J. Chem. Eng. Data **2001,** *46,* 63−68

Excess Molar Enthalpies and Excess Molar Volumes of Binary Mixtures Containing Dialkyl Carbonates + Pine Resins at (298.15 and 313.15) K

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Excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, of binary mixtures containing dimethyl carbonate (DMC), or diethyl carbonate (DEC) + α-pinene, + β-pinene, or + p-cymene have been determined using a flow microcalorimeter and a digital density meter at atmospheric pressure and at (298.15 and 313.15) K. All H_m^E and V_m^E data are positive and show symmetrical curves versus composition. The influence of temperature is marked for volumetric measurements while almost negligible for enthalpic data. Results have been correlated using the Redlich−Kister polynomial to estimate the binary interaction parameters. The calculated quantities have been qualitatively discussed in terms of thermodynamic interactions between the mixing compounds.

Introduction

Knowledge of mixing properties such as excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, is necessary to understand the molecular interactions between the components of the mixtures and to carry out practical applications in the industrial processes.

As a part of our long-term research program concerning the study of the physical properties of binary mixtures containing dialkyl carbonates[1−3] we report in this paper the excess molar enthalpies, H_m^E, and the excess molar volumes, V_m^E, of dimethyl carbonate (DMC), or diethyl carbonate (DEC) + α-pinene, + β-pinene, or + p-cymene.

Dialkyl carbonates are used as solvents for a variety of extractions of industrial importance, in the synthesis of pharmaceuticals, and in agricultural chemistry.[4−6] Particularly, in the last years the most interesting market opportunities of dimethyl carbonate are applied to gasoline additives[7] and to polycarbonate and isocyanate manufacturing.[8,9] In fact, DMC is a good biodegradable chemical which is able to substitute MTBE (butyl methyl ether), used as a gasoline additive but not biodegradable, and to substitute phosgene as a carbonylation intermediate for polycarbonate and isocyanate manufacturing.

The main constituents of the liquid phase obtained with the distillation of pine resins are α-pinene, β-pinene, p-cymene, and (S)-(−)-limonene, which are important chemicals used in the synthesis of a variety of chemicals, like synthetic resins and terpenic surfactants,[10] in the pharmaceutical and cosmetic industry.[5,6]

Even though the importance of pine resins is evident, only few papers, concerning vapor−liquid equilibrium data, are available in the literature:[10−12] no enthalpic or volumetric data have been found.

The purpose of the present work is to correlate the experimental data and to obtain information on the interactions between molecules.

Experimental Section

Chemicals. All chemicals, with stated purities ≥99 mol % from the purchaser, have been supplied from Aldrich Chemical Co., with the exception of α-pinene, which was from Fluka.

Liquids have been purified following the method described elsewere,[12] and the purities of the distillates have been checked with the aid of a gas cromatograph (Hewlett-Packard, model 5890) using an HP (cross-linked 5% Me siloxane) capillary column. The impurity contents in the final products have been less than 1 mass % for α-pinene and p-cymene and 0.8 mass % for β-pinene, DMC, and DEC. The purities of the samples have also been checked by comparing the measured densities, ρ, with those reported in the literature[13−18] and are shown in Table 1.

Coefficients A and B for the temperature dependence of the density equation of pure compounds

$$\rho = A + Bt(°\mathrm{C}) \qquad (1)$$

have been reported in Table 1 together with their standard deviation $\sigma(\rho)$.

Before measurements, pure liquids have been degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy), kept in dark bottles, and dried over molecular sieves (Union Carbide, type 4A, 1/16 in. pellets) to reduce the water content.

α-Pinene has been placed in freezer at 4 °C, as indicated by the purchaser.

