Densities, Viscosities, Refractive Indices, and Surface Tensions of 4-Methyl-2-Pentanone + Ethyl Benzoate Mixtures at (283.15, 293.15, and 303.15) K

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Densities (ρ), viscosities (η), refractive indices (n_D), and surface tensions (σ), for 4-methyl-2-pentanone + ethyl benzoate mixtures, have been measured over the whole composition range at (283.15, 293.15, and 303.15) K. The excess volumes (V^E), the viscosity deviations ($\Delta\eta$), and the excess refraction (ΔR) were calculated and show negative values. The results were fitted to a Redlich−Kister type polynomial relation, and the corresponding parameters have been derived. The results are discussed in terms of molecular interactions.

Introduction

4-Methyl-2-pentanone is a common aprotic solvent having relative dielectric constant $\epsilon = 13.11$ and dipole moment $\mu = 2.69$ D at 298.15 K.[1] 4-Methyl-2-pentanone is used in the industry of paints, varnishes, and printing inks. Esters, fairly hydrophobic solvents, are very good solvents for polymers. Ethyl benzoate is a polar solvent important from a technical viewpoint used in a variety of engineering applications, having relative dielectric constant $\epsilon = 6.02$[2] and dipole moment $\mu = 2.00$ D at 293.15 K.[3]

Thermodynamic properties of binary systems containing 4-methyl-2-pentanone or ethyl benzoate have been reported in the literature.[4−7]

A survey of the literature showed that 4-methyl-2-pentanone + ethyl benzoate mixtures have not been studied.

The program in our laboratory concerns the study of thermodynamic properties of binary organic solutions.[8,9] Here we report the experimental densities, viscosities, refractive indices, and surface tensions of the binary mixtures of 4-methyl-2-pentanone + ethyl benzoate at (283.15, 293.15, and 303.15) K. For this system no data have been previously published. The excess volumes, viscosity deviations, and excess refractions have been derived.

Experimental Section

Materials. The reagents 4-methyl-2-pentanone (Merck p.a. > 99.0%) and ethyl benzoate (Fluka > 99.0%) were used without purification. The purity of the liquids was assessed by comparing the experimental densities and refractive indices with the literature values (Table 1). The agreement was satisfactory.

The binary mixtures were prepared by mass (Mettler A210P, ±0.01 mg). The possible uncertainty in the mole fractions is estimated to be ±0.0001.

Measurements. A digital densimeter (Anton Paar, model DMA 58) was used for the determination of the densities of the pure components and the binary mixtures.

Table 1. Comparison of Experimental Densities (ρ) and Refractive Indices (n_D) of Pure Liquids with Literature Values at 298.15 K

component	ρ(exp) g·cm^{-3}	ρ(ref) g·cm^{-3}	n_D(exp)	n_D(ref)
4-methyl-2-pentanone	0.796 60	0.796 09[a] 0.796 30[b]	1.3941	1.3936[b]
ethyl benzoate	1.041 56	1.042 5[c] 1.042 1[d]	1.5032	1.5027[c] 1.5046[d]

[a] Reference 5. [b] Reference 4. [c] Reference 6. [d] Reference 7.

The sample thermostat was controlled to ±0.01 K. The estimated uncertainty of the measured densities is ±0.00001 g·cm^{-3}.

Flow times of the solvent mixtures were measured with a viscosity-measuring unit (Schott Geräte AVS 310), equipped with an Ubbelohde capillary viscometer. The temperature was maintained constant within ±0.03 K. The accuracy in the viscosity measurements was ±0.001 mPa·s.

The refractive indices at the sodium D-line were measured with a thermostated Abbe refractometer (model A. Krüss) with an error < 0.0001 unit. The thermostat temperature was constant to ±0.01 K. The detailed measuring procedures for density, viscosity, and refractive index have been described in previous papers.[8,9]

Surface tensions were measured by detachment of a platinum ring using a temperature-controlled (±0.2 K) surface tensiometer (Krüss, Model K8600). The ring was washed successively with dilute HCl and water. The tensiometer was calibrated with distilled water, and a correction factor was employed. The accuracy of the surface tension measurement was ±0.1 mN·m^{-1}.

