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Excess Molar Enthalpies and Excess Molar Volumes of Binary Mixtures Containing 1,3-Dioxolane or 1,4-Dioxane + Pine Resins at (298.15 and 313.15) K and at Atmospheric Pressure

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Excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, of binary mixtures containing 1,3-dioxolane or 1,4-dioxane + α-pinene, + *β*-pinene, or + *p*-cymene were determined at (298.15 and 313.15) K and at atmospheric pressure over the entire composition range using a flow microcalorimeter and a digital density meter. H_m^E and V_m^E are always positive, and the temperature dependence is more marked for V_m^E values. Results were fitted to the Redlich−Kister polynomials to obtain the binary adjustable parameters and the standard deviations

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Introduction

Continuing our research program involving the study of physical properties of binary mixtures containing pine resins,[1,2] we report in this paper the excess molar enthalpies, H_m^E, and the excess molar volumes, V_m^E, of 1,3-dioxolane or 1,4-dioxane + α-pinene (2,6,6-trimethylbicyclo-[3.1.1]hept-2-ene), + *β*-pinene (6,6-dimethyl-2-methylene bicyclo[3.1.1]heptane, or + *p*-cymene [1-methyl-4-(1-methylethyl)benzene] at (298.15 and 313.15) K and at atmospheric pressure. Pine resins and their derivatives are used in pharmaceutical and in cosmetic industries,[3−5] in synthetic resins, and in terpenic surfactants.[6] Particularly, α-pinene proved to be an exceptionally successful solvent for many programs in asymmetric synthesis, with asymmetric reductions being the most desirable method for synthesizing optical pure materials via chiral organoboranes.[7,8]

There are several papers regarding this subject and its pharmaceutical importance. However, only few liquid−vapor equilibrium measurements are reported in the literature, but no enthalpic or volumetric data were found. The main purpose of this paper is to extend our investigations on the binary mixtures containing pine resins + two cyclic ethers and to provide qualitative information on the interactions between the molecules of the mentioned chemicals from the measurements of H_m^E and V_m^E data.

Materials and Methods

1,3-Dioxolane (Aldrich >99.8%) and 1,4-dioxane (Fluka >99.8%) were used without further purification. α-Pinene (Fluka >99%), *β*-pinene, and *p*-cymene (both Aldrich >99%) were purified following the procedure described elsewhere.[3] The final products were obtained by removing the upper 10% and the lower 15% fractions of distillate. The purities of pine resins were checked with the aid of a gas chromatograph (Hewlett-Packard, model 5890) using an HP (cross-linked 5% siloxane) capillary column. The impurity contents were less than 1 mass % for α-pinene and 0.8 mass % for *β*-pinene and *p*-cymene. The gas cromatograph analysis confirmed the stated purities of cyclic ethers from purchasers, showing a water impurity < 0.05% for all components. Prior to use, pure chemicals were 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). α-Pinene, as suggested by the purchaser, was placed in a freezer at 4 °C.

Table 1. Densities, *ρ*, of Pure Components and Comparison with Literature Values

component	*T*/K	ρ/g·cm^{-3} exptl	ρ/g·cm^{-3} lit.
1,3-dioxolane	298.15	1.058 81	1.058 65^{9}
	313.15	1.040 08	1.039 97^{9,a}
1,4-dioxane	298.15	1.027 97	1.027 929
	298.15		1.027 97^{10}
	313.15	1.010 95	1.010 94^{9,a}
α-pinene	298.15	0.853 90	0.853 9^{10}
			0.854 8^{11}
	313.15	0.841 40	0.842 9^{11}
β-pinene	298.15	0.866 66	0.866 7^{10}
			0.865 5^{11}
	313.15	0.854 55	0.853 8^{11}
p-cymene	298.15	0.852 90	0.853 3^{10}
	298.15		0.852 1^{11}
	313.15	0.840 85	0.840 6^{11}

[a] Interpolated from ref 9.

