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Density, Refractive Index, Viscosity, and Speed of Sound in Binary Mixtures of 2-Ethoxyethanol with Dioxane, Acetonitrile, and Tetrahydrofuran at (298.15, 303.15, and 308.15) K

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Density, refractive index, viscosity, and speed of sound data in binary mixtures of 2-ethoxyethanol with dioxane, acetonitrile, and tetrahydrofuran are presented at (298.15, 303.15, and 308.15) K over the whole range of mole fractions at atmospheric pressure. These results are used to calculate excess molar volume, deviations in molar refractivity, viscosity, and isentropic compressibility. The calculated quantities are further fitted to the Redlich−Kister equation to estimate the binary interaction parameters and mean deviations from the regression lines. The sign and magnitude of the computed parameters are discussed to study the nature and type of intermolecular interactions in binary mixtures.

Introduction

The nature and type of intermolecular interactions in binary organic liquid mixtures have been studied (Aralaguppi et al., 1991, 1992a,b) in terms of the mixing parameters such as excess molar volume, V^E, deviations in molar refractivity, ΔR, deviations in viscosity, $\Delta\eta$, and deviations in isentropic compressibility, Δk_s. These parameters can be calculated from empirical equations using the values of density, ϱ, refractive index for the sodium-D line, n_D, viscosity, η, and speed of sound, u, in binary mixtures and their pure components. Such physical property data on mixtures of 2-ethoxyethanol with organic solvents are useful in process engineering design applications and other related areas. Besides, 2-ethoxyethanol finds extensive applications in a variety of areas.

As a part of our continuing research program toward the data accumulation of organic liquid mixtures (Aminabhavi et al., 1993, 1994, 1996a,b; Aminabhavi and Bindu, 1995), we present here the experimental data on ϱ, n_D, η, and u in the binary mixtures of 2-ethoxyethanol with dioxane, acetonitrile, and tetrahydrofuran at (298.15, 303.15, and 308.15) K over the entire range of mole fraction at the atmospheric pressure. From these results the V^E, ΔR, $\Delta\eta$, and Δk_s values have been calculated and these are then fitted to the Redlich−Kister equation (Redlich and Kister, 1948) to estimate the binary interaction parameters and mean deviations from the regression lines. Furthermore, the nature and type of the binary solvent−solvent interactions have been studied.

Experimental Section

Materials. All the chemicals were obtained from S. D. Fine Chemicals Ltd., Bombay, and were used directly as supplied. 2-Ethoxyethanol and tetrahydrofuran were of analytical grade while acetonitrile and dioxane were of HPLC and spectroscopic grade samples. The purity of the solvents was ascertained by comparing their density, viscosity, and refractive index values with the literature findings (Table 1). The GLC analyses were performed using a flame ionization detector (Nucon series, model 5700/5765, with fused silica columns) with a sensitivity better than 10^{-8} g of fatty acid/μL of solvent. These data for each liquid are also included in Table 1.

Measurements. Binary mixtures were prepared by mixing the calculated volumes of liquid components in airtight glass bottles. The mass measurements were done on a single-pan Mettler balance (Switzerland, Model AE-240) within the precision of ±0.0001 g. The possible error in mole fraction is less than ±0.0002.

Densities of liquids and their mixtures were obtained by using a pycnometer having a bulb volume of 20 cm^3 and a capillary with an internal diameter of 1 mm. The required buoyancy corrections have been made for the determined density values. Double distilled, deionized and degassed water with a specific conductance of $1 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$ was used for the calibration. The precision of the densities is within ±0.0002 g·cm^{-3}. All the values are an average of three independent readings, and these were reproducible within ±0.1%. For all the mixture compositions and pure solvents, triplicate measurements were performed and the average of these values was considered in all calculations.

