J. Chem. Eng. Data **2002,** *47,* 93−97

Densities, Viscosities, and Refractive Indices of Binary Mixtures Containing *n*-Hexane + Components of Pine Resins and Essential Oils at 298.15 K

Fabio Comelli and Stefano Ottani

Centro di Studio per la Fisica delle Macromolecole del CNR, via Selmi 2, I-40126 Bologna, Italy

Romolo Francesconi* and Carlo Castellari

Dipartimento di Chimica "G. Ciamician", Università degli Studi, via Selmi 2, I-40126 Bologna, Italy

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Densities, ρ, viscosities, η, and refractive indices, n_D, of binary mixtures containing *n*-hexane + α-pinene (2,6,6-trimethylbicyclo[3.1.1]hept-2-ene), + β-pinene (6,6-dimethyl-2-methylene bicyclo[3.1.1]heptane), + *p*-cymene (1-methyl-4-[1-methylethyl]benzene), + (*S*)-(−)-limonene [(−)-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 viscosity measuring system, and an Abbe refractometer, respectively. The excess molar volumes, V_m^E, deviations in viscosities, $\Delta\eta$, and deviations in molar refractions, ΔR, calculated from experimental measurements, are always negative, with the exception of the V_m^E curve referring to the hexane + linalool mixture, which shows an inversion of sign. Results were fitted to the Redlich−Kister polynomial and qualitatively discussed in terms of molecular interactions. The McAllister multibody interaction model was used to correlate the kinematic viscosities of liquid mixtures with mole fractions.

Introduction

Pine resins and essential oils are widely used in the pharmaceutical, cosmetic, and perfume industries.[1,2] In particular, α-pinene is successfully used in asymmetric reduction for synthesizing optically pure materials with chiral organoboranes.[3,4]

Following our studies on thermodynamic and bulk properties of binary mixtures containing pine resins and essential oils,[5−8] we report in this paper measurements of densities, viscosities, and refractive indices of binary mixtures containing *n*-hexane + α-pinene, + β-pinene, + p-cymene, + (*S*)-(−)-limonene, + 1,8-cineole, and + linalool at 298.15 K and at atmospheric pressure. This work is aimed to provide information about these mixtures, to investigate correlations among them, and to give a qualitative interpretation in terms of molecular interactions.

We have taken *n*-hexane as component 1 to obtain a comparison between the simple molecule of this component and those of dialkyl carbonates and ethers, studied in previous papers.[5,6,8]

No experimental data about these mixtures have been found in the literature, where only a few papers are available concerning vapor−liquid equilibrium studies.

Experimental Section

Chemicals. *n*-Hexane (Fluka, purity >99.5%) was used without further purification. α-Pinene (Fluka, purity >99%), β-pinene (Aldrich, purity 99%), p-cymene (Aldrich, purity 99%), (*S*)-(−)-limonene (Fluka, >97%), 1,8-cineole (Aldrich, purity 99%), and linalool (Aldrich, purity 97%) were purified following the procedure described elsewhere.[8] The purities of liquids were determined using a Hewlett-Packard gas chromatograph (model 5890) supplied with a HP (cross-linked 5% Me siloxane) capillary column. The purities contents, after gas chromatographic analysis, were <99.8%. α-Pinene was placed in a refrigerator at 277.15 K, as suggested by the manufacturer. 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).

The measured densities, ρ, viscosities, η, and refractive indices, n_D, compared with literature values,[8−11] are listed in Table 1.

Density Measurements. Density measurements were performed with a vibrating tube density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell (type 602) and an external bath circulator (Heto, type 01 DTB 623, Birkeród, Denmark) for temperature control with a stability of ±0.005 K. The temperature was determined using a precision thermometer (Anton Paar, type CTK 100) with an uncertainty of ±0.001 K. Samples were prepared by mass using a digital balance (Mettler, model AE 160, Switzerland) with a precision of ±0.0001 g. The accuracy in densities was better than $\pm 1.5 \times 10^{-5}$ g·cm^{-3}, corresponding to a value of $\pm 3 \times 10^{-3}$ cm^3·mol^{-1} in excess molar volume, V_m^E. Further details on sample preparation and experimental conditions are given elsewhere.[12] The apparatus was calibrated periodically with doubly distilled water and dry air, whose values are well-known from the literature.[13,14] 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 + cyclo-

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* Corresponding author. Fax: 051-2094325. E-mail: romolo@ciam.unibo.it.