Values of the densities, *ρ*, of pure chemicals were measured using a digital density meter (Anton Paar, DMA 60/602, Graz, Austria) and are reported in Table 1 and compared with literature data.[9−11] Measurements of the excess molar enthalpies, H_m^E, were carried out using a flow microcalorimeter (LKB Producer AB, model 2107, Bromma, Sweden) at (298.15 and 313.15) K, and the temperature of the apparatus was maintained within ±0.01 K. Details of the equipment and its operating procedure were described previously.[12,13]

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Table 2. Excess Molar Enthalpies, H_m^E, for Binary Mixtures Containing 1,3-Dioxolane or 1,4-Dioxane + 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}
1,3-Dioxolane (1) + α-Pinene (2)							
	T/K = 298.15				T/K = 313.15		
0.0868	464	0.7738	1271	0.0865	534	0.7733	1349
0.1597	815	0.8202	1088	0.1593	906	0.8197	1164
0.2218	1095	0.8725	825	0.2213	1178	0.8721	901
0.2754	1290	0.9012	638	0.2747	1366	0.9009	734
0.3631	1542	0.9319	463	0.3624	1594	0.9317	521
0.4318	1675	0.9480	358	0.4311	1714	0.9479	385
0.5327	1750	0.9647	248	0.5320	1785	0.9646	283
0.6031	1704	0.9821	128	0.6024	1745	0.9820	147
0.6952	1528			0.6945	1590		
1,3-Dioxolane (1) + β-Pinene (2)							
	T/K = 298.15				T/K =313.15		
0.0856	370	0.7712	1028	0.0853	403	0.7706	1164
0.1577	642	0.8180	870	0.1572	703	0.8174	1007
0.2193	839	0.8691	641	0.2186	923	0.8704	778
0.2719	1016	0.8999	501	0.2717	1091	0.8995	620
0.3597	1232	0.9310	351	0.3588	1336	0.9307	446
0.4282	1326	0.9473	269	0.4273	1433	0.9471	341
0.5291	1402	0.9642	184	0.5281	1514	0.9641	241
0.5996	1371	0.9850	77	0.5987	1495	0.9817	126
0.6920	1245			0.6912	1370		
1,3-Dioxolane (1) + p-Cymene (2)							
	T/K = 298.15				T/K = 313.15		
0.0857	149	0.7714	561	0.0854	205	0.7708	635
0.1578	293	0.8181	484	0.1573	352	0.8176	553
0.2195	413	0.8709	385	0.2188	467	0.8705	441
0.2726	506	0.9000	313	0.2719	547	0.8996	349
0.3599	628	0.931	222	0.3591	670	0.9308	262
0.4285	693	0.9473	169	0.4276	722	0.9472	200
0.5293	743	0.9643	123	0.5284	785	0.9642	141
0.5998	722	0.9818	65	0.5990	777	0.9818	74
0.6922	659			0.6915	730		
1,4-Dioxane (1) + α-Pinene (2)							
	T/K = 298.15				T/K = 313.15		
0.0720	383	0.7364	1259	0.0718	352	0.7360	1253
0.1343	676	0.7883	1111	0.1340	630	0.7879	1099
0.1888	915	0.8481	867	0.1885	842	0.8479	847
0.2366	1074	0.8816	695	0.2379	1042	0.8814	715
0.3176	1314	0.9178	497	0.3172	1270	0.9177	491
0.3829	1466	0.9371	406	0.3846	1433	0.9370	394
0.4821	1557	0.9572	277	0.4816	1542	0.9571	274
0.5538	1561	0.9781	145	0.5532	1556	0.9781	143
0.6506	1460			0.6501	1463		
1,4-Dioxane (1) + β-Pinene							
	T/K = 298.15				T/K = 313.15		
0.0710	308	0.7335	1085	0.0708	308	0.7330	1089
0.1326	548	0.7858	948	0.1323	546	0.7853	945
0.1865	731	0.8442	742	0.1861	731	0.8459	732
0.2341	893	0.8800	606	0.2351	880	0.8798	599
0.3144	1098	0.9167	440	0.3138	1076	0.9165	435
0.3794	1205	0.9362	344	0.3788	1196	0.9360	334
0.4784	1311	0.9565	238	0.4777	1302	0.9564	243
0.5501	1323	0.9778	124	0.5493	1214	0.9777	127
0.6472	1244			0.6466	1242		
1,4-Dioxane (1) + p-Cymene (2)							
	T/K = 298.15				T/K = 313.15		
0.0711	117	0.7337	528	0.0709	133	0.7332	546
0.1327	218	0.7860	475	0.1324	239	0.7856	497
0.1867	294	0.8464	365	0.1863	325	0.8460	375
0.2350	381	0.8802	304	0.2353	389	0.8799	312
0.3146	478	0.9168	219	0.3141	505	0.9166	223
0.3797	547	0.9363	166	0.3791	567	0.9361	182
0.4786	612	0.9566	120	0.4780	622	0.9565	127
0.5504	621	0.9778	62	0.5497	638	0.9778	67
0.6475	597			0.6468	616		

