Refractive Indices and Deviations in Refractive Indices for Binary Mixtures of Formamide + 1-Butanol, + 2-Butanol, + 1,3-Butanediol, and + 1,4-Butanediol at Temperatures from (293.15 to 318.15) K

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The refractive indices n of pure formamide, 1-butanol, 2-butanol, 1,3-butanediol, 1,4-butanediol, and those of their binary mixtures, with formamide as the common component, covering the whole composition range, have been measured at temperatures (293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K. From the experimental data, the deviations in refractive index (Δn) have been calculated. The variation of Δn with composition and temperature has been discussed. The extent of deviations in refractive indices for these mixtures follows the sequence 1-butanol > 2-butanol > 1,3-butanediol > 1,4-butanediol, and Δn decreases with an increase in temperature.

Introduction

The refractive indices n of liquids and liquid mixtures are required in chemical engineering for designing industrial processes. Knowledge of n of multicomponent mixtures provides information regarding the interactions in these mixtures.[1–3] Prediction of n of liquid mixtures is essential for many physicochemical calculations, which include correlation of n with density,[4] excess molar volume,[5,6] and surface tension.[6] In previous studies,[7–11] we have reported the volumetric, acoustic, transport, and refractive properties of nonaqueous binary mixtures. Here we report the refractive indices of the binary mixtures of formamide with 1-butanol, 2-butanol, 1,3-butanediol, and 1,4-butanediol over the entire composition range at six different temperatures. A literature survey indicates that there has been no temperature-dependent study of these systems from the point of view of their refractive index behavior.

The present paper reports the refractive indices of formamide + 1-butanol, + 2-butanol, + 1,3-butanediol, and + 1,4-butanediol binary mixtures, covering the entire composition range expressed by mole fraction x_1 of formamide at the temperatures (293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K. The experimental values of n have been used to calculate the deviations in refractive index (Δn), and the variations of Δn with composition and temperature were discussed in terms of molecular interactions in these mixtures.

Experimental

Formamide, 1-butanol, 2-butanol (all AR grade products from s. d. fine chemicals, India), 1,3-butanediol, and 1,4-butanediol (both products from E. Merck, Germany) used in the study were purified by using the methods described in the literature.[12,13] The mass fraction purities as determined by gas chromatography are: formamide > 0.995, 1-butanol > 0.995, 2-butanol > 0.994, 1,3-butanediol > 0.992, and 1,4-butanediol > 0.992. Before use, the chemicals were stored over 0.4 nm molecular sieves for 72 h to remove water and were degassed at low pressure. The mixtures were prepared by mass and were kept in special airtight stopper glass bottles to avoid evaporation. The weighings were done on an electronic balance with a precision of ± 0.1 mg.

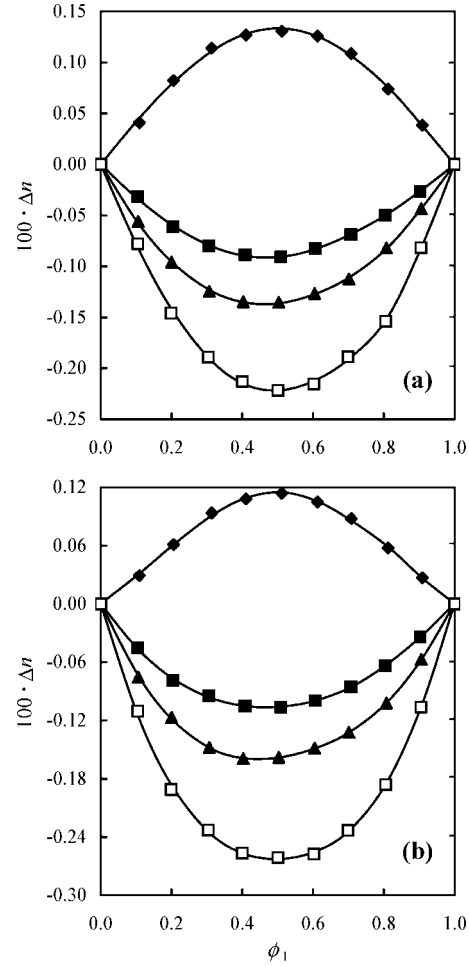

Figure 1. Plots of deviations in refractive index, Δn, vs volume fraction, ϕ_1, of formamide for the binary mixtures (a) at T/K = 298.15 and (b) at T/K = 318.15. ♦, formamide + 1-butanol; ■, formamide + 2-butanol; ▲, formamide + 1,3-butanediol; □, formamide + 1,3-butanediol; −, calculated from eq 2.

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Table 1. Values of Refractive Index, n, of Formamide (1) + Alkanol (2) Mixtures at T = (293.15 to 318.15) K as a Function of Mole Fraction x_1