10.1021/je010216w CCC: $22.00

Table 1. Comparison of Experimental Densities, ρ, Dynamic Viscosities, η, and Refractive Indices, n_D, of Pure Components with Literature Values at 298.15 K

	ρ/g·cm^{-3}		η/mPa·s		n_D	
compound	this work	lit.	this work	lit.	this work	lit.
n-hexane	0.654 86	0.65484[9]	0.295	0.2942[9]	1.3721	1.37226[9]
α-pinene	0.853 90	0.8539[9] 0.8548[12]	1.293	n.a.	1.4636	1.4632[9]
β-pinene	0.866 69	0.8667[9] 0.8655[10]	1.593	1.594[8]	1.4761	1.4768[9] 1.4748[10]
p-cymene	0.852 91	0.8533[9] 0.8521[10]	0.798	0.820[8]	1.4882	1.4885[9] 1.4865[10]
(S)-(−)-limonene	0.839 19	0.8384[9] 0.8418[10]	0.846	0.8468	1.4705	1.470710
1,8-cineole	0.920 11	0.91929 0.92029[11] 0.92009[11]	2.556	2.5598	1.4553	1.455511
linalool	0.85760 0.86238[b] 0.86238[b]	0.85810[8] 0.8622[1,b] 0.8622[1,b]	4.381	4.4658	1.4605[a]	1.4604[1,a]

[a] At 295.15 K. [b] At 273.15 K.

Table 2. Densities, ρ, and Excess Molar Volumes, V_m^E, for Binary Mixtures Containing *n*-Hexane + Components of Pine Resins and Essential Oils at 298.15 K

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}
		n-Hexane (1) + α-Pinene (2)			
0.0422	0.847 19	−0.086	0.6267	0.740 28	−0.642
0.0619	0.844 01	−0.125	0.7168	0.721 07	−0.581
0.1087	0.836 38	−0.213	0.8670	0.687 12	−0.352
0.2540	0.811 66	−0.445	0.9244	0.673 46	−0.217
0.3759	0.789 66	−0.580	0.9625	0.664 17	−0.114
0.5049	0.764 99	−0.651			
		n-Hexane (1) + β-Pinene (2)			
0.0421	0.859 51	−0.061	0.5597	0.759 98	−0.469
0.0626	0.855 97	−0.090	0.6601	0.737 88	−0.444
0.2031	0.830 91	−0.269	0.7454	0.718 29	−0.392
0.2799	0.816 55	−0.343	0.8217	0.700 1	−0.313
0.3765	0.797 82	−0.415	0.8935	0.682 32	−0.209
0.4939	0.773 92	−0.463	0.9595	0.665 51	−0.092
		n-Hexane (1) + *p*-Cymene (2)			
0.0316	0.847 84	−0.034	0.5183	0.760 96	−0.348
0.0656	0.842 32	−0.073	0.6271	0.738 95	−0.339
0.0967	0.837 21	−0.105	0.7093	0.721 59	−0.307
0.1908	0.821 33	−0.193	0.8209	0.697 01	−0.226
0.2812	0.805 50	−0.260	0.9331	0.671 01	−0.100
0.3795	0.787 56	−0.312	0.9715	0.661 80	−0.046
		n-Hexane (1) + (*S*)-(−)-Limonene (2)			
0.0279	0.835 21	−0.040	0.5543	0.748 98	−0.452
0.0568	0.831 03	−0.080	0.6701	0.726 67	−0.420
0.1130	0.822 74	−0.154	0.7542	0.709 58	−0.363
0.2079	0.808 22	−0.263	0.8966	0.678 79	−0.189
0.2991	0.793 61	−0.345	0.9273	0.671 83	−0.140
0.4219	0.772 85	−0.420	0.9720	0.661 47	−0.057
		n-Hexane (1) + 1,8-Cineole (2)			
0.0339	0.913 23	−0.041	0.6205	0.773 08	−0.385
0.0677	0.906 26	−0.084	0.7181	0.745 07	−0.340
0.1616	0.886 29	−0.188	0.8281	0.711 63	−0.248
0.2491	0.866 79	−0.270	0.8953	0.690 11	−0.166
0.3454	0.844 26	−0.338	0.9363	0.676 54	−0.106
0.4734	0.812 47	−0.389			
		n-Hexane (1) + Linalool (2)			
0.0412	0.851 51	−0.020	0.6605	0.738 65	−0.023
0.1030	0.842 16	−0.055	0.7376	0.721 05	0.030
0.2546	0.817 60	−0.110	0.8069	0.704 42	0.086
0.3645	0.798 21	−0.109	0.8815	0.685 69	0.130
0.4938	0.773 61	−0.088	0.9366	0.671 44	0.121
0.5828	0.755 43	−0.057	0.9766	0.661 00	0.064