Pure chemicals were pumped into the cell of the microcalorimeter by two automatic burets (ABU, Radiometer, Copenhagen, Denmark), and mole fractions x_1 of cyclic ethers were determined by the flow rates covering the whole mole fraction range. The uncertainties in the reported mole fractions, x_1, and excess molar enthalpies, H_m^E, are $\pm 2 \times 10^{-4}$ and <1%, respectively. The reliability of the apparatus and the method was established by measuring the excess molar enthalpies, H_m^E, of the test mixture cyclohexane + hexane over the entire composition range at 298.15 K: our results are in agreement with the literature[14] data within ±1%.

Table 3. Densities, ρ, and Experimental Excess Volumes, V_m^E, of Binary Mixtures Containing 1,3-Dioxolane or 1,4-Dioxane + 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}
1,3-Dioxolane (1) + α-Pinene (2)											
		T/K = 298.15						T/K = 313.15			
0.0369	0.856 64	0.118	0.5852	0.926 27	0.687	0.0437	0.844 14	0.118	0.5852	0.910 89	0.793
0.1121	0.862 80	0.320	0.6621	0.942 70	0.626	0.1121	0.849 94	0.354	0.6621	0.926 80	0.726
0.2536	0.876 77	0.578	0.72686	0.958 65	0.551	0.2536	0.863 17	0.663	0.7269	0.942 29	0.640
0.3502	0.888 38	0.677	0.7980	0.978 87	0.446	0.3502	0.874 32	0.775	0.7980	0.961 90	0.526
0.3962	0.894 62	0.702	0.8901	1.010 35	0.273	0.3962	0.880 31	0.808	0.8901	0.992 46	0.334
0.4856	0.908 25	0.720	0.9708	1.044 55	0.076	0.4856	0.893 44	0.831	0.9708	1.026 06	0.093
1,3-Dioxolane (1) + β-Pinene (2)											
		T/K = 298.15						T/K = 313.15			
0.0638	0.871 46	0.149	0.6996	0.959 58	0.488	0.0638	0.859 08	0.173	0.6996	0.943 64	0.570
0.1426	0.878 07	0.302	0.7593	0.974 30	0.427	0.1426	0.865 34	0.346	0.7593	0.957 90	0.500
0.2310	0.886 54	0.429	0.7972	0.984 65	0.381	0.2310	0.873 41	0.493	0.7972	0.967 92	0.447
0.3940	0.905 61	0.566	0.8611	1.004 20	0.286	0.3940	0.891 68	0.648	0.8611	0.986 87	0.338
0.4845	0.918 73	0.576	0.9493	1.036 67	0.112	0.4845	0.904 18	0.676	0.9493	1.018 50	0.133
0.5563	0.930 56	0.574	0.9818	1.050 45	0.045	0.5563	0.915 22	0.667	0.9818	1.031 95	0.052
0.6233	0.943 15	0.546				0.6233	0.927 75	0.637			
1,3-Dioxolane (1) + p-Cymene (2)											
		T/K = 298.15						T/K = 313.15			
0.0678	0.859 10	0.044	0.6092	0.935 59	0.178	0.0678	0.846 73	0.067	0.6092	0.920 39	0.250
0.1320	0.865 53	0.084	0.6585	0.946 35	0.168	0.1328	0.852 90	0.119	0.6585	0.930 80	0.238
