Density, Refractive Index, and Speed of Sound in Binary Mixtures of 2-Ethoxyethanol with Dimethyl Sulfoxide, *N,N′*-Dimethylformamide, *N,N′*-Dimethylacetamide at Different Temperatures

M. I. Aralaguppi, C. V. Jadar, and T. M. Aminabhavi*

Department of Chemistry, Karnatak University, Dharwad 580 003, India

J. D. Ortego

Department of Chemistry, Lamar University, Beaumont, Texas 77710

S. C. Mehrotra

Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431 004, India

Density and refractive index data at (298.15, 303.15, and 308.15) K, and speed of sound at 298.15 K in the binary mixtures of 2-ethoxyethanol with dimethyl sulfoxide, *N,N′*-dimethylformamide, and *N,N′*-dimethylacetamide have been measured over the entire mixture compositions. These data have been used to compute the excess molar volume, changes in molar refractivity, and isentropic compressibility of the mixtures. The results are fitted to the Redlich−Kister polynomial equation to estimate the binary coefficients and the standard errors. Furthermore, the experimental results are used to study the nature of the binary interactions in these mixtures.

Introduction

2-Ethoxyethanol is a versatile organic liquid used in chemical industries as a solvent for lacquers, oils, and resins and as an antifreeze for explosives. It is miscible with a number of organic solvents as well as water. Among the dipolar aprotic solvents, dimethyl sulfoxide (DMSO), *N,N′*-dimethylformamide (DMF), and *N,N′*-dimethylacetamide (DMAc) are the important industrial liquids that find applications in a variety of areas. To the best of our knowledge, the mixing properties of these liquids with 2-ethoxyethanol have not been measured. It was therefore decided to measure the density, ρ, refractive index, n_D, for the sodium D line, and speed of sound, u, in these mixtures. From these results, the excess molar volume, V^E, changes in Lorentz−Lorenz refractivity, ΔR, at (298.15, 303.15, and 308.15) K, and isentropic compressibility, Δk_S, at 298.15 K have been calculated. These quantities have been fitted to the Redlich−Kister equation (1948) to obtain the binary coefficients, A_n, and standard errors, σ, between the calculated and the experimental parameters.

Experimental Section

Materials. High-purity spectroscopic and HPLC grade samples of DMSO, DMF, and DMAc were purchased from s.d. Fine Chemicals Ltd., Bombay. Their gc analysis indicated a mol % purity of 99.4, 99.3, and 99.4, respectively; the moisture contents of these liquids were removed by degassing. 2-Ethoxyethanol is an AR grade sample purchased from BDH, Ltd., London, and its mol % purity as tested by gc is 99.7. All the samples were used without further purification. Experimental results of density, refractive index, and speed of sound of the pure liquids are compared at 298.15 K with the published data in Table 1.

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

liquid	ρ/g·cm^{-3}	n_D	u^b/m·s^{-1}
2-ethoxyethanol	0.9258 (0.9252)	1.4056 (1.4057)	1300 (1296)
dimethyl sulfoxide	1.0958 (1.0957)	1.4757 (1.4768)	1488 (1499)
N,N′-dimethylformamide	0.9449 (0.9442)	1.4282 (1.4293)	1462 (1451)
N,N′-dimethylacetamide	0.9372 (0.9375)	1.4341 (1.4371)	1458 (1458)

[a] Marsh, K. N., Ed. TRC Databases for Chemistry and Engineering-TRC Source Database; Texas A&M University; College Station, TX, 1996. [b] Aminabhavi, T. M.; Bindu, G. *J. Chem. Eng. Data* **1995**, *40*, 856. [c] Bracketed values are from the literature.

Measurements. The experimental details for the preparation of the binary mixtures and the measurements of density, ρ, refractive index, n_D, for the sodium D line, and speed of sound, u, are the same as published earlier (Aminabhavi et al., 1994, 1995). Mixtures were prepared by mass on a single pan Mettler balance (AE 240) within the accuracy of ±0.01 mg. The calculated mole fractions were accurate to ±0.0001 units. Density and refractivity data were obtained at (298.15, 303.15, and 308.15) K, whereas the speed of sound data were obtained at 298.15 K only. The results of density and refractive index are accurate to ±0.0002 units, while those of speed of sound are accurate to ±2 m s^{-1}. The isentropic compressibility,

* Author for correspondence. Fax: 011-91-836-347884. E-mail: unikard@ren.nic.in.