hexane at 298.15 K. Our results agree with those in the literature, showing a discrepancy with those in the literature of ±0.5% in the central range of mole fraction of benzene.[13]

Viscosity Measurements. The flow times of the pure components and their mixtures were measured using a viscosity measuring unit (Schott-Gerate AVS 310, Mains, Germany). Ubbelohde capillary viscometers (type 532, capillary No 0, 0c, 0a, I) were used with constants k = 0.001 063, 0.003 146, 0.004 993, and 0.009 937, respectively. Flow times ranged from (200 to 700) s. The viscometers were placed into a thermostat bath circulator (Lauda, type E 200, Germany) with fluctuations within ±0.005 K around the temperature set point. The uncertainty in the viscosity measurements was ±0.002 mPa·s. The viscometers were calibrated with distilled water,[9] and the average of six flow times for each liquid sample was used to compute viscosity.

Refractive Index Measurements. The refractive indices, n_D, at the sodium D-line were measured using an Abbe refractometer (Carl Zeiss, model G, Jena, Switzerland) with an error < 0.0001 units. Thermostated water was circulated into the prism of the refractometer with a circulating pump, connected to a constant-temperature bath. Calibration of the instruments was performed by measuring the n_D values of doubly distilled water, cyclohexane, and toluene, whose values are well-known from the literature.[9]

The sample mixtures were directly injected into the prism assembly of the instrument by means of an airtight syringe. An average of five measurements was taken for each sample mixture.

Results and Discussion

The experimental densities, ρ, dynamic viscosities, η, refractive indices, n_D, excess molar volumes, V_m^E, deviations in viscosities, $\Delta\eta$, and deviations in molar refractions, ΔR, of the binary mixtures at 298.15 K are reported in Tables 2 and 3. Values of V_m^E, $\Delta\eta$, and ΔR as a function of mole fraction x_1 of *n*-hexane are plotted in Figures 1−3.

The values of excess molar volumes, V_m^E, $\Delta\eta$, and ΔR were calculated using the following equations

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

$$\Delta\eta = \eta_m - \sum_{i=1}^{2}\eta_i x_i \qquad (2)$$

$$\Delta R = R_m - \sum_{i=1}^{2} R_i\varphi_i \qquad (3)$$

where x_i, M_i, and ρ_i (i = 1, 2) are the mole fractions,

Table 3. Dynamic Viscosities, η, Deviations in Viscosities, $\Delta\eta$, Refractive Indices, n_D, and Deviations in Refractive Indices, ΔR, of Binary Mixtures Containing *n*-Hexane + Components of Pine Resins and Essential Oils at 298.15 K