0.2136	0.874 32	0.122	0.7231	0.961 98	0.152	0.2136	0.861 31	0.176	0.7231	0.945 89	0.220
0.3464	0.891 01	0.166	0.8177	0.988 69	0.118	0.3464	0.877 36	0.233	0.81772	0.971 80	0.170
0.3882	0.896 97	0.171	0.8922	1.013 79	0.079	0.3882	0.883 07	0.246	0.8922	0.996 20	0.114
0.4830	0.911 88	0.183	0.9446	1.034 24	0.040	0.4830	0.897 46	0.261	0.9446	1.016 09	0.062
0.5594	0.925 64	0.181				0.5594	0.910 76	0.257			
1,4-Dioxane (1) + α-Pinene (2)											
		T/K = 298.15						T/K = 313.15			
0.451	0.857 38	0.152	0.5604	0.918 45	0.798	0.0451	0.844 82	0.163	0.5604	0.903 89	0.871
0.1117	0.862 97	0.343	0.6910	0.942 89	0.692	0.1117	0.850 18	0.370	0.6910	0.927 70	0.755
0.1817	0.869 46	0.502	0.7492	0.955 55	0.611	0.1817	0.856 42	0.547	0.7492	0.940 05	0.668
0.3188	0.884 19	0.721	0.8132	0.971 00	0.497	0.3188	0.870 66	0.782	0.8132	0.955 15	0.543
0.3882	0.892 83	0.782	0.9357	1.006 03	0.198	0.3882	0.879 03	0.847	0.9357	0.989 43	0.218
0.4561	0.902 18	0.807	0.9665	1.016 21	0.107	0.4561	0.888 09	0.879	0.9665	0.999 41	0.118
0.5272	0.913 00	0.808				0.5272	0.898 61	0.879			
1,4-Dioxane (1) + β-Pinene (2)											
		T/K = 298−15						T/K = 313.15			
0.0502	0.870 41	0.135	0.5629	0.927 73	0.691	0.0502	0.858 15	0.145	0.5629	0.913 41	0.750
0.1271	0.876 67	0.314	0.6484	0.942 09	0.641	0.1271	0.864 15	0.338	0.6484	0.927 32	0.699
0.1965	0.882 89	0.445	0.7183	0.955 35	0.570	0.1965	0.870 13	0.478	0.7183	0.940 22	0.619
0.2876	0.892 01	0.574	0.8127	0.975 75	0.436	0.2876	0.878 90	0.620	0.8127	0.960 01	0.479
0.3744	0.901 83	0.653	0.9236	1.004 46	0.205	0.3744	0.888 38	0.706	0.9236	0.987 99	0.226
0.4137	0.906 66	0.677	0.9885	1.024 18	0.035	0.4137	0.893 03	0.734	0.9885	1.007 26	0.038
0.5023	0.918 61	0.699				0.5023	0.904 58	0.759			
1,4-Dioxane (1) + p-Cymene (2)											
		T/K = 298.15						T/K = 313.15			
0.0699	0.859 01	0.070	0.6140	0.931 72	0.297	0.0699	0.847 09	0.081	0.6140	0.917 21	0.337
0.1379	0.866 20	0.128	0.6801	0.944 39	0.283	0.1379	0.853 66	0.147	0.6801	0.929 50	0.322
0.2240	0.875 49	0.195	0.7558	0.960 45	0.252	0.2240	0.862 63	0.224	0.7558	0.945 2	0.278
0.2833	0.882 45	0.230	0.8663	0.987 58	0.167	0.2833	0.869 38	0.263	0.8663	0.971 6	0.186
0.3362	0.889 05	0.256	0.9075	0.999 02	0.125	0.3362	0.875 78	0.293	0.9075	0.982 75	0.137
0.4147	0.899 63	0.287	0.9591	1.014 58	0.059	0.4147	0.886 07	0.323	0.9591	0.997 89	0.066
0.5107	0.914 00	0.312				0.5107	0.900 06	0.343			