Viscosities were measured with a Cannon Fenske viscometer (size 100, Industrial Research Glassware Ltd.). An electronic stopwatch having a precision of ±0.01 s was used to measure the flow times. Viscosity values are accurate to ±0.001 mPa·s. Triplicate measurements of flow times were reproducible within ±0.05%. Kinematic viscosity, ν, was calculated using the relation $\nu = At - B/t$, where t is the flow time of liquid levels between two marks of the viscometer and A and B are the viscometer constants determined by calibrating with pure water and pure benzene at the working temperatures. Absolute viscosities, η/mPa·s, were then calculated as $\eta = \nu\varrho$. The estimated errors in the η values are approximately ±0.05%.

Refractive indices were measured using the sodium-D line with a thermostated Abbe refractometer (Bellingham and Stanley Ltd., London). Calibration checks of the refractometer are done routinely with the help of the glass piece of known refractive index provided with the instrument. Three independent readings were taken for each composition and the average value was used to calculate the refractive index. Measurements were done at different temperatures by circulating water through the refractometer. The precision of the refractive index values is ±0.0002 units.

The speeds of sound were measured using a variable path single crystal interferometer (Mittal Enterprises, New Delhi, Model M-84) as described earlier (Aralaguppi et al.,

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Table 1. Comparison of Data for Liquids at 298.15 K with Literature[a]

liquids (mol % purity)	ϱ/g·cm^{-3}	η/mPa·s	n_D	u/m·s^{-1}
2-ethoxyethanol (>99.6)	0.9258 (0.9252)[b]	2.054 (1.850)[c]	1.4056 (1.4057)[b]	1300 (1296)[e]
dioxane (>99.4)	1.0281 (1.0280)[b]	1.321 (1.087)[d]	1.4190 (1.4191)[b]	1342 (1363)[e]
acetonitrile (>99.7)	0.7771 (0.7766)[b]	0.390 (0.341)[c]	1.3407 (1.3416)[b]	1288 (1283)[e]
tetrahydrofuran (>99.5)	0.8827 (0.8825)[b]	0.530 (0.456)[b]	1.4037 (1.4049)[b]	1288 (1289)[e]

[a] Values in parentheses refer to the literature. [b] Marsh, 1994. [c] Riddick, A. R.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; Techniques of chemistry, Vol. II.; Wiley Interscience: New York, 1986. [d] Value available at 303.15 K. [e] Aminabhavi and Bindu, 1995.

1991, 1992a,b). The instrument was calibrated by using benzene and toluene. The measured values of u at 298.15 K for benzene (1300 m·s^{-1}) and for toluene (1306 m·s^{-1}) compared well with the published data of 1301 m·s^{-1} and 1306 m·s^{-1}, respectively, of Nath and Tripathi (1983). The precision of the speed of sound data is within ±2 m·s^{-1}.

In all the physical property measurements, an INSREF model 016 AP thermostat was used at a constant digital temperature control of ±0.01 K at the desired temperature. A calibrated mercury thermometer was used as a test of temperature standard.

Results and Discussion

Experimental density, refractive index, viscosity, and speed of sound results presented in Table 2 are used to calculate V^E, ΔR, $\Delta\eta$, and Δk_s values using the general equation (Aminabhavi et al., 1993; 1994)

$$\Delta Y = Y_m - Y_1 C_1 - Y_2 C_2 \tag{1}$$

where ΔY refers to V^E/m^3·mol^{-1}, ΔR/m^3·mol^{-1}, $\Delta\eta$/mPa·s, and Δk_s/TPa^{-1}, respectively; Y_m is the measured mixture property under question, and Y_i refers to the respective pure component property. The symbols C_1 and C_2 are mixture compositions expressed in mole fraction, x_i, of the ith component for the calculation of V^E and $\Delta\eta$, and volume fraction, φ_i of the ith component for the calculation of ΔR and Δk_s, respectively. The volume fraction is calculated as

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

To compute ΔR, the required molar refractivities, R_i and R_m of the pure components and of the mixtures, respectively, were obtained using the Lorentz−Lorenz equation.

