Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Methyl Acetate + Ethylene Glycol or + Poly(ethylene glycol) in the Temperature Interval (298.15−308.15) K

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Experimental results of density, viscosity, and refractive index at 298.15, 303.15, and 308.15 K and speed of sound at 298.15 K in the binary mixtures of methyl acetate + ethylene glycol or + poly(ethylene glycol) are presented over the whole range of mixture composition. From these data, excess molar volume, V^E, deviations in viscosity, $\Delta\eta$, molar refractivity, ΔR, speed of sound, Δu, and isentropic compressibility, Δk_S, have been calculated. These quantities have been fitted to the Redlich−Kister type equation to derive the binary coefficients and standard errors.

Introduction

Physical properties of binary organic mixtures have been extensively studied in the literature of solution chemistry in view of the importance of such data in many areas of science and engineering. During our studies on drug−solvent interactions, we decided to investigate the physical properties of the binary mixtures comprising ethylene glycol (EG) and poly(ethylene glycol) (PEG-400) with esters. Unfortunately, EG is not soluble in any of the higher esters except methyl acetate (MA). With this view in mind, we decided to study the physical property data like density, ρ, viscosity, η, refractive index, n_D, for sodium D-line, and speed of sound, u, in the binary mixtures of EG or PEG with MA. The results of ρ, η, and n_D are measured at 298.15, 303.15, and 308.15 K, while those of u are measured only at 298.15 K. From these data, excess molar volume, V^E, deviations in viscosity, $\Delta\eta$, Lorenz-Lorentz molar refractivity, ΔR, speed of sound, Δu, and isentropic compressibility, Δk_S have been calculated. These are fitted to the Redlich−Kister type equation to derive the binary coefficients and standard errors.

Experimental Section

Materials. Synthesis grade samples of poly(ethylene glycol) (PEG-400) and ethylene glycol and spectroscopic grade samples of methyl acetate were procured from s.d. fine chemicals Ltd., Mumbai, India. All the samples were used without further purification as their purities exceeded 99% as tested by gas chromatography (HP 6890 Series) using a flame ionization detector with a packed column. Experimental values of ρ and n_D of the pure liquids along with their mol % purities at 298.15 K are given in Table 1. Mixtures were prepared by mass in glass stoppered bottles and used on the same day. An electronic Mettler balance (model AE 240, Switzerland) with a precision of ±0.01 mg was used. The error in mole fraction is around ±0.0002.

Measurements. Densities of liquids and their mixtures were measured using a pycnometer having a bulb volume of 15 cm^3 and a capillary bore with an internal diameter of 1 mm. Density values are accurate to ±0.0002 g·cm^{-3}.

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

liquid (mol % purity)	ρ/g.cm^{-3}		n_D	
	exptl	lit.	exptl	lit.
methyl acetate (99.4)	0.9282	0.9279[a]	1.3606	1.3589[a] 1.3606[b]
ethylene glycol	1.1061	1.1054[c]	1.4292	1.4318[d]
poly(ethylene glycol)	1.1218	1.1254[e]	1.4632	1.4650[e]

[a] Riddick et al. (1986). [b] Aminabhavi and Banerjee (1998). [c] Reddy et al. (1993). [d] Riddick et al. (1986) compared at 293.15 K. [e] *Handbook of Pharmaceutical Excipients* (1986).

Refractive indices for the sodium D-line were measured using a thermostatically controlled Abbe Refractometer (Atago 3T, made in Japan). A minimum of three independent readings were taken for each composition. The refractive index values are accurate to ±0.0002 units. Calibration procedures of the pycnometer and refractometer are the same as given earlier (Aminabhavi and Bindu, 1994, 1995; Aralaguppi et al., 1991).

