

Densities, Viscosities, Refractive Indices, and Excess Molar Enthalpies of Methyl *tert*-Butyl Ether + Components of Pine Resins and Essential Oils at 298.15 K

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Densities, ρ , viscosities, η , refractive indices, n_D , and excess molar enthalpies, H_m^E , of binary mixtures containing methyl *tert*-butyl ether (MTBE) + α -pinene (2,6,6-trimethylbicyclo[3.1.1]hept-2-ene), + β -pinene (6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane), + *p*-cymene [1-methyl-4-(1-methylethyl)benzene], + (*S*)-(-)-limonene [(*S*)-1-methyl-4-(1-methylethenyl)cyclohexene], + 1,8-cineole (1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane), and + linalool (3,7-dimethyl-1,6-octadien-3-ol) were determined at 298.15 K and at atmospheric pressure using a digital density meter, a Schott measuring system, an Abbe refractometer, and a flow microcalorimeter, respectively. The excess molar volumes, V_m^E , the deviations in viscosities, $\Delta\eta$, and in refractive indices, ΔR , and the excess molar enthalpies, H_m^E , were calculated from experimental measurements. Results were fitted to the Redlich–Kister equation to obtain the adjustable parameters and standard deviations. Results were also qualitatively discussed in terms of molecular interactions.

Introduction

Measurements of the bulk properties, such as viscosities and densities of liquids, measurements of refractive indices, and measurements of excess molar enthalpies provide insight into the molecular arrangement in liquids and help one to understand the thermodynamic properties of liquid mixtures.

Continuing our research program involving the study of bulk and excess properties of binary mixtures containing pine resins and essential oils,^{1–3} we report in this paper measurements of densities, ρ , viscosities, η , refractive indices, n_D , and excess molar enthalpies, H_m^E , of binary mixtures containing MTBE + α -pinene, + β -pinene, + *p*-cymene, + (*S*)-(-)-limonene, + 1,8-cineole, and + linalool at 298.15 K and at atmospheric pressure.

Methyl *tert*-butyl ether (MTBE), an oxygenating additive, is used presently as a blending agent in the formulation of new gasolines for enhancing the octane number as a substitute for traditional leaded products.

We have considered as being of some theoretical interest the comparison between MTBE + pine resins (this paper) and dialkyl carbonates with the same pine resins studied in a previous work.²

Pine resins (α -pinene, β -pinene, and *p*-cymene) and essential oils [(*S*)-(-)-limonene, 1,8-cineole, and linalool] are used in the pharmaceutical and cosmetic industries.^{4,5} Particularly α -pinene proved to be an exceptionally successful solvent for many chemistry programs in asymmetric reductions for synthesizing optically pure materials via chiral organoboranes.^{6,7}

The solubility of pine resins and essential oils in ethers such as MTBE is complete with respect to other solvents.

The purpose of the present paper is to correlate the experimental data and to obtain qualitative information on the interaction between molecules.

To our knowledge, no literature results for these mixtures are available.

Experimental Section

Chemicals. MTBE (Aldrich, purity = 99.8%) was used without further purification, whereas α -pinene (2,6,6-trimethylbicyclo[3.1.1]hept-2-ene) (Fluka, purity > 99%), β -pinene (6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane) (Aldrich, purity 99%), *p*-cymene [1-methyl-4-(1-methylethyl)benzene] (Aldrich, purity = 99%), (*S*)-(-)-limonene [(*S*)-1-methyl-4-(1-methylethenyl)cyclohexene] (Fluka, purity > 97%), 1,8-cineole (1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane) (Aldrich, purity = 99%), and linalool (3,7-dimethyl-1,6-octadien-3-ol) (Aldrich, purity = 97%) were distilled using a Vigreux column, 1 m long and 2.5 cm in outside diameter. The final products were obtained by discarding the upper 10% and lower 15% cuts. The purities of liquids were checked with the aid of a Hewlett-Packard gas chromatograph (model 5890) supplied with an HP (cross-linked 5% methyl siloxane) capillary column.

The impurity contents, after gas chromatographic area analysis, were <99.8%. α -Pinene was placed in refrigerator at 277.15 K, as suggested by supplier.

Before measurements, pure liquids 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).