Calorimetric Measurements. The excess molar enthalpies, H_m^E, have been determined using a flow microcalorimeter (LKB Producer AB, model 2107, Bromma, Sweden). The calibration and operation conditions have

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10.1021/je000181k CCC: $20.00

Table 1. Densities, ρ, of Pure Components and Comparison with Literature Values at 298.15 K and Coefficients *A* and *B*, Eq 1, and Standard Deviations $\sigma(\rho)$ in the Range (288.15−313.15) K

	ρ/g·cm^{-3}				
compound	this work	lit.	A	$10^4(-B)$	$10^5\sigma$
dimethyl carbonate	1.063 35	1.063 06[13] 1.063 50[14] 1.063 2[15]	1.096 52	13.28	3.6
diethyl carbonate	0.969 24	0.969 26[16] 0.969 40[17] 0.969 0[15]	0.997 35	11.29	6.3
α-pinene	0.853 90	0.853 9[16] 0.854 8[18]	0.874 67	8.31	0.8
β-pinene	0.866 66	0.866 7[16] 0.865 5[18]	0.884 75	7.48	7.6
p-cymene	0.852 88	0.853 3[16] 0.852 1[18]	0.873 06	8.06	3.8

correlation coefficient |R| ≥0.99955.

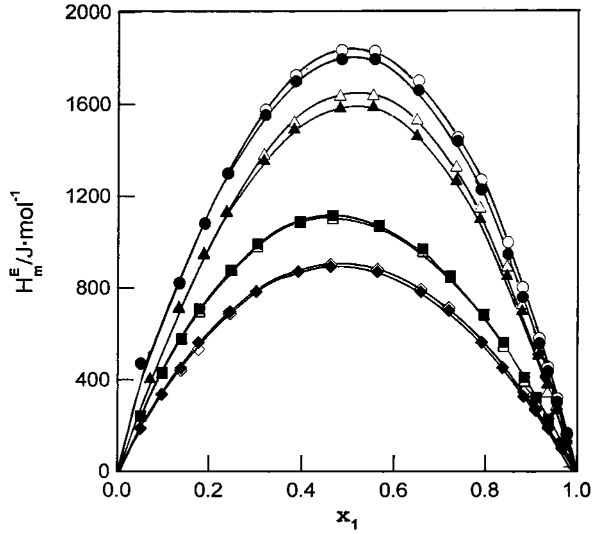

Figure 1. Excess molar enthalpies, H^E_m, of binary mixtures containing dialkyl carbonates + α-pinene or + β-pinene: (●, ▲) mixtures containing DMC + α-pinene or + β-pinene; (■, ◆) DEC + α-pinene or + β-pinene. Closed and open points are for 298.15 and 313.15 K, respectively.

been described elsewere.[19,20] Mole fractions, x_1 , of dialkyl carbonates (component 1) have been determined from fluxes be means of two automatic burets (ABU, Radiometer, Copenhagen, Denmark) necessary to pump continuously the required flow of each pure liquid into the mixing cell.

The volume of the cylinder of each buret was 2.5 cm^3, and we have selected the flow rates to cover the entire mole fraction range. The experimental uncertainties in mole fraction of dialkyl carbonates are estimated to be ±2 × 10^{-4}, which leads to uncertainties in the H^E_m values better than ±1%.

Before measurements, the apparatus has been checked on the test mixture cyclohexane + hexane, and the agreement with literature data[21] is better than ±0.5% in the central range of the thermal effect.

Volumetric Measurements. Excess molar volumes, V^E_m, reproducible to ±0.003 cm^3 mol^{-1}, have been determined from density measurements with the help of a digital density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell (Anton Paar, type 602) whose operating procedure has been described elsewere.[22]

Densities, ρ, of mixtures have been measured with an accuracy of ±1 × 10^{-5} g cm^{-3}.

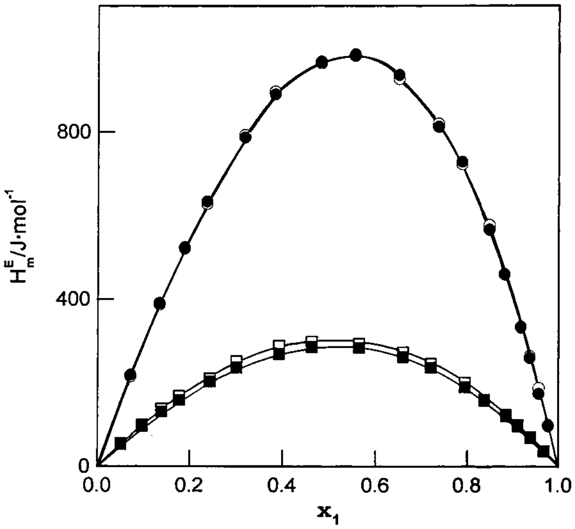

Figure 2. Excess molar enthalpies, H^E_m, of binary mixtures containing dialkyl carbonates + p-cymene: (●, ■) mixtures containing DMC or DEC, respectively. Closed and open points are for 298.15 and 313.15 K, respectively.