Viscosities were measured using a Schott-Gerate Viscometer (model AVS 350, Germany). The unit performs automated measurements of the flow-through times in capillary viscometers. Efflux times were determined on a digital display at an accuracy of 0.01 s. An AVS/S measuring stand was used for optoelectronic sensing of the meniscus. The LED in the upper part of the measuring stand generates light in the near-infrared range, which is transmitted through a glass fiber cable to the measuring levels. The light beam passes through the viscometer and reaches the input end of another light guide cable on the other side, which conducts light to a receiver in the upper part of the measuring stand. When the liquid meniscus passes through the measuring level, the light beam is darkened briefly by the optical lens effect of the meniscus and thereafter intensified for a brief period. This fluctuation of light beam produces a measuring signal that can be evaluated precisely.

The temperature of the bath (Schott Gerate, model CT 050/2, Germany) was maintained constant within ±0.01 K. The estimated error in viscosity measurement was ±0.001 mPa.s. A volume of approximately 5 cm^3 of the

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Table 2. Experimental Values of Density (ρ), Refractive Index (n_D), Viscosity (η), and Speed of Sound (u) of the Binary Mixtures at Different Temperatures

x_1	ρ/(g·cm^{-3})	n_D	η/(mPa·s)	u/(m·s^{-1})
		Ethylene Glycol (1) + Methyl Acetate (2)		
		298.15 K		
0.0000	0.9282	1.3606	0.391	1161
0.1014	0.9435	1.3680	0.543	1208
0.1953	0.9580	1.3748	0.645	1242
0.2981	0.9750	1.3820	0.829	1270
0.3974	0.9910	1.3890	1.791	1295
0.5029	1.0090	1.3960	1.850	1334
0.5992	1.0266	1.4030	2.329	1370
0.6997	1.0457	1.4100	3.499	1420
0.7990	1.0653	1.4165	5.578	1480
0.9639	1.1000	1.4270	9.086	1610
1.0000	1.1061	1.4292	15.312	1664
		303.15 K		
0.0000	0.9218	1.3582	0.372	
0.1014	0.9370	1.3653	0.507	
0.1953	0.9515	1.3710	0.599	
0.2981	0.9686	1.3790	0.756	
0.3974	0.9850	1.3860	1.008	
0.5029	1.0034	1.3935	1.633	
0.5992	1.0210	1.4008	2.026	
0.6997	1.0406	1.4080	3.025	
0.7990	1.0605	1.4150	4.658	
0.9639	1.0950	1.4250	7.673	
1.0000	1.1026	1.4282	12.242	
		308.15 K		
0.0000	0.9152	1.3550	0.355	
0.1014	0.9301	1.3620	0.473	
0.1953	0.9450	1.3683	0.561	
0.2981	0.9620	1.3760	0.701	
0.3974	0.9786	1.3831	0.921	
0.5029	0.9972	1.3905	1.439	
0.5992	1.0149	1.3970	1.781	
0.6997	1.0351	1.4048	2.643	
0.7990	1.0560	1.4120	3.989	
0.9639	1.0901	1.4221	6.317	
1.0000	1.0991	1.4274	9.945	
		PEG 400 (1) + Methyl Acetate (2)		
		298.15 K		
0.0000	0.9282	1.3606	0.391	1161
0.0965	0.9996	1.3979	1.678	1250
0.1960	1.0383	1.4188	4.638	1320
0.2957	1.0632	1.4465	9.054	1386
0.3981	1.0796	1.4422	15.374	1470
0.4979	1.0915	1.4524	23.719	1520
0.5938	1.1004	1.4540	32.391	1560
0.6972	1.1079	1.4578	42.181	1580
0.7977	1.1130	1.4609	54.524	1585
0.9068	1.1182	1.4638	67.089	1585
1.0000	1.1218	1.4632	78.815	1200
		303.15 K		
0.0000	0.9218	1.3592	0.372	
0.0965	0.9942	1.3955	1.521	
0.1960	1.0338	1.4173	4.045	
0.2957	1.0585	1.4352	7.703	
0.3981	1.0746	1.4406	12.873	
0.4979	1.0870	1.4494	19.288	
0.5938	1.0962	1.4522	26.195	
0.6972	1.1038	1.4562	33.630	
0.7977	1.1087	1.4596	43.307	
0.9068	1.1139	1.4621	52.356	
1.0000	1.1178	1.4598	60.683	
		308.15 K		
0.0000	0.9152	1.3550	0.355	
0.0965	0.9870	1.3942	1.393	
0.1960	1.0271	1.4153	3.577	
0.2957	1.0525	1.4306	6.675	
0.3981	1.0689	1.4390	10.891	
0.4979	1.0820	1.4462	16.020	
0.5938	1.0907	1.4503	21.520	
0.6972	1.0977	1.4546	27.120	
0.7977	1.1036	1.4576	34.503	
0.9068	1.1090	1.4603	41.239	
1.0000	1.1138	1.4274	50.450	