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Table 1. Comparison of Experimental Densities, ρ , Dynamic Viscosities, η , and Refractive Indices, n_D , of Pure Components with Literature Values

compound	$\rho/\text{g}\cdot\text{cm}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$		n_D	
	this work	lit.	this work	lit.	this work	lit.
MTBE	0.73536	0.7359 ⁸ 0.7356 ⁹ 0.73529 ¹⁰	0.3354	0.340 ⁸ 0.3353 ¹⁰	1.3663	1.3663 ⁹
α -pinene	0.85388	0.8539 ¹¹ 0.8548 ¹²	1.296	na	1.4635	1.4632 ¹¹ 1.4621 ¹²
β -pinene	0.86667	0.8667 ¹¹ 0.8655 ¹²	1.594	na	1.4767	1.4768 ¹¹ 1.4748 ¹²
<i>p</i> -cymene	0.85290	0.8533 ¹¹ 0.8521	0.8198	na	1.4884	1.4885 ¹¹ 1.4865 ¹²
(<i>S</i>)-(-)-limonene	0.83900	0.83944 ⁷ 0.8384 ¹¹ 0.8418 ¹²	0.8462	0.846 ⁷	1.4709	1.4707 ¹²
1,8-cineole	0.92022	0.92013 ⁷ 0.9192 ¹² 0.92029 ¹³	2.559	2.559 ⁷	1.4553	1.4555 ¹²
linalool	0.85810 0.86240 ^a	0.85809 ⁷ 0.8622 ^{2a}	4.465	4.464 ⁷	1.4601	1.4603 ⁷

^a At 293.15 K.

The measured densities, ρ , viscosities, η , and refractive indices, n_D , of pure chemicals are given in Table 1 and compared with literature.^{7–13}

Density Measurements. All solutions were prepared by mass, using a digital balance (Mettler, model AE 160) with an accuracy of $\pm 1 \times 10^{-4}$ g.

Precautions were taken, such as using samples recently prepared and reducing to a minimum the vapor space in the vessel, to avoid preferential evaporation. We have used the same operating procedure described elsewhere.¹⁴ The possible uncertainty in mole fraction x_1 of MTBE (component 1) is $< 2 \times 10^{-4}$. Densities, ρ , of the pure components and of the binary mixtures were measured using a density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell (type 602) with an uncertainty of $\pm 1.5 \times 10^{-5}$ g·cm⁻³, which lead to corresponding values in excess molar volumes of $\pm 1 \times 10^{-3}$ cm³·mol⁻¹.

The oscillator period, τ , in the vibrating U-tube was converted into density by using the equation

$$\tau = A(\tau^2 - B) \quad (1)$$

where A and B are the apparatus constant, determined with the literature density data of pure water and dry air. The apparatus and its operating procedure were described elsewhere.¹⁴

An external ultrathermostat bath circulator (Heto, type 01 DTB 623, Birkerød, Denmark) with a precision of ± 0.005 K was used to maintain constant the temperature, which was determined at (298.15 ± 0.01) K using a digital thermometer (Anton Paar, type CTK 100).

All masses were corrected for buoyancy and evaporation of the components, and all molar quantities were based on the relative atomic mass table by IUPAC.¹⁵

Before measurements, the apparatus was checked by determining V_m^E using the test mixture benzene + cyclohexane at 298.15 K. Our results agree with those of the literature,¹⁶ showing a discrepancy of $\pm 0.5\%$ in the central range of mole fraction of benzene.

Viscosimetric Measurements. The kinematic viscosities, ν , were determined experimentally by using a viscosity measuring unit (Schott Geräte AVS 310, Mains, Germany) equipped with Ubbelohde capillary viscometers (type 532, capillary no. Oc, Oa, I) having a cell constants $k =$

0.003146, 0.004993, and 0.009937, respectively, with times varying from (180 to 400) s.

The temperature was maintained constant to ± 0.005 K using a well-stirred water bath (Lauda, type E 200).

The uncertainty in viscosity measurements was $< \pm 0.002$ mPa·s.

The viscosimeter was calibrated with double-distilled water, the viscosities of which are well-known and reported in the literature.¹¹ The average of six flow times for each sample of liquid was taken for the purpose of calculation of the viscosity.