Results and Discussion

The experimental values of density, viscosity, and refractive index at (283.15, 293.15, and 303.15) K are given in Table 2. The values of excess molar volumes, V^E, and viscosity deviations, $\Delta\eta$, were calculated from the experi-

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Table 2. Experimental Densities (ρ), Viscosities (η), and Refractive Indices (n_D) of 4-Methyl-2-pentanone (1) + Ethyl Benzoate (2) Mixtures

x_1	ρ / g·cm^{-3}	η / mPa·s	n_D	x_1	ρ / g·cm^{-3}	η / mPa·s	n_D
			$T = 283.15$ K				
1.0000	0.810 41	0.675	1.4004	0.5355	0.951 10	1.299	1.4618
0.9549	0.829 76	0.748	1.4059	0.4004	0.982 06	1.519	1.4776
0.9154	0.845 74	0.791	1.4101	0.3364	0.995 12	1.642	1.4829
0.8805	0.856 07	0.829	1.4136	0.2022	1.020 46	1.929	1.4941
0.7942	0.883 39	0.931	1.4222	0.1491	1.032 47	2.053	1.4996
0.7165	0.906 00	1.040	1.4344	0.0752	1.043 07	2.350	1.5041
0.6213	0.930 02	1.162	1.4500	0.0000	1.055 65	2.799	1.5097
			$T = 293.15$ K				
1.0000	0.801 18	0.586	1.3976	0.5355	0.942 30	1.109	1.4578
0.9549	0.820 52	0.648	1.4030	0.4004	0.972 83	1.277	1.4738
0.9154	0.836 63	0.686	1.4070	0.3364	0.986 15	1.375	1.4792
0.8805	0.846 99	0.719	1.4110	0.2022	1.011 24	1.580	1.4900
0.7942	0.875 03	0.797	1.4195	0.1491	1.023 18	1.675	1.4953
0.7165	0.897 00	0.880	1.4308	0.0752	1.033 74	1.890	1.5000
0.6213	0.921 00	0.988	1.4466	0.0000	1.046 22	2.210	1.5056
			$T = 303.15$ K				
1.0000	0.791 93	0.520	1.3918	0.5355	0.932 30	0.940	1.4534
0.9549	0.811 23	0.569	1.3975	0.4004	0.963 75	1.079	1.4689
0.9154	0.827 25	0.599	1.4017	0.3364	0.976 79	1.150	1.4750
0.8805	0.837 61	0.625	1.4057	0.2022	1.001 92	1.303	1.4858
0.7942	0.865 93	0.690	1.4142	0.1491	1.013 90	1.376	1.4912
0.7165	0.888 20	0.757	1.4260	0.0752	1.024 40	1.550	1.4956
0.6213	0.912 20	0.850	1.4420	0.0000	1.036 85	1.811	1.5012

mental data according to the following equations

$$V^{\mathrm{E}} = V_{\mathrm{m}} - \sum_{i=1}^{2} V_i x_i \tag{1}$$

$$\Delta\eta = \eta_{\mathrm{m}} - \sum_{i=1}^{2} \eta_i x_i \tag{2}$$

where x_i, V_i, and η_i represent the mole fraction, molar volume, and viscosity of the ith pure component of the mixture. V_{m} and η_{m} are the molar volume and viscosity of the mixture, respectively. The molar volume, V_{m}, of the mixture was calculated from the following equation

$$V_{\mathrm{m}} = \sum_{i=1}^{2} x_i \mathrm{M}_i / \rho_{\mathrm{m}} \tag{3}$$

where ρ_{m} is the mixture density and M_i is the molecular weight of component i in the mixture. The accuracies of the excess molar volumes and viscosity deviations are estimated to be ± 0.0001 cm^3·mol^{-1} and ± 0.001 mPa·s, respectively.