Excess molar volumes, V_m^E, were calculated from the precise densities, ρ, of the samples measured by means of a vibrating glass tube densimeter (Anton Paar, model DM 60, Graz, Austria) equipped with a measuring cell (Anton Paar, type 602) and with two digital thermometers (Anton Paar DT-25 and DT-40). The procedure to prepare the samples, obtained by mass using a digital balance (Mettler, model AE 160, Switzerland), with a precision ±0.0001 g, was described in detail elsewere.[15] All masses were corrected for buoyancy and evaporation of components. All molar quantities were based on the relative atomic mass table by IUPAC.[16] The temperature of the apparatus was controlled to ±0.005 K using an external bath circulator (Heto, type 01 DTB 623, Birkeròd, Denmark). Densities, ρ, of mixtures were measured with an accuracy of $\pm 1 \times 10^{-5}$ g·m^{-3}, and the excess molar volumes, V_m^E, were accurate to ±0.003 cm^3·mol^{-1}. A calibration of the apparatus with twice distilled water[17] and dry air[18] was made for each set of measurements. Prior to measurements, the apparatus was checked by determining V_m^E using the test mixture benzene + cyclohexane at 298.15 K, and our results agree with those of the literature[19] within ±1%.

Results and Discussion

Results of measurements of H_m^E and V_m^E at (298.15 and 313.15) K are listed in Tables 2 and 3 and graphically represented in Figures 1−4. Excess molar volumes, V_m^E, were calculated from densities, ρ, from the following equation

$$V_m^E = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \qquad (1)$$

Table 4. Least-Squares Parameters, a_k, Eq 2, and Standard Deviations, $\sigma(Q_m^E)$, Eq 3, of Binary Mixtures Containing 1,3-Dioxolane or 1,4-Dioxane + Pine Resins

function	a_0	a_1	a_2	a_3	$\sigma(Q_m^E)$	function	a_0	a_1	a_2	a_3	$\sigma(Q_m^E)$
1,3-Dioxolane (1) + α-Pinene (2)											
T/K = 298.15						T/K = 313.15					
H_m^E/J·mol^{-1}	6964.6	883.0	−545.0		6.4	H_m^E/J·mol^{-1}	7101.7	823.7	533.6		7.7
V_m^E/cm^3·mol^{-1}	2.8693	−0.2847	0.1971		0.001	V_m^E/cm^3·mol^{-1}	3.3101	−0.3408	0.2345	0.3987	0.005
1,3-Dioxolane (1) + β-Pinene (2)											
T/K = 298.15						T/K = 313.15					
H_m^E/J·mol^{-1}	5592.1	936.4	−656.4	−616.7	7.7	H_m^E/J·mol^{-1}	6027.7	1057.4			6.6
V_m^E/cm^3·mol^{-1}	2.3268	−0.0718	0.1829		0.003	V_m^E/cm^3·mol^{-1}	2.7028	−0.0281	0.2101		0.002
1,3-Dioxolane (1) + p-Cymene (2)											
T/K = 298.15						T/K = 313.15					
$H_m{}^E$/J·mol^{-1}	2923.2	522.2	−362.3	606.5	4.3	$H_m{}^E$/J·mol^{-1}	3080.6	801.4	302.2		4.3
$V_m{}^E$/cm^3·mol^{-1}	0.7335	0.0440	0.0500		0.002	$V_m{}^E$/cm^3·mol^{-1}	1.0383	0.0683	0.1269		0.002
1,4-Dioxane (1) + α-Pinene (2)											
T/K = 298.15						T/K = 313.15					
H_m^E/J·mol^{-1}	6272.6	549.1	−16.2		7.5	H_m^E/J·mol^{-1}	6216.4	801−1	−352.0		9.2
V_m^E/cm^3·mol^{-1}	3.2499	−0.1011	0.1965		0.001	V_m^E/cm^3·mol^{-1}	3.5375	−0.8114	0.2207		0.001
1,4-Dioxane (1) + β-Pinene (2)											
T/K = 298.15						T/K = 313.15					
H_m^E/J·mol^{-1}	5288.9	612.0	−89.6		4.6	H_m^E/J·mol^{-1}	5235.9	45.1			4.8
V_m^E/cm^3·mol^{-1}	2.7949	0.0321	0.1073		0.001	V_m^E/cm^3·mol^{-1}	3.0311	0.0734	0.1232		0.002
1,4-Dioxane (1) + p-Cymene (2)											
T/K = 298.15						T/K = 313.15					
H_m^E/J·mol^{-1}	2467.6	631.5	−188.6		5.1	H_m^E/J·mol^{-1}	2526.7	590.4			6.1
V_m^E/cm^3·mol^{-1}	1.2197	0.2323	0.0776		0.003	V_m^E/cm^3·mol^{-1}	1.3709	0.2291	0.1095		0.002