The kinematic viscosity, ν , was obtained from the formula

$$\nu = k(t - \theta) \quad (2)$$

where k is the capillary constant, t (s) is the flowing time of the sample, and θ is the Hagenbach correction (HC). The absolute viscosity, η , was calculated from $\eta = \rho\nu$. The reported viscosity is accurate to within $< 1\%$.

Refractive Index Measurements. The refractive indices, n_D , at the sodium line were measured using an Abbe refractometer (Carl Zeiss, model G, Jena, Switzerland) with an error of < 0.0001 unit.

The temperature was kept constant to ± 0.01 K during the measurements.

Calorimetric Measurements. A flow microcalorimeter (LKB Producer, model 2107, Bromma, Sweden), equipped with two automatic burets (ABU, Radiometer, Copenhagen, Denmark) necessary to pump liquids into the mixing cell of the apparatus, was used in the measurements of H_m^E . Details of the procedure and apparatus used were described previously.^{17,18}

Mole fractions, x_1 , of MTBE were determined from flow rates with a precision of 1×10^{-4} , which leads to an error in H_m^E of $(0.5 - 1)$ J·mol⁻¹. The reliability of the calorimeter and the method was established by measuring H_m^E values of the standard system cyclohexane + hexane at 298.15 K.

Our results were in agreement with the data reported in the literature¹⁹ within $< 1\%$.

Results and Discussion

The experimental values of density, viscosity, and refractive index at 298.15 K and at atmospheric pressure are

Table 2. Experimental Densities, ρ , Dynamic Viscosities, η , Refractive Indices, n_d , Excess Molar Volumes, V_m^E , Deviations of Viscosities, $\Delta\eta$, and Deviations of Refractive Indices, ΔR , of Binary Mixtures Containing MTBE + Components of Pine Resins and Essential Oils at 298.15 K