The molar refraction deviations ΔR were calculated from the Lorentz−Lorenz[10] equation

$$\Delta R = R_{\mathrm{m}} - \sum_{i=1}^{2} R_i \varphi_i \tag{4}$$

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

$$\varphi_i = x_i V_i / \sum_{i=1}^{2} x_i V_i \tag{5}$$

The molar refraction R_i was obtained from the Lorentz−Lorenz equation

$$R_i = \frac{{n_{D(i)}}^2 - 1}{{n_{D(i)}}^2 + 2} V_i \tag{6}$$

where $n_{D(i)}$ is the refractive index for the pure components. The equation for a binary mixture becomes

$$R_{\mathrm{m}} = \frac{{n_{D(\mathrm{m})}}^2 - 1}{{n_{D(\mathrm{m})}}^2 + 2} V_{\mathrm{m}} \tag{7}$$

where $n_{D(\mathrm{m})}$ is the refractive index of the mixture and R_{m} is the molar refraction of the mixture. The molar refraction and molar refraction deviation were calculated with an accuracy of ± 0.0001 cm^3·mol^{-1}.

The experimental values of V^{E}, $\Delta\eta$, and ΔR are fitted to the Redlich−Kister[11] equation

$$Y = x_1 x_2 \sum_{k=0}^{m} \mathrm{A}_k (2x_1 - 1)^k \tag{8}$$

where Y represents the excess volume, the viscosity deviations, or the excess refraction, and A_k represents the parameters.

The standard errors, d, between the calculated and the experimental values have been estimated by using

$$d = \left[\frac{\sum (Y_{\mathrm{exp}} - Y_{\mathrm{cal}})^2}{(n - p)} \right]^{1/2} \tag{9}$$

Table 3. Parameters and Standard Deviations of Excess Functions of 4-Methyl-2-pentanone (1) + Ethyl Benzoate (2) Mixtures

function	A_0	A_1	A_2	A_3	d
		$T = 283.15$ K			
V^{E}/cm^3·mol^{-1}	−9.7500	−3.6469	−6.2293	−5.6681	0.1299
$\Delta\eta$/mPa·s	−1.5083	0.9413	−1.2804	1.4321	0.0096
ΔR/cm^3·mol^{-1}	−2.6054	−3.8225	−3.3535	1.5624	0.0617
		$T = 293.15$ K			
V^{E}/cm^3·mol^{-1}	−10.2362	−4.0411	−6.5491	−5.5857	0.1257
$\Delta\eta$/mPa·s	−0.9910	0.5425	−0.9343	1.2316	0.0055
ΔR/cm^3·mol^{-1}	−2.7081	−3.8656	−3.3153	1.7927	0.0613
		$T = 303.15$ K			
V^{E}/cm^3·mol^{-1}	−10.7169	−4.6850	−6.4337	−4.6605	0.1303
$\Delta\eta$/mPa·s	−0.7510	0.4445	−0.8805	1.0531	0.0034
ΔR/cm^3·mol^{-1}	−2.6054	−3.9657	−3.1320	1.8990	0.0657

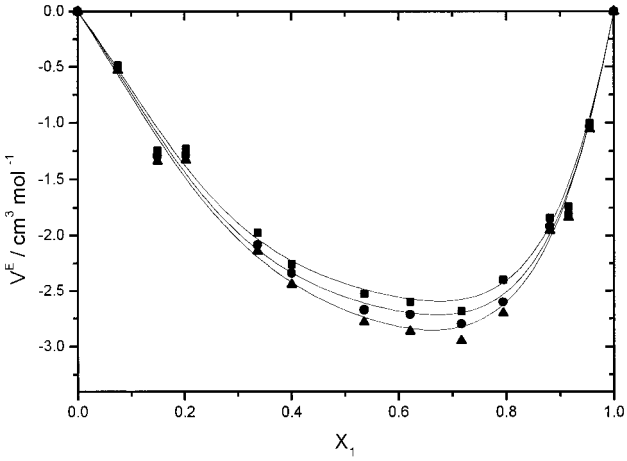

Figure 1. Excess molar volumes for 4 methyl-2-pentanone (1) + ethyl benzoate (2) mixtures at 283.15 K (■), 293.15 K (●), and 303.15 K (▲).