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

x_1	ρ/ g·cm^{-3}	n_D	u/ m·s^{-1}	x_1	ρ/ g·cm^{-3}	n_D	u/ m·s^{-1}
2-Ethoxyethanol (1) + Dimethyl Sulfoxide (2)							
298.15 K							
0.0000	1.0958	1.4757	1488	0.6041	0.9985	1.4287	1425
0.1007	1.0776	1.4668	1478	0.7299	0.9792	1.4212	1408
0.2073	1.0590	1.4583	1470	0.8041	0.9651	1.4170	1388
0.3068	1.0428	1.4507	1459	0.8973	0.9312	1.4040	1352
0.4053	1.0274	1.4430	1448	1.0000	0.9258	1.4056	1300
0.5043	1.0117	1.4359	1437				
303.15 K							
0.0000	1.0905	1.4751		0.6041	0.9937	1.4267	
0.1007	1.0725	1.4648		0.7299	0.9765	1.4192	
0.2073	1.0542	1.4569		0.8041	0.9666	1.4154	
0.3068	1.0379	1.4471		0.8973	0.9548	1.4095	
0.4053	1.0226	1.4415		1.0000	0.9210	1.4037	
0.5043	1.0070	1.4345					
308.15 K							
0.0000	1.0857	1.4719		0.6041	0.9891	1.4250	
0.1007	1.0675	1.4629		0.7299	0.9703	1.4178	
0.2073	1.0492	1.4546		0.8041	0.9552	1.4129	
0.3068	1.0333	1.4471		0.8973	0.9215	1.4031	
0.4053	1.0181	1.4399		1.0000	0.9163	1.4018	
0.5043	1.0024	1.4324					
2-Ethoxyethanol (1) + Dimethylformamide (2)							
298.15 K							
0.0000	0.9449	1.4282	1462	0.6040	0.9339	1.4153	1376
0.1032	0.9429	1.4268	1449	0.7125	0.9317	1.4128	1356
0.2030	0.9414	1.4251	1436	0.8039	0.9299	1.4106	1336
0.3040	0.9395	1.4231	1422	0.9017	0.9276	1.4080	1316
0.4033	0.9378	1.4206	1406	1.0000	0.9258	1.4056	1300
0.5009	0.9360	1.4180	1392				
303.15 K							
0.0000	0.9394	1.4260		0.6040	0.9291	1.4131	
0.1032	0.9380	1.4252		0.7125	0.9267	1.4110	
0.2030	0.9365	1.4227		0.8039	0.9253	1.4087	
0.3040	0.9346	1.4208		0.9017	0.9229	1.4060	
0.4033	0.9332	1.4185		1.0000	0.9210	1.4037	
0.5009	0.9310	1.4161					
308.15 K							
0.0000	0.9347	1.4244		0.6040	0.9244	1.4114	
0.1032	0.9332	1.4225		0.7125	0.9222	1.4091	
0.2030	0.9316	1.4204		0.8039	0.9206	1.4069	
0.3040	0.9299	1.4174		0.9017	0.9183	1.4046	
0.4033	0.9281	1.4154		1.0000	0.9163	1.4018	
0.5009	0.9263	1.4134					
2-Ethoxyethanol (1) + Dimethylacetamide (2)							
298.15 K							
0.0000	0.9372	1..4341	1458	0.6022	0.9314	1.4192	1378
0.1039	0.9361	1.4339	1452	0.7056	0.9301	1.4160	1361
0.2049	0.9353	1.4318	1440	0.7940	0.9289	1.4130	1344
0.3035	0.9344	1.4293	1428	0.8984	0.9275	1.4091	1320
0.4001	0.9335	1.4261	1413	1.0000	0.9258	1.4056	1300
0.5016	0.9325	1.4228	1396				
303.15 K							
0.0000	0.9325	1.4346		0.5016	0.9278	1.4202	
0.1039	0.9315	1.4323		0.6022	0.9266	1.4169	
0.2049	0.9307	1.4300		0.7056	0.9254	1.4146	
0.3035	0.9297	1.4264		0.7940	0.9242	1.4110	
0.4001	0.9293	1.4227		0.8984	0.9224	1.4080	
				1.000	0.9210	1.4037	
308.15 K							
0.0000	0.9278	1.4323		0.5016	0.9232	1.4184	
0.1039	0.9270	1.4294		0.6022	0.9221	1.4153	
0.2049	0.9260	1.4271		0.7056	0.9208	1.4118	
0.3035	0.9251	1.4244		0.7940	0.9196	1.4087	
0.4001	0.9243	1.4218		0.8984	0.9178	1.4048	
				1.000	0.9163	1.4018	

k_S, was calculated from the density and speed of sound using, $k_S = 1/u^2\rho$. The experimental temperature was controlled within $\pm$0.01 K as measured by the digital display.