All measurements have been determined at a constant temperature using an external ultrathermostat bath circulator (Heto, type 01 DTB 623, Birkeròd, Denmark), precision ±0.005 K, and temperatures have been detected with two digital thermometers (Anton Paar, DT 25, and DT 40). Mole fractions, x_1, of dialkyl carbonates have been obtained by mass, using a digital balance (Mettler, model AE 160, Switzerland) with an accuracy of ±0.0001 g. All masses have been corrected for buoyancy and evaporation of components. All molar quantities have been based on the relative atomic mass table by IUPAC.[23]

Before measurements, the apparatus has been checked by determining V^E_m using the test mixture benzene + cyclohexane at 298.15 K. Our results agree with those of the literature,[24] showing a discrepancy of ±0.5% in the central range of mole fraction of benzene.

A calibration with twice-distilled water[25] and dry air[26] has been made for each set of measurements.

Results and Discussion

The experimental results of the excess molar enthalpies, H^E_m, and the excess molar volumes, V^E_m, at atmospheric pressure and at (298.15 and 313.15) K are listed in Tables 2 and 3 as a function of the mole fraction x_1 and are graphically represented in Figures 1−4.

Table 2. Excess Molar Enthalpies, H_m^E, for Binary Mixtures Containing Dialkyl Carbonates + Pine Resins

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
Dimethyl Carbonate (1) + α-Pinene (2)				Diethyl Carbonate (1) + α-Pinene (2)			
T/K = 298.15				T/K = 298.15			
0.0728	473	0.7386	1439	0.0517	241	0.6627	971
0.1356	825	0.7902	1227	0.0983	432	0.7236	851
0.1906	1084	0.8498	949	0.1406	575	0.7970	684
0.2389	1300	0.8828	759	0.1791	708	0.8396	562
0.3201	1554	0.9187	559	0.2466	877	0.8871	409
0.3857	1700	0.9378	436	0.3038	991	0.9128	322
0.4850	1795	0.9576	304	0.3960	1089	0.9402	227
0.5566	1795	0.9784	159	0.4659	1115	0.9692	119
0.6532	1660			0.5669	1073		
T/K = 313.15				T/K = 313.15			
0.0725	469	0.7378	1454	0.0516	239	0.6620	960
0.1351	820	0.7895	1269	0.0981	428	0.723	845
0.1899	1081	0.8491	1000	0.1403	578	0.7966	682
0.2381	1298	0.8824	802	0.1786	695	0.8392	544
0.3192	1577	0.9184	581	0.2460	876	0.8868	393
0.3846	1725	0.9375	456	0.3032	981	0.9126	321
0.4839	1834	0.9575	318	0.3949	1086	0.9400	226
0.5555	1831	0.9783	166	0.4652	1102	0.9691	119
0.6522	1703			0.5662	1070		
Dimethyl Carbonate (1) + β-Pinene (2)				Diethyl Carbonate (1) + β-Pinene (2)			
T/K = 298.15				T/K = 298.15			
0.0718	409	0.7358	1272	0.0510	189	0.6593	783
0.1339	714	0.7877	1107	0.0970	338	0.7206	701
0.1883	950	0.8477	859	0.1388	450	0.7922	563
0.2362	1134	0.8813	705	0.1769	563	0.8376	454
0.3169	1363	0.9176	514	0.2438	697	0.8856	326
0.3821	1499	0.9369	388	0.3007	784	0.9116	267
0.4813	1591	0.9570	276	0.3920	873	0.9393	187
0.5529	1595	0.9780	144	0.4622	894	0.9687	99
0.6498	1468			0.5633	872		
T/K = 313.15				T/K = 313.15			
0.0714	409	0.7348	1316	0.0508	185	0.6585	794
0.1333	720	0.7869	1160	0.0967	334	0.7199	714
0.1875	958	0.8471	914	0.1384	442	0.7941	564
0.2353	1140	0.8808	728	0.1764	533	0.8372	451
0.3158	1388	0.9172	529	0.2432	689	0.8852	346
0.3810	1530	0.9476	350	0.2999	786	0.9114	274
0.4801	1631	0.9568	292	0.3912	874	0.9391	193
0.5517	1646	0.9779	153	0.4613	903	0.9686	102
0.6487	1539			0.5624	882		
Dimethyl Carbonate (1) + p-Cymene (2)				Diethyl Carbonate (1) + p-Cymene (2)			
T/K = 298.15				T/K = 298.15			
0.0718	220	0.736	812	0.0510	52	0.6596	262
0.1340	391	0.7879	723	0.0971	96	0.7209	237
0.1884	521	0.8479	567	0.1390	131	0.7948	190
0.2364	634	0.8814	461	0.1771	159	0.8379	158
0.3171	787	0.9177	335	0.2440	203	0.8857	121
0.3824	890	0.9369	260	0.3009	237	0.9117	96
0.4816	968	0.9571	175	0.3923	269	0.9394	68
0.5532	982	0.9781	98	0.4625	286	0.9687	36
0.6501	936			0.5635	284		
T/K = 313.15				T/K = 313.15			
0.0715	216	0.7351	820	0.0509	55	0.6588	273
0.1335	388	0.7871	723	0.0968	100	0.7202	246
0.1877	525	0.8473	577	0.1386	138	0.7943	201
0.2355	629	0.8809	460	0.1766	169	0.8373	160
0.3161	793	0.9173	333	0.2434	211	0.8853	124
0.3813	897	0.9367	266	0.3002	252	0.9115	99
0.4804	966	0.9569	189	0.3915	289	0.9392	71
0.5520	986	0.9780	100	0.4616	298	0.9686	37
0.6490	927			0.5627	294		