x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	n_d	$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\eta/\text{mPa}\cdot\text{s}$	$\Delta R/\text{cm}^3\cdot\text{mol}^{-1}$
MTBE (1) + α -Pinene (2)						
0.0598	0.84855	1.1959	1.4593	-0.015	-0.043	-0.213
0.1280	0.84228	1.0911	1.4544	-0.031	-0.082	-0.432
0.2151	0.83392	0.9713	1.4478	-0.051	-0.118	-0.667
0.3570	0.81943	0.8048	1.4362	-0.077	-0.148	-0.943
0.4839	0.80542	0.6762	1.4248	-0.091	-0.155	-1.068
0.5691	0.79540	0.5379	1.4167	-0.096	-0.146	-1.069
0.6514	0.78521	0.6030	1.4082	-0.093	-0.132	-1.022
0.7236	0.77583	0.4866	1.4006	-0.087	-0.114	-0.908
0.8254	0.76178	0.4221	1.3889	-0.065	-0.081	-0.673
0.9034	0.75038	0.3790	1.3793	-0.042	-0.049	-0.417
0.9583	0.74197	0.3576	1.3722	-0.019	-0.018	-0.191
MTBE (1) + β -Pinene (2)						
0.0493	0.86193	1.4853	1.4727	-0.045	-0.046	-0.182
0.1076	0.85615	1.3643	1.4679	-0.098	-0.094	-0.372
0.2248	0.84398	1.1424	1.4579	-0.193	-0.168	-0.679
0.3540	0.82952	0.9300	1.4461	-0.268	-0.218	-0.901
0.4390	0.81937	0.8092	1.4377	-0.305	-0.232	-0.987
0.5239	0.80864	0.7038	1.4289	-0.322	-0.231	-1.009
0.6457	0.79217	0.5826	1.4150	-0.314	-0.199	-0.958
0.7594	0.77548	0.4855	1.4009	-0.264	-0.153	-0.788
0.8663	0.75853	0.4100	1.3864	-0.179	-0.094	-0.516
0.9007	0.75276	0.3873	1.3814	-0.138	-0.073	-0.407
0.9651	0.74161	0.3495	1.3719	-0.053	-0.030	-0.154
MTBE (1) + <i>p</i> -Cymene (2)						
0.0616	0.84783	0.7751	1.4835	-0.097	-0.015	-0.196
0.1556	0.83971	0.7225	1.4754	-0.230	-0.022	-0.465
0.3301	0.82316	0.6338	1.4586	-0.412	-0.026	-0.828
0.4987	0.80515	0.5524	1.4401	-0.502	-0.026	-0.974
0.5665	0.79726	0.5253	1.4319	-0.511	-0.025	-0.974
0.6911	0.78164	0.4605	1.4156	-0.473	-0.024	-0.870
0.7665	0.77145	0.4272	1.4047	-0.416	-0.021	-0.752
0.8304	0.76227	0.3998	1.3949	-0.339	-0.018	-0.607
0.8734	0.75582	0.3814	1.3882	-0.273	-0.015	-0.473
0.9298	0.74697	0.3583	1.3789	-0.163	-0.011	-0.274
0.9644	0.74134	0.3467	1.3727	-0.089	-0.006	-0.151
MTBE (1) + (<i>S</i>)-(-)-Limonene (2)						
0.0694	0.83395	0.807	1.4660	-0.068	-0.003	-0.276
0.1591	0.82704	0.755	1.4592	-0.140	-0.010	-0.591
0.2570	0.81900	0.700	1.4513	-0.202	-0.015	-0.864
0.3599	0.80996	0.641	1.4422	-0.248	-0.021	-1.084
0.4910	0.79749	0.572	1.4297	-0.284	-0.024	-1.221
0.6599	0.77960	0.486	1.4120	-0.282	-0.023	-1.125
0.7344	0.77095	0.449	1.4031	-0.259	-0.022	-1.005
0.8017	0.76267	0.418	1.3947	-0.220	-0.019	-0.830
0.8714	0.75360	0.386	1.3854	-0.163	-0.015	-0.592
0.9373	0.74452	0.356	1.3759	-0.092	-0.011	-0.319
0.9672	0.74021	0.344	1.3715	-0.051	-0.008	-0.167
MTBE (1) + 1,8-Cineole (2)						
0.0390	0.91539	2.3646	1.4531	-0.069	-0.108	-0.187
0.1663	0.89862	1.8327	1.4455	-0.263	-0.357	-0.708
0.2659	0.88437	1.4910	1.4390	-0.383	-0.477	-1.022
0.3790	0.86686	1.1884	1.4308	-0.485	-0.528	-1.280
0.4562	0.85843	1.0199	1.4247	-0.532	-0.525	-1.386
0.5768	0.83228	0.7958	1.4143	-0.555	-0.481	-1.420
0.6621	0.81554	0.6632	1.4065	-0.530	-0.424	-1.318
0.7385	0.79947	0.5702	1.3986	-0.476	-0.347	-1.169
0.8408	0.77618	0.4604	1.3871	-0.347	-0.229	-0.835
0.9020	0.76118	0.4049	1.3796	-0.235	-0.148	-0.559
0.9701	0.74348	0.3547	1.3705	-0.078	-0.047	-0.188
MTBE (1) + Linalool (2)						
0.0756	0.85255	3.6915	1.4560	-0.236	-0.405	-0.518
0.1208	0.84927	3.3138	1.4535	-0.365	-0.599	-0.790
0.1819	0.84457	2.8561	1.4497	-0.527	-0.808	-1.144
0.3063	0.83405	2.0928	1.4415	-0.802	-1.065	-1.703
0.3763	0.82747	1.7611	1.4365	-0.918	-1.112	-1.915
0.5129	0.81301	1.2500	1.4255	-1.053	-1.067	-2.139
0.5989	0.80258	0.9982	1.4175	-1.056	-0.969	-2.128
0.7222	0.78556	0.7171	1.4047	-0.941	-0.749	-1.854
0.8148	0.77088	0.5569	1.3936	-0.746	-0.532	-1.441
0.9106	0.75360	0.4273	1.3806	-0.421	-0.272	-0.793
0.9692	0.74191	0.3605	1.3714	-0.158	-0.100	-0.302