Table 3. Estimated Parameters of Excess Functions for Mixtures

function	temp/K	A_0	A_1	A_2	σ
2-Ethoxyethanol (1) + Dimethyl Sulfoxide (2)					
$V^E/10^6$ m^3 mol^{-1}	298.15	−5.908	1.932	5.752	0.577
	303.15	−4.895	7.283	−9.992	0.263
	308.15	−6.225	1.970	6.338	0.593
$\Delta R/10^6$ m^3 mol^{-1}	298.15	−2.103	−1.482	−0.909	0.025
	303.15	−2.079	−1.829	−3.051	0.089
	308.15	−2.151	−1.385	−0.381	0.076
Δk_S/TPa^{-1}	298.15	−237.5	−227.5	−189.0	3.925
2-Ethoxyethanol (1) + Dimethylformamide (2)					
$V^E/10^6$ m^3 mol^{-1}	298.15	−0.631	0.011	0.314	0.011
	303.15	−0.733	−0.127	−0.019	0.019
	308.15	−0.705	−0.016	−0.023	0.010
$\Delta R/10^6$ m^3 mol^{-1}	298.15	−0.576	−0.277	−0.148	0.007
	303.15	−0.609	−0.223	0.185	0.012
	308.15	−0.800	−0.038	0.410	0.009
Δk_S/TPa^{-1}	298.15	−96.33	−24.34	14.75	0.968
2-Ethoxyethanol (1) + Dimethylacetamide (2)					
$V^E/10^6$ m^3 mol^{-1}	298.15	−0.468	0.178	0.112	0.004
	303.15	−0.590	0.057	0.368	0.029
	308.15	−0.526	0.151	0.124	0.011
$\Delta R/10^6$ m^3 mol^{-1}	298.15	0.577	−0.565	0.538	0.009
	303.15	0.146	0.020	0.815	0.026
	308.15	0.306	−0.127	−0.260	0.006
Δk_S/TPa^{-1}	298.15	−89.47	1.49	−14.82	0.973

Results and Discussion

The excess molar volume, V^E, and other mixing properties such as changes in Lorentz−Lorenz molar refractivity, ΔR, and isentropic compressibility, Δk_S, of the mixtures were calculated by using the results of ρ, n_D, and u given Table 2 using the following equations (Aminabhavi et al., 1994, 1995):

$$V^E = V_m - V_1x_1 - V_2x_2 \tag{1}$$

$$\Delta Y = Y_m - Y_1x_1 - Y_2x_2 \tag{2}$$

where V_m represents the molar volume of the mixture calculated as suggested before (Aminabhavi et al., 1994, 1995); V_1 and V_2 are the molar volumes of the pure components; x_i represents the mole fraction of the ith component of the mixture; ΔY represents respectively ΔR and Δk_S; and Y_m is the respective mixture property, viz, molar refractivity, R, calculated from the Lorentz−Lorenz relation for mixtures and their pure components and k_S as obtained from the speed of sound data. For the calculation of ΔR, the volume fraction, Φ_i, is used instead of mole fraction (Aminabhavi et al., 1994, 1995).

The calculated results of V^E and ΔR at (298.15 and 308.15) K and Δk_S at 298.15 K for the binary mixtures of 2-ethoxyethanol with DMSO, DMF, and DMAc are presented respectively in Figures 1−3. It is observed that in all the cases, V^E results are negative, suggesting the specific hydrogen-bond type interactions between the hydroxy group of 2-ethoxyethanol and the sulfoxide group in DMSO and of the amide groups in DMF and DMAc. However, the negative V^E values decrease, i.e., the absolute V^E values increase from DMSO to DMAc via DMF, suggesting the decreased interactions of these molecules in the 2-ethoxyethanol environment. The effects of temperature on the V^E results are more significant with the mixtures of 2-ethoxyethanol + DMF and + DMAc, but show no greater dependence on temperature for 2-ethoxyethanol + DMSO mixtures. The V^E results of the mixtures decrease with increasing temperature.

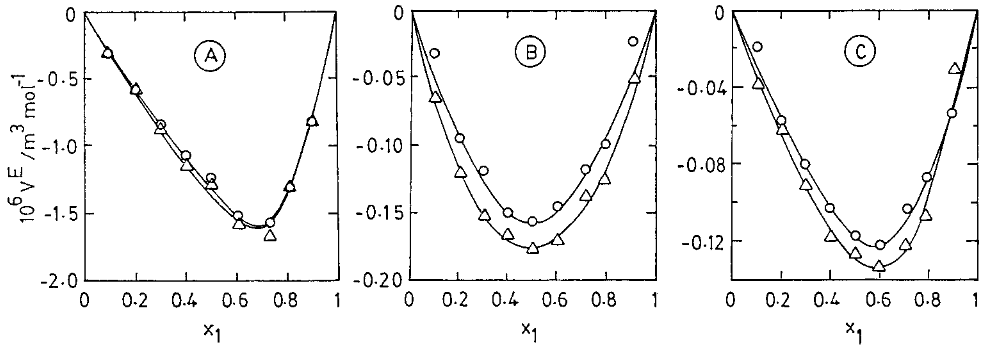

Figure 1. Dependence of excess molar volume for mixtures of 2-ethoxyethanol with (A) DMSO, (B) DMF, and (C) DMAc at (○) 298.15 K and (△) 308.15 K.

