J. Chem. Eng. Data 1995, 40, 811−814

Excess Molar Enthalpies, Densities, and Excess Molar Volumes of Binary Mixtures Containing Esters of Carbonic Acid at 298.15 and 313.15 K

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Excess molar enthalpies, H_m^E, densities, ϱ, and excess molar volumes, V_m^E, of the binary mixtures propylene carbonate + dimethyl carbonate, propylene carbonate + diethyl carbonate and dimethyl carbonate + diethyl carbonate have been determined at 298.15 and 313.15 K. The excess molar enthalpies are positive for all mixtures while the excess molar volumes are positive only for the dimethyl carbonate + diethyl carbonate system. The absolute values of V_m^E for the mixtures containing propylene carbonate increase with the increase of temperature while for dimethyl carbonate + diethyl carbonate a smaller variation with temperature is noted.

Introduction

Esters of carbonic acid find a wide range of applications as solvents in industry, in the synthesis of pharmaceuticals, and in agricultural chemicals. Particularly, in recent years, much interest has been shown in the properties of propylene carbonate, a dipolar aprotic solvent, which has been used in mixtures of organic electrolytes for some lithium batteries owing to its inertness toward alkali metals (Janz and Tomkins, 1973; Jasinky, 1970; Moumouzias and Ritzoulis, 1992).

We report in this paper, as part of a systematic study on the physical properties of esters of carbonic acid (Francesconi and Comelli, 1994, 1995; Comelli and Francesconi, 1994), the excess molar enthalpies, H_m^E, and the excess molar volumes, V_m^E, of binary mixtures containing propylene carbonate + dimethyl carbonate, propylene carbonate + diethyl carbonate and dimethyl carbonate + diethyl carbonate at 298.15 and 313.15 K. To our knowledge, no measurements have been reported previously for the mixtures studied.

Experimental Section

Materials. The chemicals used were supplied by Aldrich. Their purities and densities are listed in Table 1 and compared with the literature values. All the substances were used without further purification and kept in dark stoppered bottles over molecular sieves (Acros Chimica type 4A, 8−12 mesh, 1/16 in. beads) before each set of measurements. Samples were prepared by mass with a precision of $\pm 1 \times 10^{-4}$ g. All measurements were corrected for buoyancy and for evaporation of components. All molar quantities are based on the 1993 IUPAC recommendations.

Table 1. Purity and Density, ϱ, of the Pure Compounds at 298.15 K

component	purity/(mass %)	ϱ/(g·cm^{-3}) this work	ϱ/(g·cm^{-3}) lit.
propylene carbonate	99.7	1.199 51	1.199 5[a]
dimethyl carbonate	99.0	1.063 30	1.063 50[b]
diethylc arbonate	+99	0.969 27	0.969 26[c]

[a] Moumouzias et al. (1991). [b] Garcia et al. (1992). [c] Riddik et al. (1986).

Calorimetric Measurements. Excess molar enthalpies, H_m^E, were determined at (298.15 or 313.15 ± 0.001) K (IPTS-68) and at atmospheric pressure by means of an LKB flow microcalorimeter (model 2107, LKB, AB Produkter, Bromma, Sweden) equipped with two identical autoburets (ABU-Radiometer, Copenhagen, Denmark), used to pump liquids through the mixing cell of the calorimeter. Calibration of the apparatus, operating procedure, and other details are described elsewere (Monk and Wadso, 1968; Francesconi and Comelli, 1986). The flow microcalorimeter was checked by measuring the standard cyclohexane + hexane mixture to evaluate the accuracy of the experimental technique in comparison with that of the literature (Benson, 1974). The discrepancy between the H_m^E values measured and published was less than ±0.5% over the central range of concentration. The uncertainties in the measured H_m^E are estimated to be on the order of ±(0.5−1) J·mol^{-1}.