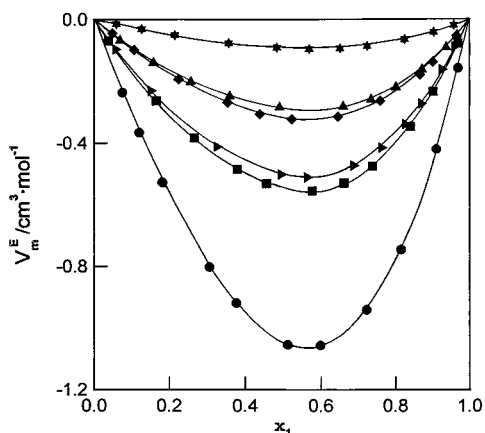


Figure 1. Excess molar volumes, V_m^E , versus the mole fraction x_1 of MTBE (1) + α -pinene (2) (\star), + β -pinene (2) (\blacklozenge), + p -cymene (2) (\blacktriangleright), + (S)-(-)-limonene (2) (\blacktriangle), + 1,8-cineole (2) (\blacksquare), and + linalool (2) (\bullet) at 298.15 K: solid line, Redlich–Kister equation.

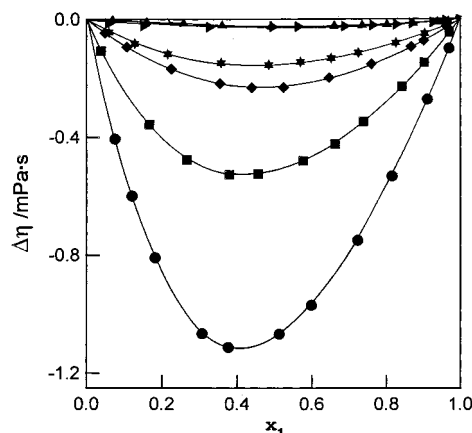


Figure 2. Deviation of viscosity, $\Delta\eta$, versus the mole fraction x_1 of MTBE (1) + α -pinene (2) (\star), + β -pinene (2) (\blacklozenge), + p -cymene (2) (\blacktriangleright), + (S)-(-)-limonene (2) (\blacktriangle), + 1,8-cineole (2) (\blacksquare), and + linalool (2) (\bullet) at 298.15 K: solid line, Redlich–Kister equation.

Table 3. Excess Molar Enthalpies, H_m^E , for Binary Mixtures Containing MTBE + Components of Pine Resins and Essential Oils 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	$H_m^E/\text{J}\cdot\text{mol}^{-1}$
MTBE (1) + α -Pinene (2)					
0.0525	91.2	0.3996	295.7	0.8419	111.0
0.0998	154.4	0.4700	298.4	0.8887	66.7
0.1426	190.7	0.5710	283.4	0.9141	51.3
0.1815	218.9	0.6664	245.6	0.9411	30.4
0.2497	258.3	0.7269	206.3	0.9696	12.3
0.3073	278.1	0.7997	148.6	0.9771	10.0
MTBE (1) + β -Pinene (2)					
0.0518	35.3	0.3960	191.0	0.8400	102.8
0.0985	65.7	0.4663	204.5	0.8872	74.8
0.1408	91.4	0.5673	202.4	0.9130	58.7
0.1793	114.9	0.6631	181.3	0.9403	40.7
0.2469	145.9	0.7420	159.3	0.9692	21.2
0.3041	170.7	0.7973	126.6	0.9767	16.1
MTBE (1) + p -Cymene (2)					
0.0519	11.5	0.3963	-4.4	0.8400	-4.1
0.0986	15.5	0.4666	-8.1	0.8874	-3.0
0.1410	15.5	0.5676	-9.1	0.9131	-2.5
0.1795	13.8	0.6633	-7.3	0.9403	-2.0
0.2471	7.9	0.7242	-6.5	0.9692	-1.3
0.3044	2.8	0.7975	-5.0		
MTBE (1) + (S)-(-)-Limonene (2)					
0.0406	-50.6	0.4036	20.5	0.8904	40.3
0.0534	-61.6	0.4743	47.3	0.9155	30.4
0.1014	-83.5	0.5751	70.5	0.9420	20.2
0.1447	-87.2	0.6701	76.5	0.9701	11.0
0.1841	-80.1	0.7303	70.4	0.9774	9.5
0.2529	-53.4	0.8024	55.3		
0.3109	-24.6	0.8441	47.2		
MTBE (1) + 1,8-Cineole (2)					
0.0551	9.0	0.4115	36.7	0.8483	21.4
0.1044	14.7	0.4824	35.7	0.8935	17.4
0.1488	17.9	0.5831	35.6	0.9180	14.4
0.1890	20.3	0.6773	33.1	0.9438	9.1
0.2591	27.4	0.7366	30.0	0.9711	6.3
0.3179	30.2	0.8075	25.8	0.9781	4.4
MTBE (1) + Linalool (2)					
0.0588	-35.5	0.4287	-229.8	0.8572	-157.4
0.1111	-67.3	0.5000	-248.7	0.9000	-117.9
0.1579	-95.8	0.6001	-254.4	0.9231	-90.4
0.2000	-118.3	0.6925	-242.6	0.9474	-68.2
0.2729	-160.1	0.7501	-222.2	0.9730	-35.2
0.3334	-194.4	0.8182	-185.8	0.9796	-27.0