Table 3. Estimated Parameters of Excess Functions for Mixtures

function	temp/K	A_0	A_1	A_2	σ
		Ethylene Glycol (1) + Methyl Acetate (2)			
$V^E/10^{-6}$(m^3·mol^{-1})	298.15	−1.879	0.167	−0.734	0.031
	303.15	−1.823	0.154	−0.269	0.014
	308.15	−1.657	0.172	−0.135	0.032
$\Delta\eta$/(mPa·s)	298.15	−22.59	24.96	−28.78	1.427
	303.15	−18.35	18.11	−19.26	1.029
	308.15	−14.55	13.92	−14.70	0.828
$\Delta R/10^{-6}$(m^3·mol^{-1})	298.15	−0.478	−0.108	−0.062	0.009
	303.15	−0.520	0.064	−0.312	0.014
	308.15	−0.631	−0.242	−0.450	0.020
Δu/(m·s^{-1})	298.15	−321.2	333.1	−19.7	6.21
Δk_S/(TPa^{-1})	298.15	−151.1	190.5	−226.3	5.42
		PEG 400 (1) + Methyl Acetate (2)			
$V^E/10^{-6}$(m^3·mol^{-1})	298.15	−4.343	−3.833	−2.930	0.086
	303.15	−4.388	−4.259	−3.205	0.124
	308.15	−3.757	−5.316	−0.845	0.104
$\Delta\eta$/(mPa·s)	298.15	−64.11	−13.68	3.49	0.367
	303.15	−45.06	−14.18	4.62	0.339
	308.15	−36.94	−2.24	−12.27	0.511
$\Delta R/10^{-6}$ (m^3·mol^{-1})	298.15	−97.57	−63.71	−78.95	0.670
	303.15	−98.31	−65.18	−69.92	0.457
	308.15	−91.85	−56.20	−0.09	1.873
Δu/(m·s^{-1})	298.15	1287	−1351	1611	50.5
Δk_S/(TPa^{-1})	298.15	−335	−529	−3543	91.3

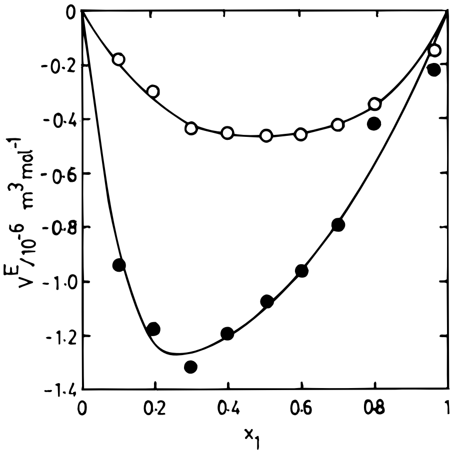

Figure 1. Plots of V^E vs x_1 at 298.15 K for mixtures of ethylene glycol + methyl acetate (○) and poly(ethylene glycol) + methyl acetate (●).

liquid was taken in the viscometer, and it was allowed to equilibrate to the desired bath temperature for about 7 to 10 min. The viscosity of the liquids and their mixtures was then calculated as $\eta = t\cdot k\cdot \rho$, where k is the viscometer constant (0.01035 mm^2/s^2), ρ is the density of the liquid, and t is efflux time in seconds. The viscometer constant, k, was determined by using comparative measurements with reference viscometers, of which the constants were determined from the Physikalisch-Technischen Bundesanstalt, D-38116 Braunschweig. The value of k is valid for liquids with a surface tension of 20 to 30 mN/m and an acceleration of the fall of 9.8125 m/s^2. For temperatures up to 100 °C, it is not required to pay attention to the heat expansion of the viscometer.