x_1	η/mPa·s	$\Delta\eta$/mPa·s	n_D	ΔR/cm^3·mol^{-1}
n-Hexane (1) + α-Pinene (2)				
0.0422	1.207	−0.044	1.4604	−0.105
0.06195	1.165	−0.067	1.4590	−0.142
0.1087	1.077	−0.108	1.4555	−0.236
0.2540	0.842	−0.198	1.4445	−0.442
0.3759	0.699	−0.219	1.4348	−0.535
0.5049	0.577	−0.212	1.4237	−0.571
0.6267	0.487	−0.181	1.4124	−0.541
0.7168	0.430	−0.147	1.4035	−0.475
0.8670	0.355	−0.073	1.3877	−0.263
0.9244	0.326	−0.044	1.3812	−0.156
0.9625	0.310	−0.023	1.3768	−0.071
n-Hexane (1) + *β*-Pinene (2)				
0.0421	1.455	−0.083	1.4728	−0.071
0.0626	1.392	−0.119	1.4711	−0.109
0.2031	1.055	−0.274	1.4592	−0.313
0.2799	0.914	−0.315	1.4523	−0.398
0.3765	0.772	−0.332	1.4432	−0.476
0.4939	0.634	−0.318	1.4316	−0.514
0.5597	0.570	−0.296	1.4248	−0.510
0.6601	0.488	−0.249	1.4140	−0.464
0.7454	0.427	−0.198	1.4042	−0.401
0.8217	0.381	−0.145	1.3952	−0.304
0.8935	0.344	−0.089	1.3864	−0.183
0.9595	0.312	−0.035	1.3776	−0.081
n-Hexane (1) + *p*-Cymene (2)				
0.0316	0.768	−0.014	1.4854	−0.055
0.0656	0.745	−0.020	1.4824	−0.107
0.0967	0.723	−0.026	1.4795	−0.159
0.1908	0.662	−0.040	1.4707	−0.278
0.2812	0.599	−0.057	1.4618	−0.366
0.3795	0.538	−0.069	1.4515	−0.438
0.5183	0.474	−0.063	1.4362	−0.466
0.6271	0.424	−0.059	1.4232	−0.446
0.7093	0.393	−0.049	1.4129	−0.395
0.8209	0.349	−0.036	1.3981	−0.283
0.9331	0.314	−0.014	1.3821	−0.125
0.9715	0.971	−0.038	1.3764	−0.056
n-Hexane (1) + (*S*)-(−)-Limonene (2)				
0.0279	0.825	−0.005	1.4684	−0.069
0.0568	0.806	−0.009	1.4663	−0.132
0.1130	0.759	−0.025	1.4620	−0.255
0.2079	0.686	−0.046	1.4545	−0.425
0.2991	0.622	−0.059	1.4468	−0.557
0.4219	0.549	−0.065	1.4357	−0.677
0.5543	0.477	−0.063	1.4230	−0.704
0.6701	0.421	−0.055	1.4113	−0.625
0.7542	0.386	−0.045	1.4022	−0.522
0.8966	0.334	−0.017	1.3856	−0.246
0.9273	0.326	−0.009	1.3817	−0.178
0.9720	0.305	−0.006	1.3759	−0.064
n-Hexane (1) + 1,8-Cineole (2)				
0.0339	2.317	−0.162	1.4526	−0.115
0.0677	2.110	−0.293	1.4504	−0.221
0.1616	1.642	−0.548	1.4444	−0.457
0.2491	1.325	−0.668	1.4386	−0.625
0.3454	1.063	−0.712	1.4319	−0.756
0.4734	0.800	−0.686	1.4221	−0.860
0.6205	0.593	−0.561	1.4097	−0.851
0.7181	0.491	−0.441	1.4006	−0.772
0.8281	0.400	−0.284	1.3898	−0.579
0.8953	0.359	−0.173	1.3830	−0.395
0.9363	0.330	−0.110	1.3787	−0.261
n-Hexane (1) + Linalool (2)				
0.0412	3.820	−0.392	1.4572	−0.189
0.1030	3.130	−0.830	1.4535	−0.436
0.2546	1.952	−1.388	1.4435	−0.932
0.3645	1.418	−1.474	1.4353	−1.184
0.4938	0.995	−1.369	1.4250	−1.316
0.5828	0.792	−1.208	1.4172	−1.312
0.6605	0.637	−1.046	1.4101	−1.222
0.7376	0.525	−0.843	1.4023	−1.079
0.8069	0.445	−0.640	1.3947	−0.897
0.8815	0.372	−0.408	1.3864	−0.600
0.9366	0.330	−0.224	1.3798	−0.348
0.9766	0.306	−0.085	1.3749	−0.139