reported in Table 2, and excess molar enthalpies are given in Table 3 as a function of mole fraction, x_1 , and are graphically represented in Figures 1–4.

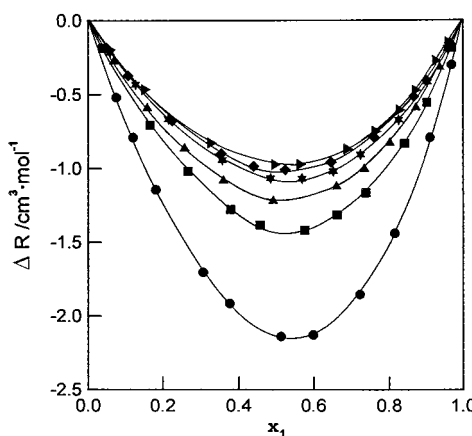


Figure 3. Deviation of refractive indices, ΔR , versus the mole fraction x_1 of MTBE (1) + α -pinene (2) (\star), + β -pinene (2) (\blacklozenge), + p -cymene (2) (\blacktriangleright), + (S)-(-)-limonene (2) (\blacktriangle), + 1,8-cineole (2) (\blacksquare), and + linalool (2) (\bullet) at 298.15 K: solid line, Redlich–Kister equation.

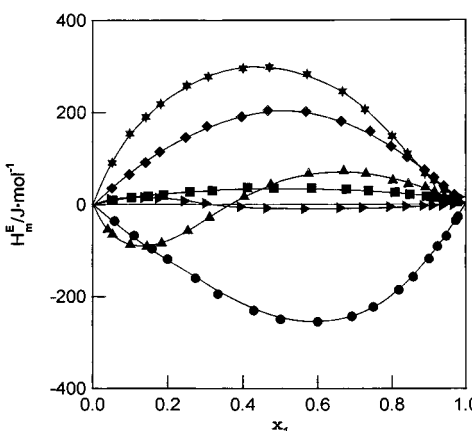


Figure 4. Excess molar enthalpies, H_m^E , versus the mole fraction x_1 of MTBE (1) + α -pinene (2) (\star), + β -pinene (2) (\blacklozenge), + p -cymene (2) (\blacktriangleright), + (S)-(-)-limonene (2) (\blacktriangle), + 1,8-cineole (2) (\blacksquare), and + linalool (2) (\bullet) at 298.15 K: solid line, Redlich–Kister equation.

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

$$V_m^E = (x_1 M_1 + x_2 M_2) / \rho - x_1 M_1 / \rho_1 - x_2 M_2 / \rho_2 \quad (3)$$

Table 4. Least-Squares Parameters, a_k , Equation 9, and Standard Deviations, $\sigma(Q_m^E)$, Equation 10, of Binary Mixtures Containing MTBE + Components of Pine Resins and Essential Oils at 298.15 K