Volumetric Measurements. Densities, ϱ, of pure liquids and binary mixtures were measured at 298.15 or 313.15 K and atmospheric pressure using an Anton Paar digital vibrating tube density meter (model 60/602, Anton Paar, Graz, Austria) with a precision of $\pm 10^{-6}$ for the measured period. The temperature of the U-shaped tube was checked using two calibrated digital thermometers (Anton Paar DT 100-25 and DT 100-40) with an accuracy of ±0.01 K while an Hetotherm bath circulator (Heto type 01 DBT 623, Birkerød, Denmark) maintained the temperature constant to within ±0.005 K.

Distilled and degassed water (ϱ(298.15 K) = 0.997 047 g·cm^{-3}) and dry air were used as calibration substances (Wagenreth and Blanke, 1971; Kohlrausch, 1968). The

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0021-9568/95/1740-0811$09.00/0

Table 2. Experimental Excess Molar Enthalpies, H^{E}_{m}, Adjustable Parameters, a_k, and Standard Deviation, $\sigma(H^{E}_{m})$, According to Eq 2 for Binary Mixtures Containing Esters of Carbonic Acid at 298.15 and 313.15 K

x_1	$H^{E}_{m}/(J\cdot mol^{-1})$	x_1	$H^{E}_{m}/(J\cdot mol^{-1})$
Propylene Carbonate (1) − Dimethyl Carbonate (2)			
$T = 298.15$ K			
0.0474	55	0.5989	77
0.0905	85	0.6656	66
0.1106	95	0.7491	53
0.1423	106	0.7993	43
0.1993	114	0.8566	31
0.2491	114	0.8884	23
0.3323	109	0.9228	16
0.3989	102	0.9598	8
0.4988	91		
$a_0 = 360.6$; $a_1 = -240.3$; $a_2 = 312.2$; $a_3 = -373.7$; $a_4 = 141.6$; $\sigma(H^{E}_{m})/(J\cdot mol^{-1}) = 0.8$			
$T = 313.15$ K			
0.0340	58	0.6003	80
0.0658	91	0.6669	70
0.1112	113	0.7502	54
0.1429	119	0.8001	45
0.2001	124	0.8573	34
0.2502	123	0.8890	25
0.3335	119	0.9232	17
0.4002	112	0.9600	9
0.5002	97		
$a_0 = 393.1$; $a_1 = -305.2$; $a_2 = 174.8$; $a_3 = -108.2$; $a_4 = 571.8$; $a_5 = -555.2$; $\sigma(H^{E}_{m})/(J\cdot mol^{-1}) = 1.1$			
Propylene Carbonate (1) − Diethyl Carbonate (2)			
$T = 298.15$ K			
0.0668	138	0.6824	276
0.1066	211	0.7412	244
0.1518	264	0.8112	189
0.1926	293	0.8514	156
0.2636	328	0.8958	110
0.3231	348	0.9197	85
0.4172	353	0.9450	58
0.4884	344	0.9717	32
0.5888	320		
$a_0 = 1375$; $a_1 = -383.2$; $a_2 = 475.2$; $a_3 = -369.2$; $\sigma(H^{E}_{m})/(J\cdot mol^{-1}) = 3.3$			
$T = 313.15$ K			
0.0482	147	0.6833	292
0.0919	234	0.7420	254
0.1523	292	0.8118	204
0.1933	316	0.8519	162
0.2644	354	0.8962	119
0.3240	379	0.9200	93
0.4183	383	0.9452	63
0.4895	374	0.9718	33
0.5899	346		
$a_0 = 1497$; $a_1 = -487.3$; $a_2 = 167.3$; $a_3 = 101.3$; $a_4 = 897.4$; $a_5 = -1074$; $\sigma(H^{E}_{m})/(J\cdot mol^{-1}) = 3.6$			
Dimethyl Carbonate (1) − Diethyl Carbonate (2)			
$T = 298.15$ K			
0.0565	32	0.6834	156
0.1070	62	0.7421	140
0.1523	79	0.8119	113
0.1934	98	0.8520	96
0.2645	124	0.8962	71
0.3241	146	0.9201	59
0.4184	165	0.9453	39
0.4896	171	0.9719	20
0.5899	171		
$a_0 = 689.2$; $a_2 = 92.1$; $\sigma(H^{E}_{m})/(J\cdot mol^{-1}) = 1.5$			
$T = 313.15$ K			
0.0565	27	0.6831	146
0.1069	51	0.7418	132
0.1522	75	0.8117	111
0.1932	89	0.8518	88
0.2643	114	0.8995	66
0.3238	132	0.9200	52
0.4181	154	0.9452	35
0.4892	162	0.9718	19
0.5896	162		
$a_0 = 650.9$; $a_1 = 105.7$; $a_2 = -42.9$; $\sigma(H^{E}_{m})/(J\cdot mol^{-1}) = 1.8$			