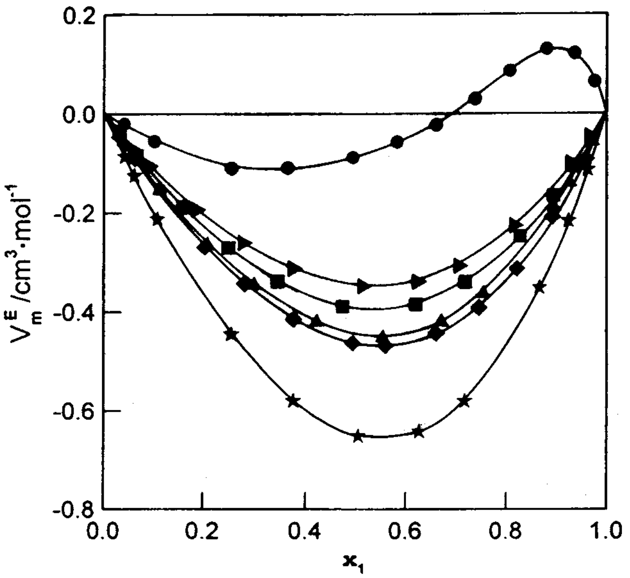

Figure 1. Excess molar volumes, V_m^E, vs the mole fraction, x_1, of *n*-hexane (1) + α-pinene (2) (★), + *β*-pinene (2) (◆), + *p*-cymene (2) (solid triangle pointing right), + (*S*)-(−)-limonene (2) (▲), + 1,8-cineole (2) (■), and + linalool (2) (●) at 298.15 K. The full lines are calculated with the Redlich−Kister equation.

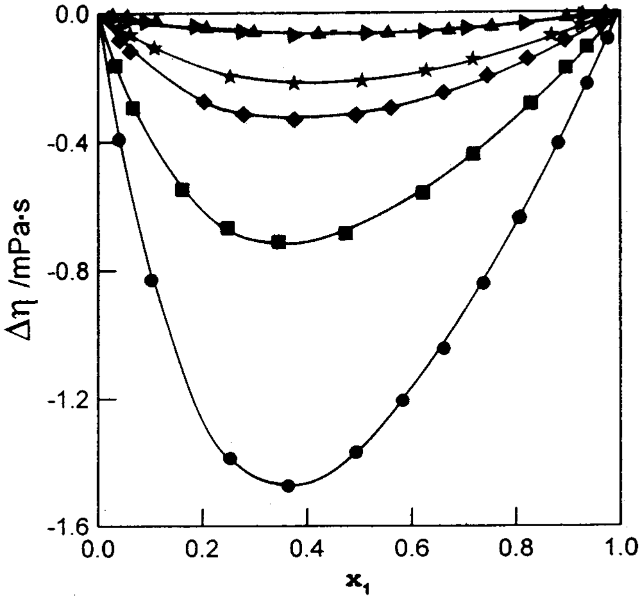

Figure 2. Deviation of viscosity, $\Delta\eta$, vs the mole fraction, x_1, of *n*-hexane (1) + α-pinene (2) (★), + *β*-pinene (2) (◆), + *p*-cymene (2) (solid triangle pointing right), + (*S*)-(−)-limonene (2) (▲), + 1,8-cineole (2) (■), and + linalool (2) (●) at 298.15 K. The full lines are calculated with the Redlich−Kister equation.

molecular weights, and densities of pure *n*-hexane and component 2, respectively.

η_i and η_m represent the viscosities of the *i*th pure component and of the mixture, respectively.

R_i and R_m, in the Lorentz−Lorenz eq 3, are the molar refractions of pure components and of the mixture, respectively, and φ_i is the volume fraction of component *i*, given as

$$\varphi_i = x_i V_i / \sum_{i=1}^{2} x_i V_i \tag{4}$$

where $V_i = M_i/\rho_i$.