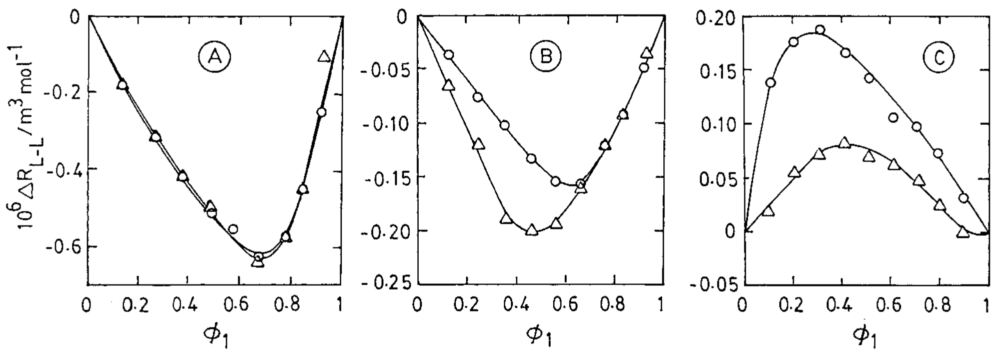

Figure 2. Dependence of changes in molar refractivity for mixtures of 2-ethoxyethanol with (A) DMSO, (B) DMF, and (C) DMAc at (○) 298.15 K and (△) 308.15 K.

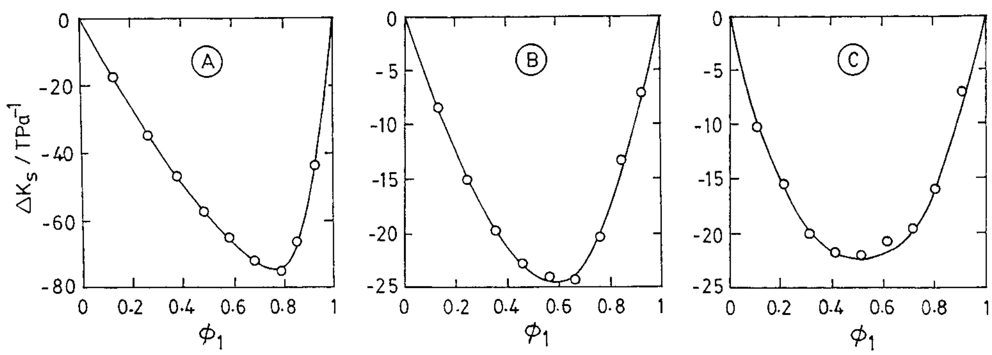

Figure 3. Dependence of changes in isentropic compressibility for mixtures 2-ethoxyethanol with (A) DMSO, (B) DMF, and (C) DMAc at 298.15 K.

The results of ΔR for 2-ethoxyethanol + DMSO and + DMF mixtures are negative, suggesting higher electronic perturbations of the molecular orbitals of the mixing liquids. On the other hand, for 2-ethoxyethanol + DMAc mixtures, these results are positive. Similar to the temperature dependence of the V^E results, the ΔR values for the DMSO-containing mixtures do not exhibit any significant dependence on temperature. In all the binary mixtures, the results of Δk_S are negative, further supporting the specific interactions in these mixtures. It may be noted that the results of Δk_S increase from DMSO to DMAc via DMF, which has the same sequence as exhibited by the V^E results.

The calculated results of V^E, ΔR, and Δk_S are fitted to the Redlich−Kister equation (1948) to estimate the binary coefficients and standard errors using the procedure outlined earlier (Aminabhavi et al., 1994). The best fitted parameter values, A_n (where n = 3), along with the standard errors, σ, are presented in Table 3 for all the systems at all the temperatures.

Literature Cited

Aminabhavi, T. M.; Bindu, G. Density, viscosity, refractive index, and speed of sound in aqueous mixtures of N,N′-dimethyl sulfoxide, N,N′-dimethylacetamide, acetonitrile, ethylene glycol, 1,4-dioxane, tetrahydrofuran, 2-methoxyethanol, and 2-ethoxyethanol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 856.

Aminabhavi, T. M.; Phyade, H. T. S.; Khinnavar, R. S.; Bindu, G.; Hansen, K. C. Densities, refractive indices, speeds of sound, and shear viscosities of diethylene glycol dimethyl ether with ethyl acetate, methyl benzoate, ethyl benzoate, and diethyl succinate in the temperature range from 298.15 to 318.15 K. *J. Chem. Eng. Data* **1994**, *39*, 251.

Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345.

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