The calculated values of V^E, ΔR, $\Delta\eta$, and Δk_s have been fitted to the Redlich−Kister equation (Redlich and Kister, 1948) to estimate the coefficients A_i from the least-squares method using the Marquardt algorithm (Marquardt, 1963). It was found that the number of coefficients A_i required for the best fit (i.e., to produce minimum error) in all cases was 3, viz., A_0, A_1, and A_2. The values of mean deviations, σ, were calculated using the relation published earlier (Aminabhavi et al., 1993, 1994). The estimated results of A_i and σ are presented in Table 3.

The precision of V^E results are within ±0.05 m^3·mol^{-1}. These data for mixtures of 2-ethoxyethanol with dioxane at 298.15 K and 308.15 K are presented in Figure 1. Smooth lines are drawn through the calculated points. The values of V^E are positive which increase systematically from 298.15 to 308.15 K, suggesting the mild dispersion type interactions between mixing components. The results of $\Delta\eta$ at 298.15 K are negative and these increase with increasing temperature. Similarly, the ΔR values at 298.15 K are negative and decrease with increasing temperature. Also, the Δk_s values at 298.15 K are negative.

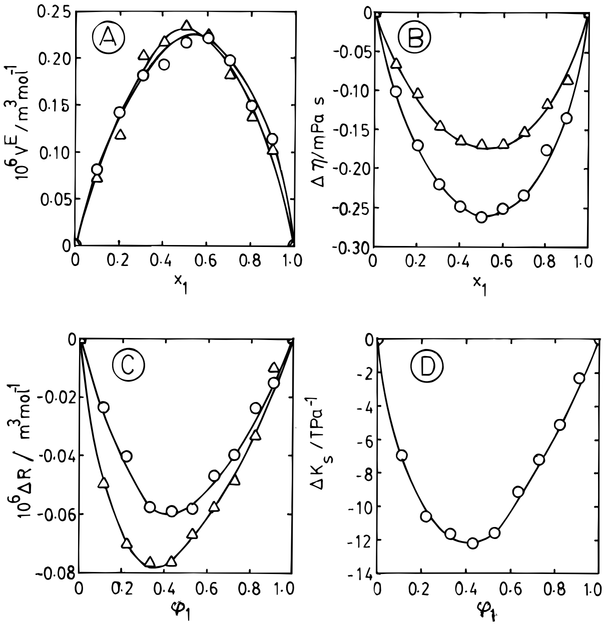

Figure 1. Dependence of excess parameters for 2-ethoxyethanol (1) + dioxane (2) mixtures at (○) 298.15 K and (△) 308.15 K: (A) excess molar volume; (B) deviations in viscosity; (C) deviations in molar refractivity; (D) deviations in isentropic compressibility.

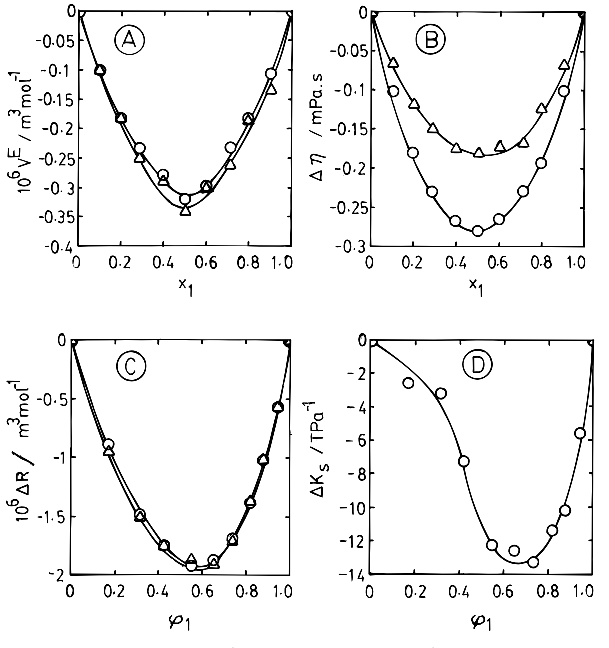

Figure 2. Dependence of excess parameters for 2-ethoxyethanol (1) + acetonitrile (2) mixtures at (○) 298.15 K and (△) 308.15 K: (A) excess molar volume; (B) deviations in viscosity; (C) deviations in molar refractivity; (D) deviations in isentropic compressibility.