ρ values have been used to calculate the excess molar volumes, V_m^E, with the following equation

$$V_m^E = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \qquad (2)$$

where x_i, M_i, and ρ_i (i = 1, 2) are the mole fractions, molecular weights, and densities of pure components 1 and 2, respectively.

Each set of experimental values of H_m^E and V_m^E is fitted to a Redlich−Kister polynomial of the type

$$Q_m^E = x_1x_2\sum_{k\geq 0} a_k(x_1 - x_2)^k \qquad (3)$$

by an unweighted least-squares method, where Q_m^E refers to H_m^E/J·mol^{-1} or V_m^E/cm^3·mol^{-1}, x_1, x_2 are the molar frac-

Table 3. Densities, ρ, and Experimental Excess Volumes, V_m^E, of Binary Mixtures Containing Dialkyl Carbonates + Pine Resins

x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}
Dimethyl Carbonate (1) + α-Pinene (2)						Diethyl Carbonate (1) + α-Pinene (2)					
T/K = 298.15						T/K = 298.15					
0.0410	0.857 48	0.195	0.5781	0.933 72	1.045	0.0338	0.856 32	0.107	0.5617	0.906 68	0.652
0.1113	0.864 24	0.475	0.6352	0.946 16	0.989	0.0895	0.860 53	0.258	0.6263	0.914 53	0.614
0.1975	0.873 68	0.732	0.6822	0.957 21	0.937	0.2150	0.870 99	0.498	0.7554	0.931 56	0.471
0.3317	0.891 12	0.977	0.7660	0.979 29	0.789	0.2431	0.873 51	0.536	0.8159	0.940 13	0.384
0.4092	0.902 88	1.048	0.8658	1.010 41	0.525	0.3402	0.882 71	0.630	0.8943	0.951 97	0.240
0.4884	0.916 39	1.069	0.9597	1.045 87	0.178	0.4007	0.888 83	0.661	0.9716	0.964 43	0.071
						0.4806	0.897 40	0.673			
T/K = 313.15						T/K = 313.15					
0.0410	0.844 79	0.222	0.5781	0.917 73	1.160	0.3383	0.843 75	0.117	0.5617	0.891 84	0.715
0.1113	0.851 15	0.535	0.6352	0.929 67	1.106	0.0895	0.847 78	0.270	0.6263	0.899 40	0.672
0.1975	0.860 11	0.818	0.6822	0.940 40	1.040	0.2150	0.857 66	0.544	0.7554	0.915 82	0.516
0.3317	0.876 75	1.089	0.7660	0.961 76	0.876	0.2431	0.860 06	0.584	0.8159	0.924 13	0.417
0.4092	0.888 04	1.165	0.8658	0.991 93	0.583	0.3402	0.868 84	0.689	0.8943	0.935 53	0.266
0.4884	0.901 01	1.192	0.9597	1.026 40	0.198	0.4007	0.874 69	0.724	0.9716	0.947 62	0.077
						0.4806	0.882 91	0.737			
Dimethyl Carbonate (1) + β-Pinene (2)						Diethyl Carbonate (1) + β-Pinene (2)					
T/K = 298.15						T/K = 298.15					
0.0587	0.871 76	0.226	0.6128	0.949 61	0.902	0.0409	0.869 41	0.095	0.6151	0.920 13	0.485