Table 3. Experimental Densities, ρ, Excess Molar Volumes, V^{E}_{m}, Adjustable Parameters, a_k, and Standard Deviations, $\sigma(V^{E}_{m})$, According to Eq 2 for Binary Mixtures Containing Esters of Carbonic Acid at 298.15 and 313.15 K

x_1	$\rho/(g\cdot cm^{-3})$	$V^{E}_{m}/(cm^{3}\cdot mol^{-1})$	x_1	$\rho/(g\cdot cm^{-3})$	$V^{E}_{m}/(cm^{3}\cdot mol^{-1})$
Propylene Carbonate (1) − Dimethyl Carbonate (2)					
$T = 298.15$ K					
0.0139	1.06557	−0.032	0.5391	1.14154	−0.349
0.0555	1.07233	−0.116	0.5864	1.14774	−0.329
0.1646	1.08927	−0.272	0.6336	1.15386	−0.306
0.2184	1.09721	−0.315	0.7118	1.16382	−0.255
0.3119	1.11066	−0.365	0.7708	1.17125	−0.210
0.3596	1.11733	−0.376	0.8612	1.18248	−0.133
0.4203	1.12566	−0.377	0.9303	1.19098	−0.069
0.4492	1.12960	−0.375	0.9855	1.19770	−0.014
0.4983	1.13616	−0.363			
$a_0 = -1.4520$; $a_1 = 0.5639$; $a_2 = -0.2115$; $a_3 = 0.1157$; $\sigma(V^{E}_{m})/(cm^{3}\cdot mol^{-1}) = 0.0011$					
$T = 313.15$ K					
0.0139	1.04578	−0.039	0.5391	1.12431	−0.413
0.0555	1.05276	−0.133	0.5864	1.13068	−0.390
0.1646	1.07034	−0.315	0.6336	1.13694	−0.361
0.2184	1.07863	−0.372	0.7118	1.14716	−0.302
0.3119	1.09253	−0.431	0.7708	1.15477	−0.250
0.3596	1.09939	−0.442	0.8612	1.16629	−0.161
0.4203	1.10798	−0.445	0.9303	1.17497	−0.086
0.4492	1.11201	−0.442	0.9855	1.18181	−0.018
0.4983	1.11878	−0.429			
$a_0 = -1.7140$; $a_1 = 0.6820$; $a_2 = -0.2561$; $\sigma(V^{E}_{m})/(cm^{3}\cdot mol^{-1}) = 0.0011$					
Propylene Carbonate (1) − Diethyl Carbonate (2)					
$T = 298.15$ K					
0.0232	0.97343	−0.051	0.6255	1.09836	−0.462
0.0968	0.98702	−0.206	0.6632	1.10753	−0.436
0.2158	1.00974	−0.379	0.7064	1.11826	−0.400
0.2866	1.02382	−0.447	0.7764	1.13629	−0.330
0.3801	1.04310	−0.498	0.8315	1.15104	−0.263
0.4538	1.05896	−0.512	0.9158	1.17463	−0.142
0.5000	1.06921	−0.510	0.9534	1.18556	−0.080
0.5491	1.08038	−0.498	0.9929	1.19735	−0.013
0.5915	1.09026	−0.480			
$a_0 = -2.0392$; $a_1 = 0.3032$; $a_2 = -0.0938$; $\sigma(V^{E}_{m})/(cm^{3}\cdot mol^{-1}) = 0.0012$					
$T = 313.15$ K					
0.0232	0.95656	−0.069	0.6255	1.08240	−0.544
0.0968	0.97031	−0.248	0.6632	1.09159	−0.514
0.2158	0.99327	−0.450	0.7064	1.10235	−0.472
0.2866	1.00745	−0.526	0.7764	1.12041	−0.391
0.3801	1.02688	−0.587	0.8315	1.13517	−0.312
0.4538	1.04284	−0.603	0.9158	1.15876	−0.171
0.5000	1.05313	−0.600	0.9534	1.16967	−0.099
0.5491	1.06434	−0.586	0.9929	1.18142	−0.018
0.5915	1.07427	−0.565			
$a_0 = -2.3973$; $a_1 = 0.3603$; $a_2 = -0.1746$; $\sigma(V^{E}_{m})/(cm^{3}\cdot mol^{-1}) = 0.0017$					
Dimethyl Carbonate (1) − Diethyl Carbonate (2)					
$T = 298.15$ K					
0.0207	0.97053	0.006	0.6318	1.01943	0.093
0.0655	0.97341	0.022	0.6714	1.02349	0.089
0.1980	0.98249	0.058	0.7109	1.02767	0.084
0.3150	0.99128	0.081	0.7768	1.03499	0.071
0.3852	0.99692	0.091	0.8269	1.04083	0.060
0.4467	1.00213	0.095	0.9121	1.05143	0.034
0.5093	1.00770	0.097	0.9485	1.05622	0.021
0.5617	1.01256	0.097	0.9877	1.06157	0.065
0.5856	1.01487	0.096			
$a_0 = 0.3901$; $a_1 = 0.0397$; $\sigma(V^{E}_{m})/(cm^{3}\cdot mol^{-1}) = 0.0005$					
$T = 313.15$ K					
0.0207	0.95353	0.007	0.6319	1.00085	0.099
0.0655	0.95630	0.026	0.6714	1.00479	0.095
0.1980	0.96510	0.063	0.7108	1.00883	0.090
0.3150	0.97358	0.089	0.7768	1.01593	0.077
0.3852	0.97906	0.097	0.8269	1.02160	0.063
0.4467	0.98410	0.102	0.9121	1.03187	0.036
0.5093	0.98948	0.105	0.9485	1.03651	0.022
0.5617	0.99419	0.105	0.9877	1.04170	0.005
0.5856	0.99644	0.102			
$a_0 = =.4198$; $a_1 = 0.0326$; $\sigma(V^{E}_{m})/(cm^{3}\cdot mol^{-1}) = 0.0008$					