As shown in Figure 2, the V^E values for mixtures of 2-ethoxyethanol and acetonitrile are negative and decrease with increasing temperature. Acetonitrile, a more polar molecule than dioxane, exerts stronger specific interactions when compared to dioxane, thus giving negative V^E. These negative values may be due to the breaking of the hydrogen

Table 2. Experimental Densities (ϱ), Viscosities (η), Refractive Indices (n_D), and Speeds of Sound (u) of Binary Mixtures at Different Temperatures

X_1	ϱ/g·cm^{-3}	η/mPa·s	n_D	u/m·s^{-1}	X_1	ϱ/g·cm^{-3}	η/mPa·s	n_D	u/m·s^{-1}
2-Ethoxyethanol (1) + Dioxane (2)									
298.15 K									
0.0000	1.0281	1.321	1.4190	1342	0.6020	0.9612	1.511	1.4098	1320
0.1009	1.0156	1.293	1.4171	1346	0.7004	0.9518	1.600	1.4087	1312
0.2023	1.0036	1.299	1.4154	1344	0.8031	0.9425	1.733	1.4076	1308
0.3051	0.9920	1.324	1.4137	1340	0.8976	0.9341	1.844	1.4065	1300
0.4014	0.9818	1.367	1.4124	1336	1.000	0.9258	2.054	1.4056	1300
0.4990	0.9715	1.424	1.4110	1328					
303.15 K									
0.0000	1.0224	1.086	1.4178		0.6020	0.9561	1.228	1.4081	
0.1009	1.0101	1.069	1.4156		0.7004	0.9470	1.299	1.4069	
0.2023	0.9981	1.066	1.4135		0.8031	0.9377	1.400	1.4058	
0.3051	0.9866	1.085	1.4119		0.8976	0.9292	1.487	1.4047	
0.4014	0.9763	1.119	1.4106		1.0000	0.9210	1.646	1.4037	
0.4990	0.9665	1.162	1.4093						
308.15 K									
0.0000	1.0167	1.0000	1.4156		0.6020	0.9510	1.120	1.4059	
0.1009	1.0045	0.982	1.4131		0.7004	0.9420	1.183	1.4048	
0.2023	0.9929	0.992	1.4114		0.8031	0.9328	1.268	1.4038	
0.3051	0.9811	1.000	1.4096		0.8976	0.9245	1.344	1.4028	
0.4014	0.9710	1.028	1.4083		1.0000	0.9163	1.480	1.4018	
0.4990	0.9610	1.070	1.4071						
2-Ethoxyethanol (1) + Acetonitrile (2)									
298.15 K									
0.0000	0.7771	0.390	1.3407	1288	0.6026	0.8899	1.128	1.3905	1303
0.1016	0.8041	0.458	1.3529	1284	0.7122	0.9016	1.346	1.3943	1304
0.2016	0.8267	0.546	1.3622	1288	0.7978	0.9097	1.524	1.3989	1305