function	a_0	a_1	a_2	a_3	$\sigma(Q_m^E)$
MTBE (1) + α -Pinene (2)					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.3720	-0.1269			0.0005
$\Delta\eta/\text{mPa}\cdot\text{s}$	-0.6142	0.1195	-0.0520		0.0016
$\Delta R/\text{cm}^3\cdot\text{mol}^{-1}$	-4.2899	-0.5925			0.0032
$H_m^E/\text{J}\cdot\text{mol}^{-1}$	1190.0	-190.00	-9.7236		1.6
MTBE (1) + β -Pinene (2)					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-1.2771	-0.3329			0.0013
$\Delta\eta/\text{mPa}\cdot\text{s}$	-0.9147	0.1237			0.0028
$\Delta R/\text{cm}^3\cdot\text{mol}^{-1}$	-4.0427	-0.4068	-0.2468		0.0024
$H_m^E/\text{J}\cdot\text{mol}^{-1}$	820.16	3.5300	-117.89		1.2
MTBE (1) + p -Cymene (2)					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-2.0117	-0.4905	-0.1496		0.0014
$\Delta\eta/\text{mPa}\cdot\text{s}$	-0.0958	0.0273	0.0018		
$\Delta R/\text{cm}^3\cdot\text{mol}^{-1}$	-3.9021	-0.5233			0.0056
$H_m^E/\text{J}\cdot\text{mol}^{-1}$	-34.931	-37.116	163.08	-141.96	0.2
MTBE (1) + (S)-(-)-Limonene (2)					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-1.1426	-0.2845	-0.2107		0.0008
$\Delta\eta/\text{mPa}\cdot\text{s}$	-0.0939	-0.0388	-0.0175		0.0018
$\Delta R/\text{cm}^3\cdot\text{mol}^{-1}$	-4.8714	-0.6156	0.0899		0.0052
$H_m^E/\text{J}\cdot\text{mol}^{-1}$	224.44	543.43	-776.40	431.40	1.5
MTBE (1) + 1,8-Cineole (2)					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-2.1868	-0.5469	-0.1161	0.0785	0.0010
$\Delta\eta/\text{mPa}\cdot\text{s}$	-2.0692	0.6565	-0.2029		0.0027
$\Delta R/\text{cm}^3\cdot\text{mol}^{-1}$	-5.6522	-0.8431	-0.0177		0.0049
$H_m^E/\text{J}\cdot\text{mol}^{-1}$	144.15	17.548	28.026		1.0
MTBE (1) + Linalool (2)					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-4.1769	-1.0963	-0.1583		0.0013
$\Delta\eta/\text{mPa}\cdot\text{s}$	-4.3318	1.5903	-0.3567	-0.2078	0.0033
$\Delta R/\text{cm}^3\cdot\text{mol}^{-1}$	-8.5487	-1.4771	-0.1215		0.0051
$H_m^E/\text{J}\cdot\text{mol}^{-1}$	-990.73	-393.44			1.7

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

The deviation in viscosity, $\Delta\eta$, was calculated from definition

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (4)$$

where η_1 , η_2 , and η are the viscosities of pure components and of mixture, respectively.

The molar refraction deviations, ΔR , were calculated from the Lorentz–Lorenz equation

$$\Delta R = R_m - \sum_{i=1}^2 R_i\varphi_i \quad (5)$$

where R_i and R_m are the molar refractions of pure components and of mixture, respectively, and φ_i is the volume fraction of component i given as

$$\varphi_i = x_i V_i / \sum_{i=1}^2 x_i V_i \quad (6)$$

where $V_i = M_i/\rho_i$.

The molar refraction, R_i , was obtained from the formula (Lorentz–Lorenz)

$$R_i = \{[n_{D(0)}^2 - 1]/[n_{D(0)}^2 + 2]\} V_i \quad (7)$$

where $n_{D(0)}$ is the refractive index for the pure components.

The equation for binary mixture becomes

$$R_m = \{[n_{D(m)}^2 - 1]/[n_{D(m)}^2 + 2]\} V_m \quad (8)$$

where $n_{D(m)}$ is the refractive index of the mixture, $V_m = (x_1M_1 + x_2M_2)/\rho$, and R_m is the molar refraction of the mixture.

The molar refraction and molar refraction deviation, ΔR , were calculated with an accuracy of $\pm 0.0001 \text{ cm}^3\cdot\text{mol}^{-1}$. The variation of V_m^E , $\Delta\eta$, ΔR , and H_m^E with composition are expressed by the Redlich–Kister equation

$$Q_m^E = x_1x_2 \sum_{k=0}^8 a_k(x_1 - x_2)^k \quad (9)$$

where Q_m^E refers to V_m^E , $\Delta\eta$, ΔR , and H_m^E .