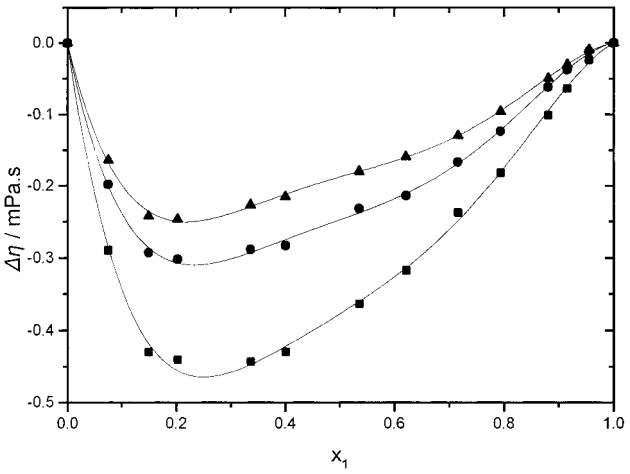

Figure 2. Viscosity deviations of 4-methyl-2-pentanone (1) + ethyl benzoate (2) mixtures at 283.15 K (■), 293.15 K (●), and 303.15 K (▲).

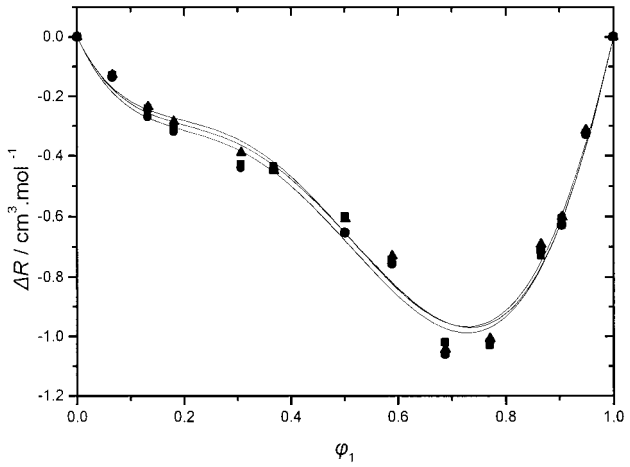

Figure 3. Molar refraction deviations versus the volume fraction for 4-methyl-2-pentanone (1) + ethyl benzoate (2) mixtures at 283.15 K (■), 293.15 K (●), and 303.15 K (▲).

where n is the number of experimental points and p is the number of estimated parameters. The values of A_k and d are presented in Table 3. The excess volumes and viscosity deviations are shown in Figures 1 and 2, respectively. The symbols represent the experimental values, and the lines, the curve-fitting procedure according to the Redlich−Kister equation.

The V^E values are negative for all mixtures, indicating interactions between unlike molecules. V^E becomes more negative with the temperature increase, and the minima are observed at the high mole fraction of 4-methyl-2-pentanone.

The $\Delta\eta$ values are also negative and increase with increasing temperature. The variation of $\Delta\eta$ with the strength of interaction is reverse to that of V^E, being less negative as the strength of interaction between unlike molecules increases.[12,13]

The molar refraction deviations are shown in Figure 3. The ΔR values are negative over the whole composition range for all mixtures. The values are independent of temperature, as predicted by the theory that the molar refraction depends only on the wavelength of the light used for measurement.[14,15]

As shown in Figure 4, the temperature coefficient for V^E is negative, that for $\Delta\eta$ is positive, and that for ΔR is close to zero.