The speed of sound values were measured using a variable-path single-crystal interferometer (Mittal Enterprises, model M-84, New Delhi) as described earlier by Aralaguppi et al. (1991). The interferometer was used at a frequency of 4 kHz and was calibrated using water and benzene. The speed of sound values are accurate to ±2 m·s^{-1}. From the speed of sound data, the values of isentropic compressibilities, k_S in TPa^{-1} units, have been calculated as $k_S = 1/u^2\rho$.

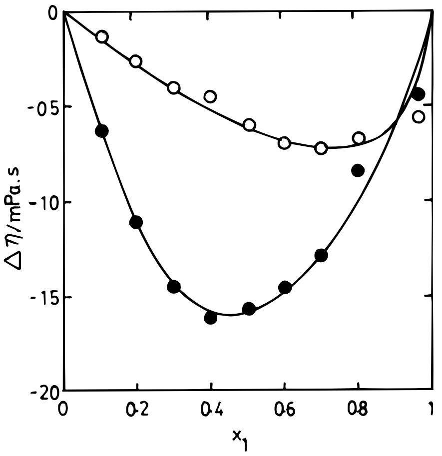

Figure 2. Plots of $\Delta\eta$ vs x_1 at 298.15 K for the binary mixtures given in Figure 1.

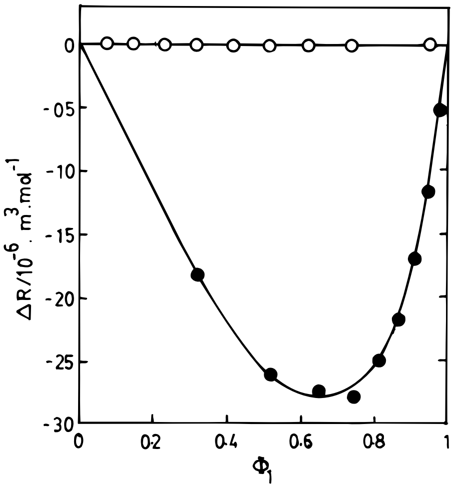

Figure 3. Plots of ΔR vs ϕ_1 at 298.15 K for the binary mixtures given in Figure 1.

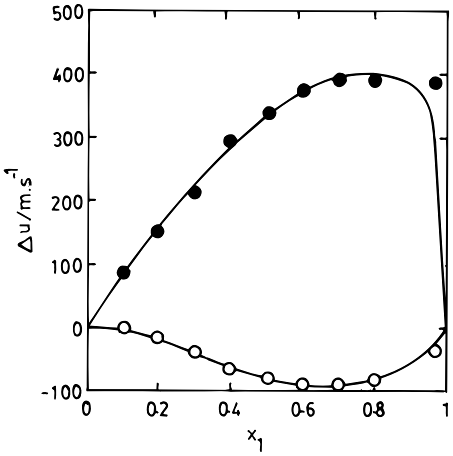

Figure 4. Plots of Δu vs x_1 at 298.15 K for the binary mixtures given in Figure 1.

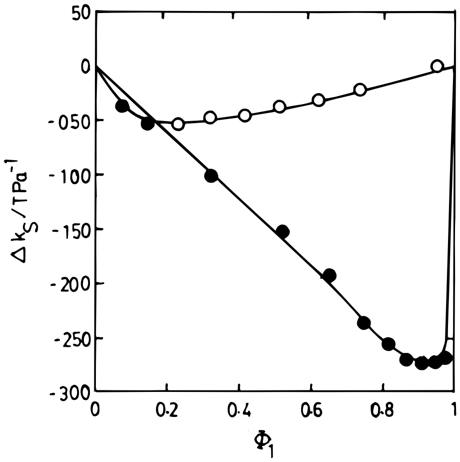

Figure 5. Plots of Δk_S vs ϕ_1 at 298.15 K for the binary mixtures given in Figure 1.