0.2865	0.8433	0.638	1.3700	1292	0.8997	0.9184	1.786	1.4018	1303
0.4004	0.8626	0.790	1.3780	1298	1.0000	0.9258	2.054	1.4056	1300
0.5026	0.8776	0.946	1.3850	1300					
303.15 K									
0.0000	0.7715	0.333	1.3391		0.6026	0.8849	0.921	1.3881	
0.1016	0.7986	0.389	1.3485		0.7122	0.8960	1.075	1.3929	
0.2016	0.8213	0.461	1.3605		0.7978	0.9048	1.236	1.3964	
0.2865	0.8382	0.535	1.3677		0.8997	0.9136	1.435	1.4001	
0.4004	0.8573	0.655	1.3759		1.0000	0.9210	1.646	1.4037	
0.5026	0.8725	0.781	1.3824						
308.15 K									
0.0000	0.7660	0.319	1.3366		0.6026	0.8799	0.845	1.3856	
0.1016	0.7933	0.370	1.3466		0.7122	0.8920	0.978	1.3905	
0.2016	0.8160	0.435	1.3573		0.7978	0.9000	1.122	1.3949	
0.2865	0.8330	0.501	1.3657		0.8997	0.9090	1.295	1.3983	
0.4004	0.8523	0.608	1.3751		1.0000	0.9163	1.480	1.4018	
0.5026	0.8676	0.721	1.3799						
2-Ethoxyethanol (1) + Tetrahydrofuran (2)									
298.15 K									
0.0000	0.8827	0.530	1.4037	1288	0.6012	0.9147	1.232	1.4040	1304
0.1003	0.8883	0.593	1.4034	1280	0.7048	0.9200	1.503	1.4038	1312
0.2025	0.8938	0.677	1.4031	1284	0.7983	0.9236	1.701	1.4040	1316
0.3008	0.8990	0.787	1.4036	1288	0.8839	0.9257	1.898	1.4053	1318
0.4030	0.9044	0.908	1.4040	1292	1.0000	0.9258	2.054	1.4056	1300
0.5069	0.9098	1.057	1.4038	1296					
303.15 K									
0.0000	0.8773	0.450	1.3996		0.6012	0.9097	1.011	1.4020	
0.1003	0.8828	0.502	1.4010		0.7048	0.9151	1.223	1.4027	
0.2025	0.8885	0.571	1.4009		0.7983	0.9188	1.381	1.4029	
0.3008	0.8944	0.660	1.4012		0.8839	0.9208	1.546	1.4029	
0.4030	0.8994	0.756	1.4016		1.0000	0.9210	1.646	1.4037	
0.5069	0.9050	0.874	1.4013						
308.15 K									
0.0000	0.8718	0.429	1.3968		0.6012	0.9048	0.930	1.3997	
0.1003	0.8773	0.475	1.3984		0.7048	0.9102	1.091	1.4004	
0.2025	0.8833	0.539	1.3983		0.7983	0.9140	1.242	1.4002	
0.3008	0.8892	0.618	1.3991		0.8839	0.9160	1.385	1.4008	
0.4030	0.8942	0.702	1.3991		1.0000	0.9163	1.480	1.4018	
0.5069	0.9000	0.808	1.4001						