0.1749	0.883 32	0.575	0.6832	0.964 91	0.834	0.1332	0.876 03	0.268	0.6629	0.925 45	0.456
0.2799	0.895 66	0.774	0.7476	0.980 55	0.739	0.2001	0.881 19	0.362	0.7454	0.935 12	0.385
0.3662	0.907 26	0.880	0.8094	0.997 31	0.615	0.2704	0.886 94	0.434	0.8498	0.948 28	0.257
0.4162	0.914 66	0.917	0.8992	1.025 39	0.368	0.3854	0.897 07	0.505	0.9345	0.959 78	0.123
0.5195	0.931 75	0.939	0.9585	1.046 72	0.169	0.4912	0.907 19	0.521	0.9833	0.966 77	0.034
						0.5676	0.915 02	0.506			
T/K = 313.15						T/K = 313.15					
0.0587	0.859 35	0.248	0.6128	0.933 65	0.992	0.0409	0.857 12	0.105	0.6151	0.905 24	0.531
0.1750	0.870 27	0.630	0.6832	0.948 37	0.916	0.1332	0.863 35	0.293	0.6629	0.910 31	0.499
0.2799	0.881 98	0.854	0.7476	0.963 44	0.811	0.2001	0.868 23	0.394	0.7454	0.919 55	0.422
0.3662	0.892 99	0.979	0.8094	0.979 58	0.676	0.2704	0.873 66	0.474	0.8498	0.932 16	0.283
0.4162	0.900 08	1.016	0.8992	1.006 68	0.407	0.3854	0.883 26	0.551	0.9345	0.943 20	0.136
0.5195	0.916 49	1.035	0.9585	1.027 34	0.184	0.4912	0.892 89	0.570	0.9833	0.949 91	0.038
						0.5676	0.900 36	0.553			
Dimethyl Carbonate (1) + p-Cymene (2)						Diethyl Carbonate (1) + p-Cymene (2)					
T/K = 298.15						T/K = 298.15					
0.0776	0.861 20	0.142	0.6249	0.947 76	0.549	0.0480	0.857 17	0.020	0.5660	0.910 57	0.121
0.2155	0.877 83	0.349	0.7097	0.967 90	0.501	0.1207	0.863 81	0.048	0.6203	0.917 09	0.119
0.3635	0.898 97	0.497	0.7876	0.988 92	0.424	0.1828	0.869 70	0.067	0.7202	0.929 64	0.105
0.4417	0.911 81	0.541	0.8496	1.007 73	0.337	0.2758	0.878 87	0.091	0.8507	0.947 24	0.070
0.5212	0.926 29	0.562	0.8832	1.018 80	0.279	0.3221	0.883 60	0.101	0.9310	0.958 81	0.037
0.5706	0.936 12	0.561	0.9449	1.041 11	0.143	0.4381	0.895 97	0.117	0.9903	0.967 74	0.007
						0.5014	0.903 06	0.121			
T/K = 313.15						T/K = 313.15					
0.0776	0.848 77	0.162	0.6249	0.931 95	0.599	0.0480	0.844 91	0.030	0.5660	0.896 02	0.146
0.2155	0.864 65	0.398	0.7097	0.951 33	0.548	0.1207	0.851 25	0.064	0.6203	0.902 27	0.142
0.3635	0.885 01	0.548	0.7876	0.971 62	0.460	0.1828	0.856 88	0.086	0.7202	0.914 29	0.126
0.4417	0.897 37	0.592	0.8496	0.989 74	0.366	0.2758	0.865 65	0.116	0.8507	0.931 17	0.083
0.5212	0.911 30	0.613	0.8832	1.000 45	0.299	0.3221	0.870 18	0.126	0.9310	0.942 28	0.044
0.5706	0.920 78	0.610	0.9449	1.021 95	0.154	0.4381	0.882 03	0.144	0.9903	0.950 85	0.008
						0.5014	0.8888	0.147			