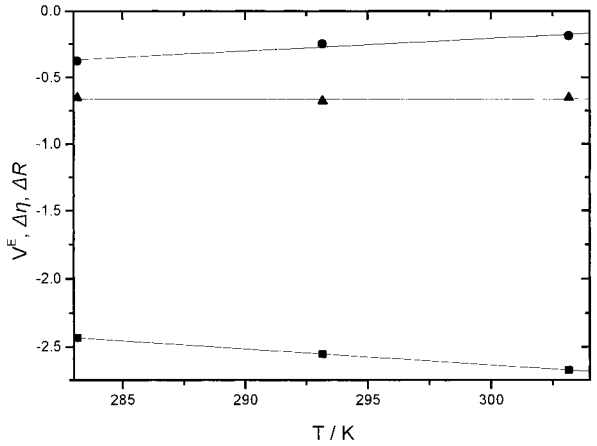

Figure 4. Temperature dependence of the equimolar excess volumes (■), viscosity deviation (●), and excess refraction (▲) for 4-methyl-2-pentanone (1) + ethyl benzoate (2) mixtures.

Table 4. Surface Tension (σ) of 4-Methyl-2-pentanone (1) + Ethyl Benzoate (2) Mixtures

	σ/mN·m^{-1}						
T/K	x_1 = 1.0000	x_1 = 0.9549	x_1 = 0.9154	x_1 = 0.8805	x_1 = 0.7942	x_1 = 0.7165	x_1 = 0.6213
283.15	24.6	26.3	26.8	27.4	28.2	29.1	30.1
293.15	23.6	25.1	25.6	26.1	27.0	27.8	28.8
303.15	22.6	23.9	24.3	24.7	25.7	26.5	27.5
	σ/mN·m^{-1}						
T/K	x_1 = 0.5355	x_1 = 0.4004	x_1 = 0.3364	x_1 = 0.2022	x_1 = 0.1491	x_1 = 0.0752	x_1 = 0.0000
283.15	31.0	32.1	32.6	33.7	34.3	35.3	36.1
293.15	29.7	31.1	31.7	32.7	33.4	34.2	35.0
303.15	28.3	29.6	30.3	31.7	32.3	33.2	34.0

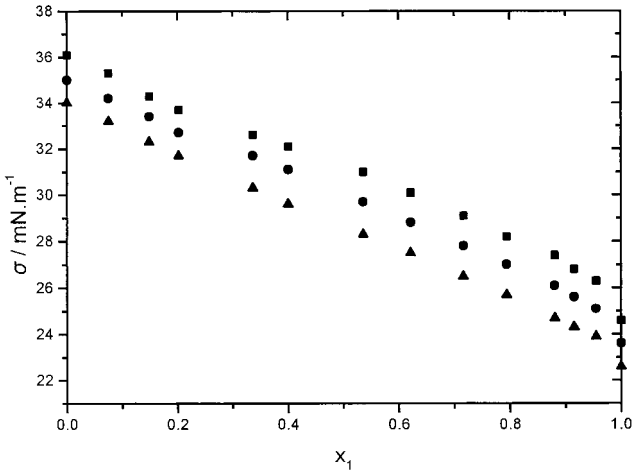

Figure 5. Surface tension of 4-methyl-2-pentanone (1) + ethyl benzoate (2) mixtures at 283.15 K (■), 293.15 K (●), and 303.15 K (▲).

The surface tensions (σ) of binary mixtures of 4-methyl-2-pentanone + ethyl benzoate are tabulated in Table 4 and are shown versus the mole fraction of 4-methyl-2-pentanone in Figure 5.

In the systems studied, surface tension decreased with increasing temperature for any given mole fraction of 4-methyl-2-pentanone.

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