *n*-alkoxy-and *n*-alkoxyethoxy-ethanols at 288.15, 298.15, and 313.15 K

Alkoxy- and alkoxyethoxy-ethanol	T (K)	a_0	a_1	a_2	a_3	$\sigma(H_m^E)$ (J mol^{-1})
2-Methoxyethanol	288.15	3082.3	1258.7	594.3	656.6	4.4
	298.15	3658.6	997.5	262.3	809.8	3.8
	313.15	3193.5	1087.3	355.9	692.0	4.6
2-Ethoxyethanol	288.15	3991.0	823.0	762.5	1096.8	4.5
	298.15	4663.9	854.8	524.6	847.0	5.2
	313.15	4110.9	889.3	489.5	814.7	4.3
2-Butoxyethanol	288.15	4942.8	651.2	2274.6	1128.5	3.5
	298.15	5303.9	757.9	1841.6	645.2	7.1
	313.15	6128.2	808.2	1068.3	804.7	5.6
2-(2-Methoxyethoxy)ethanol	288.15	787.3	1246.7	890.5	1430.0	2.5
	298.15	1004.3	1291.4	622.2	1239.5	2.3
	313.15	1528.9	1559.1	477.5	780.9	2.6
2-(2-Ethoxyethoxy)ethanol	288.15	1609.5	992.9	1060.3	1858.3	4.4
	298.15	2431.7	1445.4	419.8	1234.7	3.8
	313.15	1835.8	1014.7	833.3	1771.0	3.6
2-(2-Butoxyethoxy)ethanol	288.15	2473.9	625.5	1367.0	2162.8	3.7
	298.15	2813.7	857.7	1408.7	2300.5	4.3
	313.15	3616.9	1315.2	770.3	1786.2	4.6

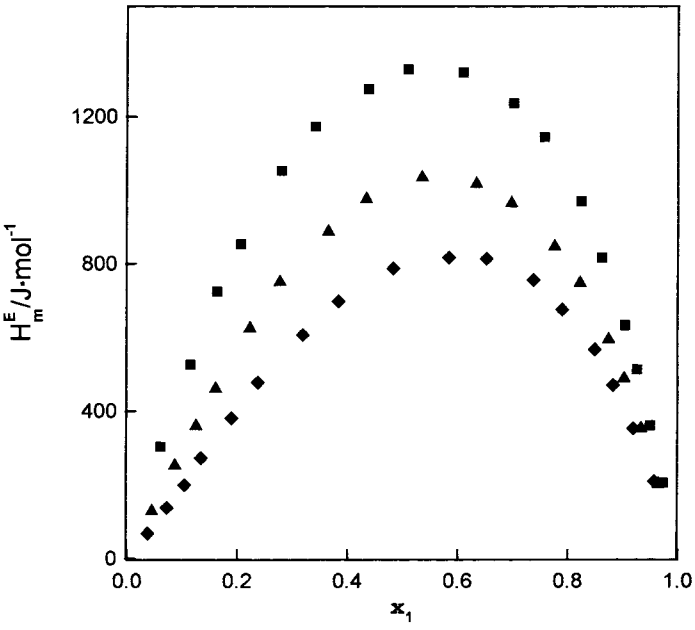

Fig. 1. Excess molar enthalpies, H^E_m, of propylene carbonate + *n*-alkoxyethanols at 298.15 K. (◆), (▲), (■) Refer to mixtures containing 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol, respectively.

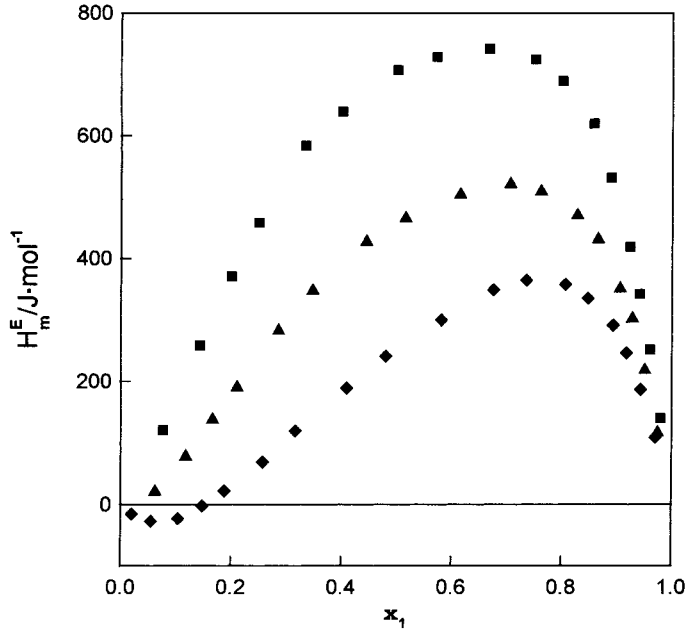

Fig. 2. Excess molar enthalpies, H^E_m, of propylene carbonate + *n*-alkoxyethoxy-ethanols at 298.15 K. (◆), (▲), (■) Refer to mixtures containing 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, and 2-(2-butoxyethoxy)ethanol, respectively.