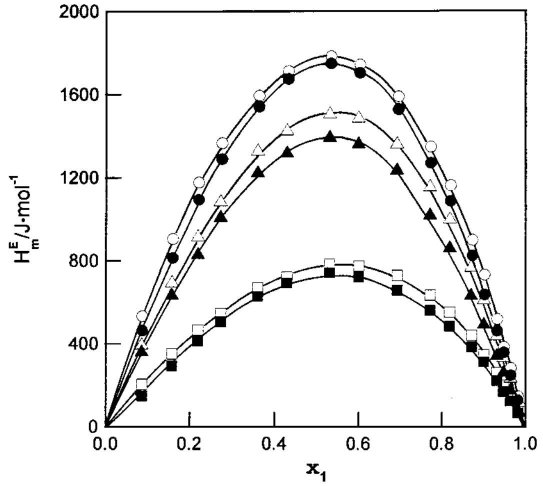

Figure 1. Excess molar enthalpies, H_m^E, for binary mixtures containing 1,3-dioxolane (1) + α-pinene (2) (●), + β-pinene (2) (▲), or + p-cymene (2) (■). Closed and open points are for (298.15 and 313.15) K. The solid curves were drawn from eq 2.

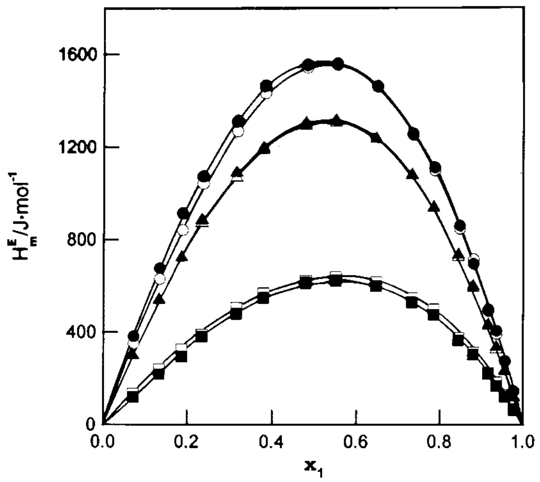

Figure 2. Excess molar enthalpies, H_m^E, for binary mixtures containing 1,3-dioxane (1) + α-pinene (2) (●), + β-pinene (2) (▲), or + p-cymene (2) (■). Closed and open points are for (298.15 and 313.15) K. The solid curves were drawn from eq 2.

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.