Table 4. Least-Squares Parameters, a_k, Eq 7, and Standard Deviations, $\sigma(Q^E_m)$, of Binary Mixtures Containing *n*-Hexane + Components of Pine Resins and Essential Oils at 298.15 K

function	a_0	a_1	a_2	a_3	a_4	$\sigma(Q^E_m)$
			n-Hexane (1) + α-Pinene (2)			
V^E_m/cm^3·mol^{-1}	−2.6043	−0.5563	−0.0573			0.0011
$\Delta\eta$/mPa·s	−0.8615	0.3211				0.0025
ΔR/cm^3·mol^{-1}	−2.2949	−0.0981	−0.0884	0.3645		0.0040
			n-Hexane (1) + β-Pinene (2)			
V^E_m/cm^3·mol^{-1}	−1.8566	−0.3656	−0.0746	−0.0667		0.0013
$\Delta\eta$/mPa·s	−1.2637	0.5470	−0.2555	0.1074		0.0009
ΔR/cm^3·mol^{-1}						0.0045
			n-Hexane (1) + *p*-Cymene (2)			
V^E_m/cm^3·mol^{-1}	−1.3878	−0.2347				0.0009
$\Delta\eta$/mPa·s	−0.2631	0.0466				0.0029
ΔR/cm^3·mol^{-1}	−1.8724	−0.1081				0.0025
			n-Hexane (1) + (*S*)-(−)-Limonene (2)			
V^E_m/cm^3·mol^{-1}	−1.7849	−0.3340				0.0011
$\Delta\eta$/mPa·s	−0.2697	0.0376				0.0023
ΔR/cm^3·mol^{-1}	−2.8142	−0.2538	0.3693	0.2633		0.0031
			n-Hexane (1) + 1,8-Cineole (2)			
V^E_m/cm^3·mol^{-1}	−1.1089	−0.2586				0.0011
$\Delta\eta$/mPa·s	−2.6642	1.3319	−0.7456	0.4234		0.0024
ΔR/cm^3·mol^{-1}	−1.5715	−0.2586				0.0011
			n-Hexane (1) + Linalool (2)			
V^E_m/cm^3·mol^{-1}	−0.3381	0.4792	0.2025	1.2831	1.6006	0.0015
$\Delta\eta$/mPa·s	−5.4356	2.9343	−1.5844	0.4804		0.0032
ΔR/cm^3·mol^{-1}	−5.2697	−0.6742	−0.0116			0.0060

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

$$R_i = \{[n^2_{D(i)} - 1]/[n^2_{D(i)} + 2]\}V_i \tag{5}$$

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

The equation of the molar refraction R_m for the binary mixture is

$$R_m = \{[n^2_{D(m)} - 1]/[n^2_{D(m)} + 2]\}V_m \tag{6}$$

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

The variation of V^E_m, $\Delta\eta$, and ΔR, as a function of composition, is expressed by the Redlich−Kister equation

$$Q^E_m = x_1x_2\sum_{k\geq 0} a_k(x_1 - x_2)^k \tag{7}$$

where Q^E_m refers to V^E_m, $\Delta\eta$, and ΔR.

The adjustable parameters a_k were determined by fitting the experimental values to eq 7 with the least-squares method, and the results are given in Table 4. The tabulated standard deviations, $\sigma(Q^E_m)$, reported in Table 4 were defined as in previous papers.[5,6]