The adjustable parameters a_k were determined by fitting the experimental values to eq 8 with least-squares methods, and the results are given in Table 4. The tabulated standard deviations, $\sigma(Q_m^E)$ reported in Table 4 were defined as

$$\sigma(Q_m^E) = |\phi_{\min}/(N - n)|^{0.5} \quad (10)$$

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

$$\phi = \sum_{k=1}^N \eta_k^2 \quad (11)$$

where $\eta_k = Q_m^E, \text{calcd} - Q_m^E$; Q_m^E is the experimental value and Q_m^E, calcd is evaluated through eq 8.

Figures 1–4 show values of V_m^E , $\Delta\eta$, ΔR , and H_m^E for the binary mixtures of MTBE with the six compounds. To obtain some useful information on the connection between chemical properties, and structures of the molecules, the mixtures MTBE + pine resins and MTBE + essential oils will be considered separately.

As to the mixtures of MTBE + pine resins, the figures show negative values of ΔR , V_m^E , and $\Delta\eta$. The quite different behavior of these pine resins in mixtures with dialkyl carbonates² is noteworthy because they show positive values of V_m^E . Values of H_m^E are positive for α -pinene and β -pinene (with maxima ranging between 200 and 300 $\text{J}\cdot\text{mol}^{-1}$), in the same order which was found for the mixtures of dialkyl carbonates⁶ with the same pine resins (with maxima ranging between 1500 and 1800 $\text{J}\cdot\text{mol}^{-1}$), whereas p -cymene shows very small values in mixtures with MTBE and positive values in mixtures with dialkyl carbonates.

The different behavior of volumetric data V_m^E and the larger values of H_m^E observed for the mixtures containing pine resins + dialkyl carbonates suggest that the interactions of double bonds of pinenes are stronger with the ethereal oxygen of MTBE than with the C=O group of carbonates; hence, marked volume contractions for the mixtures with MTBE and large values of H_m^E for mixtures with alkyl carbonates are observed (H_m^E may be assumed to be approximately proportional to $E_{11} + E_{22} - 2E_{12}$, E_{ij} being the interaction energy between molecules i and j).

Values of V_m^E , $\Delta\eta$, and ΔR for the mixtures of MTBE with essential oils are always negative. Absolute values are in the order linalool > cineole > limonene. The H_m^E values are negative for linalool and positive for cineole, whereas

the mixtures with limonene show a sign inversion of H_m^E as a function of the mole fraction of MTBE.

An interesting comparison of H_m^E data may be made between the systems linalool + MTBE (Figure 4) and linalool + 1,8-cineole⁷ (in both cases alcohol + ether, respectively). The former mixture shows negative values (with a minimum of $\sim -250 \text{ J}\cdot\text{mol}^{-1}$) and the latter positive values (with a maximum of $\sim 120 \text{ J}\cdot\text{mol}^{-1}$).

These low absolute values of H_m^E and the nearly symmetrical curves allow the application of the Prigogine model²⁰ to the above-mentioned mixtures. The calculated values of E_{11} , E_{22} , and E_{12} (alcohol is component 1) lead to a good agreement between calculated and experimental values of H_m^E .

$E_{22} - 2E_{12}$ results are more negative for the first mixture, which leads to $H_m^E \approx E_{11} + E_{22} - 2E_{12}$ negative and positive for the binary mixtures of linalool + MTBE or + cineole, respectively.

Particularly, the more negative value of $E_{22} - 2E_{12}$ obtained for the system linalool + MTBE implies, at the molecular level, the prevailing of interactions between the OH group of linalool and the lone pair of electrons of O in MTBE (linear ether), with respect to the corresponding O atom in cineole (cyclic ether).

This result is significant because in the solid state, despite the bulk of the molecule, the cyclic ether cineole shows the O atom well exposed to the approach of some compounds, thus acting as a monodentate ligand. Moreover, cineole may form also hydrogen-bonded complexes.²¹

On the contrary, the literature on MTBE in the solid state reports no examples of this kind, probably due to the prevailing of steric hindrance in the solid state for MTBE.

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