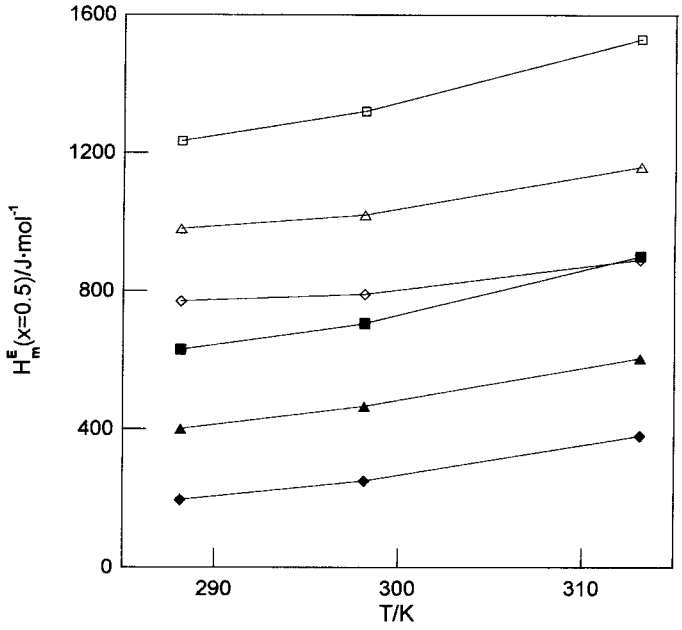

Fig. 3. Values of equimolar $H_m^E(x_1 = 0.5)$ (J mol^{-1}) as a function of temperature, T (K), of mixtures containing propylene carbonate + n-alkoxy- and n-alkoxyethoxy-ethanols. (◆), (▲), (■) Refer to mixtures containing 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol while (◇), (△), (□) refer to mixtures containing 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, and 2-(2-butoxyethoxy)ethanol, respectively.

temperature and chain length (the sign is identical).

2. Asymmetry of H_m^E curves become more marked in mixtures containing propylene carbonate.

Moreover, if the mixtures of this paper are compared with the mixtures containing propylene carbonate + alkylalkanols [26], the latter show much larger values of H_m^E, which may suggest that the ethereal groups of n-alkoxy or n-alkoxyethoxy-ethanols give rise to strong bonding with the carboxylic groups of substituted carbonate with a consequent lowering of the thermal effect in mixing.

References

[1] R. Francesconi, F. Comelli, J. Chem. Eng. Data 41 (1996) 1397.
[2] F. Comelli, M.C. Righetti, Thermochim. Acta 306 (1997) 37.
[3] F. Comelli, R. Francesconi, S. Ottani, J. Chem. Eng. Data 43 (1998) 333.
[4] F. Comelli, R. Francesconi, C. Castellari, J. Chem. Eng. Data 44 (1999) 144.
[5] S. Tobishima, M. Arakawa, Y. Yamaki, Electrochim. Acta 33 (1988) 239.
[6] J.-P. Gabano, Lithium Batteries, Academic Press, New York, 1983.
[7] G. Pistoia, Lithium Batteries. In: Industrial Chemistry Library, Vol. 5, Elsevier, Amsterdam, 1994.
[8] P.K. Muhuri, D.K. Hazra, J. Chem. Eng. Data 40 (1995) 582.
[9] T. Treszcranowicz, Thermochim. Acta 160 (1990) 253.
[10] G. Moumouzias, G. Ritzoulis, J. Chem. Eng. Data 42 (1997) 710.
[11] G. Moumouzias, D. Ponopoulos, G. Ritzoulis, J. Chem. Eng. Data 36 (1991) 20.
[12] M.L. Jansen, H.L. Yeager, J. Phys. Chem. 78 (1974) 1380.
[13] E. Wilhelm, E. Jmenez, G. Roux-Desgranges, G. Grolier, J. Solution Chem. 20 (1) (1991) 17.
[14] J.A. Riddick, W.S. Bunger, T.K. Sakano, Organic Solvents, 4th Edition, Wiley/Interscience, New York, 1986.
[15] A. Pal, G. Dass, A Kumar, J. Chem. Eng. Data 44 (1999) 2.
[16] M.A. Rubio, J.A. Gonzales, I.G. De la Fuente, J.C. Cobos, J. Chem. Eng. Data 43 (1998) 479.
[17] J. Cobos, I. Garcia, C. Casanova, Roux-Desgranges, J.-P.E. Grolier, Int. DATA Ser., Sel. Data Mixtures, Ser. A (1989) (1) 65.
[18] M.C. Martin, M.J. Cocero, R.B. Mato, J. Chem. Eng. Data 39 (1994) 535.
[19] D. Venkatesulu, P. Venkatesu, M.V. Prabhakara Rao, J. Chem. Eng. Data 42 (1997) 365.

[20] A. Pal, S. Sharma, J. Chem. Eng. data 43 (1998) 21.
[21] Handbook of Tables for Organic Compound Identification, 3rd Edition, The Chemical Rubber Co., Cranwood Parkway, Cleveland, OH, 1968.
[22] P. Monk, I. Wadso, Acta Chem. Scand. 22 (1968) 1842.
[23] R. Francesconi, F. Comelli, J. Chem. Eng. Data 31 (1986) 250.
[24] G.C. Benson, Int. DATA Ser., Sel. Data Mixtures, Ser. A (1974) (1), 19.
[25] R. Francesconi, C. Castellari, F. Comelli, J. Chem. Eng. Data (1999), in press.
[26] C. Comelli, R. Francesconi, C. Castellari, J. Chem. Eng. Data 44 (1999) 739.