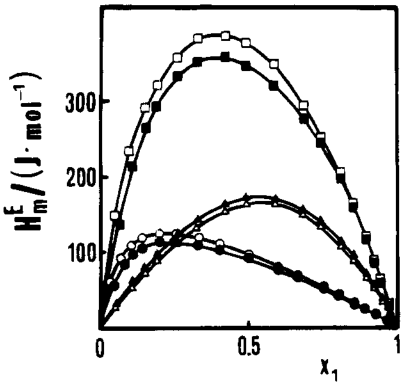

Figure 1. Excess molar enthalpies, H^E_m, at 298.15 and 313.15 K for the binary mixtures containing esters of carbonic acid as a function of the mole fraction of component 1. Experimental results: (circles) propylene carbonate + dimethyl carbonate; (squares) propylene carbonate + diethyl carbonate; (triangles) dimethyl carbonate + diethyl carbonate. Black and white points refer to 298.15 or 313.15 K, respectively. The solid lines are curves calculated from eq 2 using the parameters a_k of Table 2.

apparatus and the measurement procedure are reported elsewere (Fermeglia and Lapasin, 1988). Densities were determined with an estimated precision of 1 × 10^{-5} g·cm^{-3}, corresponding to an uncertainty in V^E_m on the order of 0.002 cm^3·mol^{-1}.