tions of dialkyl carbonates and component 2, and a_k are the adjustable parameters. The a_k values are given in Table 4 together with the standard deviation $\sigma(Q_m^E)$, defined as

$$\sigma(Q_m^E) = |\phi_{min}/(N - n)|^{0.5} \tag{4}$$

with N and n the number of experimental points and of parameters, whereas ϕ_{min} is the minimum value of the objective function ϕ, defined as

$$\phi = \sum_{k=1}^{N} {\eta_k}^2 \tag{5}$$

where $\eta_k = Q_{m,calcd}^E - Q_m^E$; Q_m^E is the experimental value, and $Q_{m,calcd}^E$ is evaluated through eq 3.

Values of H_m^E are positive and very large, in the range (1000−2000) J·mol^{-1} for mixtures containing α-pinene and β-pinene and (250−1000) J·mol^{-1} for p-cymene. In going from DEC to DMC, values of H_m^E are almost doubled for mixtures containing α-pinene and β-pinene and quadrupled for those containing p-cymene. Instead, the influence of temperature on H_m^E is meaningless.

Analysis of the molecular structure of pine resins and alkyl carbonates may help in understanding the thermal behavior of the mixtures in terms of intermolecular interactions.

In fact, attention may be focused on the intermolecular forces between the double bond of α-pinene and β-pinene or the π electrons in the benzene ring of p-cymene and the C=O group in the alkyl carbonates. Interactions between β-pinene and alkyl carbonates will be stronger than the

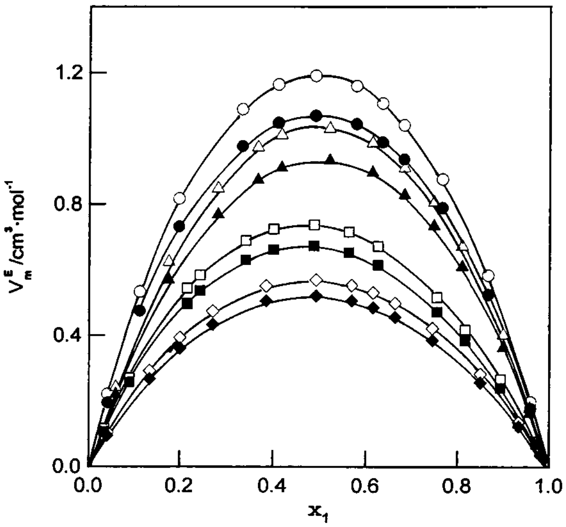

Figure 3. Excess molar volumes, V^E_m, of binary mixtures containing dialkyl carbonates + α-pinene or + β-pinene: (●, ▲) mixtures containing DMC + α-pinene or + β-pinene; (■, ◆) DEC + α-pinene or + β-pinene. Closed and open points are for 298.15 and 313.15 K, respectively.

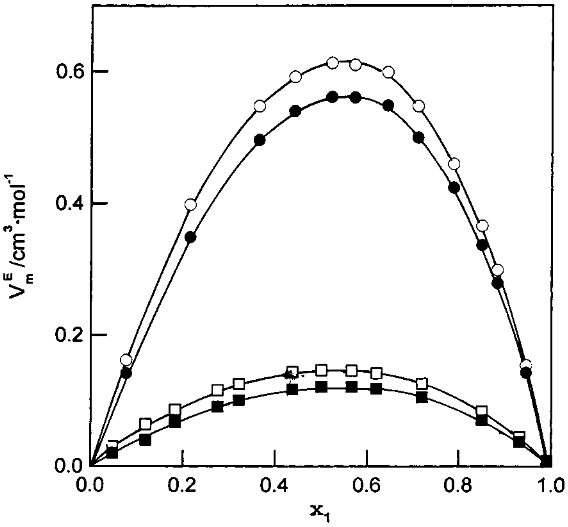

Figure 4. Excess molar volumes, V^E_m, of binary mixtures containing dialkyl carbonates + p-cymene: (●, ■) mixtures containing DMC or DEC, respectively. Closed and open points are for 298.15 and 313.15 K, respectively.