In all the property measurements (except viscosity), an INSREF, model 016 AP thermostat was used at a constant digital temperature display accurate to ±0.01 K. The results of ρ, η, n_D, and u compiled in Table 2 represent the average of three independent measurements for each composition of the mixture.

The Julabo immersion cooler (FT 200), Julabo Labortechnik Gmbh, Germany, was employed to cool the temperature of the bath. This unit is installed at the intake of a heating circulator to draw the heat away from the circulating bath liquid. The immersion probe is connected to the instrument with a flexible and insulated tube. To prevent the immersion probe from icing, it should be completely immersed into the bath liquid.

Results and Discussion

Experimental values of density are used to calculate V^E of the mixtures as

$$V^E/(\mathrm{m^3 mol^{-1}}) = \frac{M_1x_1 + M_2x_2}{\rho_m} - \frac{M_1x_1}{\rho_1} - \frac{M_2x_2}{\rho_2} \qquad (1)$$

where M_1 and M_2 are the molecular weights of components 1 and 2, ρ_1 and ρ_2 are the densities, and x_1, x_2 are the mole fractions of the respective components. The symbol ρ_m stands for mixture density. The deviations in viscosity, refractivity, speed of sound, and isentropic compressibility have been calculated as

$$\Delta Y = Y_m - Y_1x_1 - Y_2x_2 \qquad (2)$$

where ΔY (=$\Delta\eta$, ΔR, Δu, and Δk_S), Y_1, and Y_2 refer to the respective pure component properties, viz., η, R, u, and k_S. To compute R, the Lorentz–Lorenz equation is used. Also, while computing ΔR and Δk_S, we have used the volume fraction, ϕ_i (=$(x_iV_i)/\sum_i x_iV_i$) (where V_i is molar volume of the ith component), instead of mole fraction, x_i. Each of the above excess functions have been fitted to the Redlich–Kister (1948) type equation

$$V^E \text{ (or } \Delta Y) = x_1x_2\sum_{j=0}^{k} A_j\,(x_2 - x_1)^{j-1} \qquad (3)$$

to derive the coefficients A_i (i.e., $A_i = 0$ to 2) from the least-squares procedures using the Marquardt (1963) algorithm. The standard errors, σ, are calculated as

$$\sigma = (\sum(V^E_{cal} \text{ (or } \Delta Y_{cal}) - V^E_{obs} \text{ (or } \Delta Y_{obs}))/(n-m))^{1/2} \quad (4)$$

where n represents the number of data points and m the number of coefficients. The fitted parameter values along with the calculated standard deviations are presented in Table 3. The third-degree polynomial was suitable for the fitting procedure. While fitting the ΔR and Δk_S results, volume fraction was used instead of mole fraction.

The plots of V^E vs x_1 for the binary mixtures at 298.15 K are displayed in Figure 1. For both the mixtures V^E is negative throughout the composition range, and for EG + MA mixtures the negative V^E is about three times higher than observed for PEG + MA mixtures. The results of $\Delta\eta$ vs x_1 at 298.15 K shown in Figure 2 are also negative and exhibit almost the same trends as those of V^E results. Figure 3 displays the plots of ΔR vs x_1 at 298.15 K. The results of ΔR for EG + MA mixtures are very small and negative, whereas large negative values of ΔR are observed for PEG + MA mixtures. On the other hand, from the plots of Δu vs x_1 at 298.15 K displayed in Figure 4, it is found that the Δu values are positive for PEG + MA and negative for EG + MA mixtures. The results of Δk_S vs ϕ_1 shown in Figure 5 exhibit negative values for both the mixtures.

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