Before measurements, the density meter was checked with benzene + cyclohexane, for which values are accurately known by Wilhelm (1985) (our value of V^E_m at x = 0.5 is 0.652 cm^3·mol^{-1}, lit. value 0.6514 cm^3·mol^{-1}). The excess molar volumes, V^E_m, were evaluated from densities according to

$$V^E_m = (x_1M_1 + x_2M_2)/\varrho - x_1M_1/\varrho_1 - x_2M_2/\varrho_2 \qquad (1)$$

where x_i, M_i, and ϱ_i are the mole fraction, molar mass, and density of component i, respectively.

Results and Discussion

Excess molar enthalpies, H^E_m, are listed in Table 2 and densities, ϱ, and excess molar volumes, V^E_m, are reported in Table 3. Both H^E_m and V^E_m are graphically represented in Figures 1 and 2.

The results were correlated as a function of composition, using the Redlich–Kister equation

$$Q^E_m = x_1x_2\sum_{k\geq 0} a_k(x_1 - x_2)^k \qquad (2)$$

where $Q^E_m = H^E_m/(J \cdot mol^{-1})$ or $V^E_m/(cm^3 \cdot mol^{-1})$. The adjustable parameters a_k and standard deviations $\sigma(Q^E_m)$, the same as defined in Francesconi and Comelli (1994), were estimated by the unweighted least-squares method and are reported in Tables 2 and 3.

Values of H^E_m are positive for the three mixtures but show a different behavior with respect to temperature. A very small decrease of H^E_m with increasing temperature is observed for dimethyl carbonate + diethyl carbonate, while for the mixtures containing the cyclic ester propylene carbonate, H^E_m increases with temperature, more so for the mixture with dimethyl carbonate.

The shape of the H^E_m vs x_1 curve is asymmetrical for the mixtures containing the cyclic ester and nearly symmetric for the mixture dimethyl carbonate + diethyl carbonate. Mixtures containing cyclic ester have negative V^E_m values while those with the noncyclic esters have (smaller) positive values of V^E_m. The binary mixtures with a cyclic ester show V^E_m values which decrease with an increase in temperature, while for dimethyl carbonate + diethyl carbonate V^E_m shows a negligible temperature dependence.

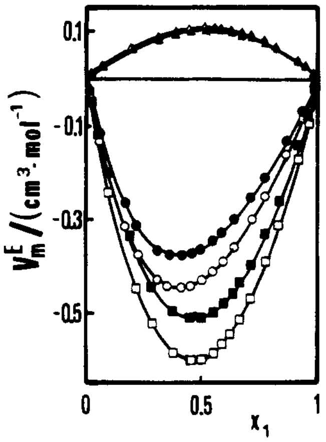

Figure 2. Excess molar volumes, V^E_m, at 298.15 and 313.15 K for the binary mixtures containing esters of carbonic acid as a function of the mole fraction of component 1. Experimental results: (circles) propylene carbonate + dimethyl carbonate; (squares) propylene carbonate + diethyl carbonate; (triangles) dimethyl carbonate + diethyl carbonate. Black and white points refer to 298.15 or 313.15 K, respectively. The solid lines are curves calculated from eq 2 using the parameters a_k of Table 3.

An attempt was made to interpret our data by comparing the experimental points with the values calculated from known theories (Flory, 1965; Lacombe and Sanchez, 1976). However, no satisfactory interpretation was obtained, owing to the complexity of the interaction pattern between the cyclic molecule of propylene carbonate and the linear molecules of the dialkyl carbonates. These conclusions line up with those attained by Perron et al. (1992) who have investigated mixtures of aprotic solvents.

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Received for review January 24, 1995. Accepted March 29, 1995.[⊗]

JE950024Z

[⊗] Abstract published in *Advance ACS Abstracts*, June 1, 1995.