Table 4. Least-Squares Parameters, a_k, Eq 3, and Standard Deviations, $\sigma(Q^E_m)$, Eq 4, of Binary Mixtures Containing Dialkyl Carbonates + Pine Resins

function	a_0	a_1	a_2	$\sigma(Q^E_m)$
Dimethyl Carbonate (1) + α-Pinene (2)				
T/K = 298.15				
H^E_m/J·mol^{-1}	7239.7	284.2		6.6
V^E_m/cm^3·mol^{-1}	4.2827	−0.1580	0.6581	0.002
T/K = 313.15				
H^E_m/J·mol^{-1}	7372.9	453.3		6.8
V^E_m/cm^3·mol^{-1}	4.7660	−0.1988	0.7647	0.002
Dimethyl Carbonate (1) + β-Pinene (2)				
T/K = 298.15				
H^E_m/J·mol^{-1}	6410.0	314.8		5.9
V^E_m/cm^3·mol^{-1}	3.7669	0.0341	0.5052	0.002
T/K = 313.15				
H^E_m/J·mol^{-1}	6593.8	496.2		6.6
V^E_m/cm^3·mol^{-1}	4.1603	0.0192	0.5086	0.003
Dimethyl Carbonate (1) + p-Cymene (2)				
T/K = 298.15				
H^E_m/J·mol^{-1}	3895.6	701.8		6.0
V^E_m/cm^3·mol^{-1}	2.2340	0.4106	0.2061	0.002
T/K = 313.15				
H^E_m/J·mol^{-1}	3902.7	693.9		6.4
V^E_m/cm^3·mol^{-1}	2.4434	0.3710	0.2960	0.003
Diethyl Carbonate (1) + α-Pinene (2)				
T/K = 298.15				
H^E_m/J·mol^{-1}	4469.4	−473.9		4.8
V^E_m/cm^3·mol^{-1}	2.6800	−0.3469	0.2395	0.002
T/K = 313.15				
H^E_m/J·mol^{-1}	4432.8	−507.2		6.2
V^E_m/cm^3·mol^{-1}	2.9400	−0.3585	0.1935	0.003
Diethyl Carbonate (1) + β-Pinene (2)				
T/K = 298.15				
H^E_m/J·mol^{-1}	3591.4	−344.1		5.1
V^E_m/cm^3·mol^{-1}	2.0836	−0.1961	0.1605	0.001
T/K = 313.15				
H^E_m/J·mol^{-1}	3605.2	−249.0		7.1
V^E_m/cm^3·mol^{-1}	2.2768	−0.2032	0.1842	0.001
Diethyl Carbonate (1) + p-Cymene (2)				
T/K = 298.15				
H^E_m/J·mol^{-1}	1145.0	62.5		1.5
V^E_m/cm^3·mol^{-1}	0.4838	0.0744	0.0356	0.001
T/K = 313.15				
H^E_m/J·mol^{-1}	1197.6	39.2		3.0
V^E_m/cm^3·mol^{-1}	0.5871	0.0501	0.0774	0.001

ones between α-pinene, owing to the greater availability of the C=C group in β-pinene, whereas the cooperative effect of CH_3 and $CH(CH_3)_2$ in p-cymene will lead to a relevant negative charge in the benzene ring, ortho and meta with respect to the CH_3 group.

The interaction energy E_{12} between the alkyl carbonates and the second components will be in the order p-cymene > β-pinene > α-pinene, which explains the values of H^E_m in the reverse order if the approximated expression $H^E_m \propto E_{11} + E_{22} - 2E_{12}$ is considered for the heat of mixing. The same results were obtained in a previous paper for the mixtures phenetole + α-pinene or + β-pinene.[27]

Moreover, these interaction energies E_{12} will be larger when DEC is the second component, due to the large effect of C_2H_5 groups, with respect to the CH_3 groups, in the polarization of the C=O group of alkyl carbonates. The analogous trend in the V^E_m curves may be a confirmation of the prevailing of interaction energies with respect to package and steric hindrance effects, in the volume changes on mixing. Finally, these latter effects seem to be the origin of the relatively large temperature dependence of V^E_m on temperature

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Received for review June 19, 2000. Accepted September 18, 2000.

JE000181K