The results of H_m^E and V_m^E for each mixture were fitted to a Redlich−Kister polynomial

$$Q_m^E = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \tag{2}$$

where Q_m^E refers to H_m^E/J·mol^{-1} or V_m^E/cm^3·mol^{-1}, x_1 and x_2 are the molar fractions of cyclic ethers and component 2, and a_k are the adjustable parameters obtained by the least-squares method, with all points weighted equally. The a_k values are given in Table 4 together with the standard deviation $\sigma(Q_m^E)$, defined as

$$\sigma(Q_m^E) = |\phi_{\min}/(N - n)|^{0.5} \tag{3}$$

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

$$\phi = \sum_{k=1}^{N} {\eta_k}^2 \tag{4}$$

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 2.

Values of H_m^E are positive and in the order α-pinene > β-pinene > p-cymene. The same trend is observed in the V_m^E curves.

The temperature dependence is positive and sensible for the volumetric data and almost negligible for the thermochemical data. These results are the same as those obtained in previous papers dealing with the same pine resins in mixture with phenetole, dimethyl carbonate, and diethyl

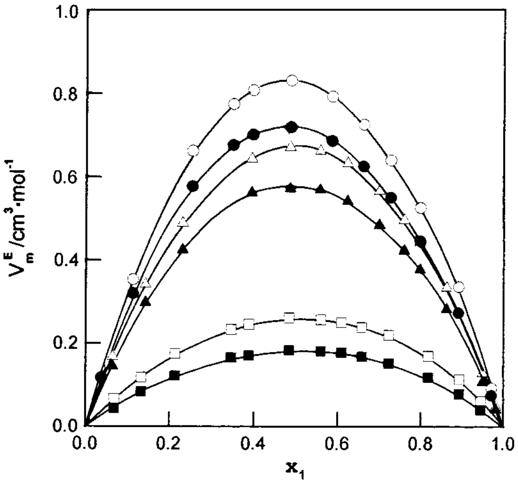

Figure 3. Excess molar volumes, V_m^E, for binary mixtures containing 1,3-dioxolane (1) + α-pinene (2) (●), + β-pinene (2) (▲), or + p-cymene (2) (■). Closed and open points are for (298.15 and 313.15) K. The solid curves were drawn from eq 2.

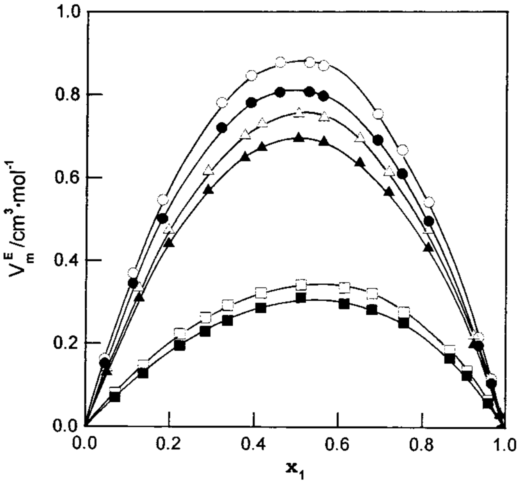

Figure 4. Excess molar volumes, V_m^E, for binary mixtures containing 1,4-dioxane (1) + α-pinene (2) (●), + β-pinene (2) (▲), or + p-cymene (2) (■). Closed and open points are for (298.15 and 313.15) K. The solid curves were drawn from eq 2.

carbonate,[1,2] thus confirming the previous analysis on the thermodynamic interactions between molecules in the binary mixtures.

Particularly, if we refer to the approximated expression $H_m^E \propto E_{11} + E_{22} - 2E_{12}$, where E_{ij} is the interaction energy between molecules *i* and *j*, the H_m^E curves imply a larger E_{12} interaction for β-pinene, with respect to α-pinene. This conclusion may find an explanation in the allyl character of β-pinene,[20] showing a double bond highly delocalized and then strongly interacting with the oxygen atoms of ethers, whereas α-pinene shows a sterically hindered localized double bond.

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