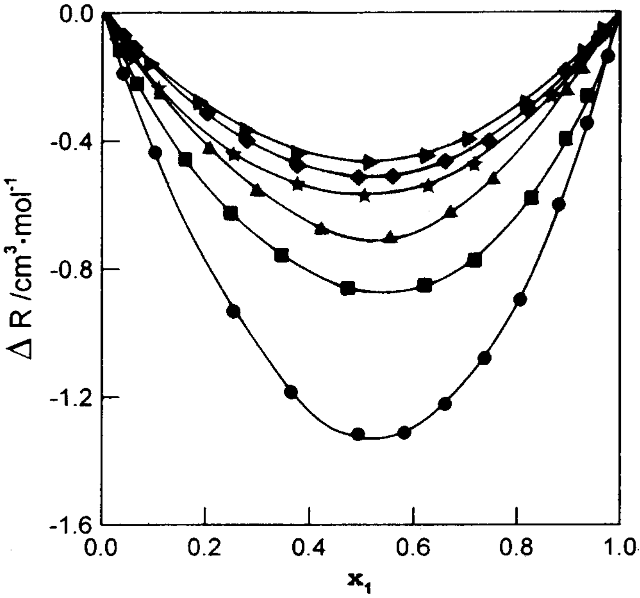

Figure 3. Deviation of refractive indices, ΔR, **vs** the mole fraction, x_1, of *n*-hexane (1) + α-pinene (2) (★), + β-pinene (2) (◆), + *p*-cymene (2) (solid triangle pointing right), + (*S*)-(−)-limonene (2) (▲), + 1,8-cineole (2) (■), and + linalool (2) (●) at 298.15 K. The full lines are calculated with the Redlich−Kister equation.

McAllister's multibody interaction model,[17] widely used to correlate the kinematic viscosity ν of liquid mixtures with mole fraction, was applied to our data. We used the three-body model defined as

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln \nu_{12} + 3x_1x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln(x_1 + x_2M_2/M_1) + 3x_1^2x_2 \ln[(2 + M_2/M_1)/3] + 3x_1x_2^2 \ln[(1 + 2M_2/M_1)/3] + x_2^3 \ln(M_2/M_1) \tag{8}$$

and the four-body model given by

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3x_2 \ln \nu_{1112} + 6x_1^2x_2^2 \ln \nu_{1122} + 4x_1x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln(x_1 + x_2M_2/M_1) + 4x_1^3x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^2x_2^2 \ln[(1 + M_2/M_1)/2] + 4x_1x_2^3 \ln[(1 + 3M_2/M_1)/4] + x_2^4 \ln(M_2/M_1) \tag{9}$$

where ν_{12}, ν_{21}, ν_{1112}, ν_{1122}, and ν_{2221} are the model param-

Table 5. Coefficients of McAllister's Models and Standard Deviations for Kinematic Viscosities

three-body model			four-body model			
ν_{12}	ν_{21}	$\sigma/(\times 10^{-6}$ m^2 s$^{-1})$	ν_{1112}	ν_{1122}	ν_{2221}	$\sigma/(\times 10^{-6}$ m^2 s$^{-1})$
			n-Hexane (1) + α-Pinene (2)			
0.636	0.905	0.002	0.578	0.761	1.213	0.002
			n-Hexane (1) + β-Pinene (2)			
0.6474	0.9640	0.0005	0.5844	0.8016	1.3555	0.0003
			n-Hexane (1) + *p*-Cymene (2)			
0.570	0.690	0.002	0.529	0.639	0.892	0.002
			n-Hexane (1) + (*S*)-(−)-Limonene (2)			
0.592	0.767	0.002	0.569	0.633	1.023	0.001
			n-Hexane (1) + 1,8-Cineole (2)			
0.702	1.172	0.003	0.626	0.903	1.721	0.003
			n-Hexane (1) + Linalool (2)			
0.778	1.851	0.003	0.644	1.312	2.665	0.002

eters. Table 5 records the calculated results, showing that practically the two models are equivalent.

The values of V_m^E, $\Delta\eta$, and ΔR represented in Figures 1−3 are all negative, with the exception of the excess volumes of the mixture *n*-hexane (1) + linalool (2), showing a sign inversion at about $x_1 = 0.7$. These trends agree with the results obtained with the mixtures of MTBE with the same pine resins and essential oils,[8] whereas previous measurements on the mixtures of dialkyl carbonates or cyclic diethers (1,3-dioxolane, 1,4-dioxane) with the same pine resins[6] lead to values of V_m^E that are always positive.

Since *n*-hexane may be conceived to have small interactions with molecules of pine resins and essential oils, in comparison with those of mono- and diethers, the relatively large negative values of all measured physical quantities seem to indicate the prevailing of packaging among small molecules of *n*-hexane and the large molecules of the second component.

According to this model, however, it is quite difficult to explain the differences between the behaviors of the different mixtures, where the shape and dimensions of molecules show a wide range of variations.

Acknowledgment

The authors thank Mr. Gianni Bragaglia (I.Co.C.E.A−CNR−Bologna) for his valuable technical assistance with the measurements.

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Received for review August 1, 2001. Accepted November 6, 2001.

JE010216W