bonds in 2-ethoxyethanol due to the interaction of acetonitrile. The acetonitrile being a more polar molecule reinforces the 2-ethoxyethanol−acetonitrile interaction which competes with the hydrogen bond of the 2-ethoxyethanol. The $\Delta\eta$ values are also negative and increase with increasing temperature. Similarly, the results of ΔR are negative and exhibit no dependence on temperature and thus, a common curve is drawn for all the temperatures.

Table 3. Estimated Parameters of Excess Functions for Mixtures

function	temp/K	A_0	A_1	A_2	σ	function	temp/K	A_0	A_1	A_2	σ
					2-Ethoxyethanol (1) + Dioxane (2)						
$V^E/10^6$ m^3·mol^{-1}	298.15	0.855	−0.128	0.242	0.009	$\Delta R/10^6$ m^3·mol^{-1}	298.15	−0.234	0.056	0.064	0.002
	303.15	0.852	−0.038	0.198	0.012		303.15	−0.266	0.145	−0.004	0.004
	308.15	0.923	−0.068	0.142	0.015		308.15	−0.286	0.171	−0.088	0.004
$\Delta\eta$/mPa·s	298.15	−1.032	0.102	−0.283	0.009	Δk_S/TPa^{-1}	298.15	−46.26	23.16	−5.680	0.332
	303.15	−0.800	0.074	−0.179	0.007						
	308.15	−0.681	0.081	−0.153	0.006						
					2-Ethoxyethanol (1) + Acetonitrile (2)						
$V^E/10^6$ m^3·mol^{-1}	298.15	−1.224	0.020	0.247	0.010	$\Delta R/10^6$ m^3·mol^{-1}	298.15	−7.505	−2.337	−0.889	0.023
	303.15	−1.233	−0.056	0.303	0.027		303.15	−7.529	−2.101	−1.237	0.017
	308.15	−1.278	0.090	0.169	0.016		308.15	−7.483	−2.127	−1.427	0.025
$\Delta\eta$/mPa·s	298.15	−1.114	0.025	−0.063	0.005	Δk_S/TPa^{-1}	298.15	−38.28	−54.90	−20.59	0.929
	303.15	−0.857	0.048	−0.062	0.006						
	308.15	−0.734	0.043	−0.067	0.006						
					2-Ethoxyethanol (1) + Tetrahydrofuran (2)						
$V^E/10^6$ m^3·mol^{-1}	298.15	−1.327	2.291	−1.876	0.015	$\Delta R/10^6$ m^3·mol^{-1}	298.15	−1.125	−0.726	−0.866	0.015
	303.15	−1.444	2.200	−1.741	0.029		303.15	−1.028	−0.809	−0.273	0.020
	308.15	−1.478	2.255	−1.732	0.028		308.15	−0.954	−0.925	−0.620	0.024
$\Delta\eta$/mPa·s	298.15	−0.960	−0.596	0.995	0.017	Δk_S/TPa^{-1}	298.15	−11.32	−133.0	−101.6	1.788
	303.15	−0.718	−0.517	0.880	0.016						
	308.15	−0.614	−0.389	0.674	0.013						

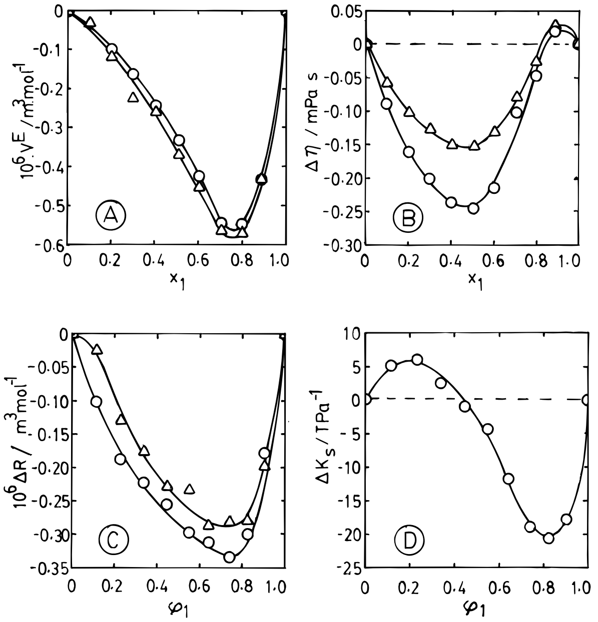

Figure 3. Dependence of excess parameters for 2-ethoxyethanol (1) + tetrahydrofuran (2) mixtures at (○) 298.15 K and (△) 308.15 K: (A) excess molar volume; (B) deviations in viscosity; (C) deviations in molar refractivity; (D) deviations in isentropic compressibility.

The results of Δk_s are negative and exhibit a skewed behavior at higher mole fractions.

The results of 2-ethoxyethanol + tetrahydrofuran mixtures are presented in Figure 3. Tetrahydrofuran is a more polar molecule ($\mu = 1.75$) than acetonitrile, and thus it has more negative V^E. The minimum of the curve is shifted toward higher mole fraction, i.e., at $x_1 \simeq 0.75$, and the curve is somewhat skewed. This is suggestive of the specific interactions between tetrahydrofuran and 2-ethoxyethanol. Similarly, the results of $\Delta\eta$ and ΔR are negative and exhibit a skewed behavior. On the other hand, the results of Δk_s show a sigmoidal curve with their values varying from positive to negative.

To the best of our knowledge, the mixture properties presented here have not been published earlier and hence we cannot compare the present results with the literature findings.

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