	T/K					
x_1	293.15	298.15	303.15	308.15	313.15	318.15
	Formamide + 1-Butanol					
0.0000	1.3994	1.3974	1.3953	1.3933	1.3913	1.3893
0.1093	1.4023	1.4003	1.3983	1.3963	1.3943	1.3923
0.2057	1.4052	1.4032	1.4012	1.3992	1.3973	1.3954
0.3138	1.4086	1.4067	1.4048	1.4029	1.4011	1.3992
0.4104	1.4119	1.4101	1.4083	1.4065	1.4047	1.4029
0.5115	1.4158	1.4141	1.4124	1.4107	1.4090	1.4073
0.6124	1.4203	1.4187	1.4171	1.4155	1.4139	1.4123
0.7081	1.4252	1.4238	1.4223	1.4208	1.4194	1.4179
0.8123	1.4316	1.4303	1.4290	1.4277	1.4264	1.4251
0.9086	1.4389	1.4378	1.4367	1.4357	1.4345	1.4334
1.0000	1.4475	1.4467	1.4459	1.4451	1.4442	1.4433
	Formamide + 2-Butanol					
0.0000	1.3972	1.3951	1.3931	1.3911	1.3891	1.3871
0.1043	1.3993	1.3973	1.3953	1.3933	1.3913	1.3893
0.2043	1.4017	1.3996	1.3977	1.3958	1.3939	1.3919
0.3056	1.4045	1.4025	1.4007	1.3989	1.3970	1.3951
0.4083	1.4079	1.4061	1.4043	1.4026	1.4008	1.3990
0.5093	1.4119	1.4102	1.4085	1.4068	1.4051	1.4034
0.6063	1.4165	1.4149	1.4133	1.4118	1.4102	1.4086
0.7068	1.4222	1.4207	1.4193	1.4179	1.4164	1.4149
0.8042	1.4289	1.4276	1.4263	1.4251	1.4237	1.4224
0.9024	1.4372	1.4361	1.4350	1.4340	1.4328	1.4317
1.0000	1.4475	1.4467	1.4459	1.4451	1.4442	1.4433
	Formamide + 1,3-Butanediol					
0.0000	1.4412	1.4391	1.4370	1.4349	1.4329	1.4308
0.1061	1.4410	1.4389	1.4368	1.4348	1.4328	1.4307
0.2004	1.4409	1.4389	1.4369	1.4349	1.4329	1.4309
0.3068	1.4411	1.4391	1.4372	1.4352	1.4333	1.4314
0.4026	1.4414	1.4395	1.4377	1.4358	1.4340	1.4321
0.5033	1.4419	1.4401	1.4384	1.4366	1.4349	1.4331
0.6046	1.4425	1.4409	1.4393	1.4377	1.4360	1.4344
0.7013	1.4434	1.4419	1.4404	1.4389	1.4374	1.4359
0.8073	1.4445	1.4432	1.4419	1.4406	1.4393	1.4379
0.9058	1.4459	1.4448	1.4437	1.4427	1.4415	1.4404
1.0000	1.4475	1.4467	1.4459	1.4451	1.4442	1.4433
	Formamide + 1,4-Butanediol					
0.0000	1.4451	1.4431	1.4411	1.4391	1.4372	1.4352
0.1052	1.4445	1.4425	1.4405	1.4385	1.4365	1.4345
0.1988	1.4440	1.4420	1.4400	1.4380	1.4361	1.4341
0.3041	1.4437	1.4418	1.4399	1.4380	1.4361	1.4342
0.4002	1.4436	1.4418	1.4400	1.4382	1.4364	1.4345
0.5009	1.4437	1.4420	1.4403	1.4386	1.4369	1.4351
0.6022	1.4440	1.4424	1.4408	1.4392	1.4376	1.4359
0.6992	1.4445	1.4431	1.4416	1.4401	1.4386	1.4370
0.8051	1.4452	1.4439	1.4426	1.4413	1.4400	1.4386
0.9050	1.4463	1.4452	1.4441	1.4430	1.4419	1.4407
1.0000	1.4475	1.4467	1.4459	1.4451	1.4442	1.4433

The probable uncertainty in the mole fraction was estimated to be less than ± 0.0001.

The refractive indices of pure liquids and their binary mixture were measured by using a thermostated Abbe refractometer. The refractometer was calibrated by measuring the refractive indices of triply distilled water and toluene at desired temperatures. The values of refractive index were obtained using sodium D light. The uncertainty of refractive index measurements was within ± 0.0001. The temperature of the test liquids between the prisms during the measurements was maintained to an uncertainty of ± 0.01 K by circulating water through the jacket around the prisms from an electronically controlled thermostatic water bath (JULABO, model ME-31A, Germany). The reliability of experimental measurements of n was ascertained by comparing the experimental data of pure liquids with the corresponding values available in the literature[12] at 298.15 K. The experimental values of n of pure formamide with 1-butanol, 2-butanol, and 1,3-butanediol obtained at 298.15 K are 1.4467, 1.3973, 1.3951, and 1.4391, respectively, and the corresponding literature[12] values are 1.44682, 1.3973, 1.3950, and 1.4390, respectively.

Table 2. Coefficients, A_i, of Equation 2 of $100\cdot\Delta n$ and Standard Deviations, σ, for Formamide + Alkanol Mixtures at Different Temperatures

T/K	A_1	A_2	A_3	A_4	A_5	$100\cdot\sigma$
	Formamide + 1-Butanol					
293.15	0.4582	0.3996	0.2433	0.0877	−0.0337	0.0024
298.15	0.4362	0.4020	0.2416	0.0518	−0.1246	0.0029
303.15	0.4146	0.4239	0.2582	−0.0082	−0.2154	0.0028
308.15	0.3944	0.4499	0.2382	−0.1059	−0.1786	0.0027
313.15	0.3735	0.4187	0.2657	−0.0649	−0.2908	0.0026
318.15	0.3533	0.3971	0.3065	−0.0494	−0.4171	0.0018
	Formamide + 2-Butanol					
293.15	−0.2654	−0.2781	−0.2168	−0.0680	0.0739	0.0007
298.15	−0.2793	−0.2820	−0.2351	−0.0900	0.0852	0.0010
303.15	−0.2966	−0.2886	−0.1696	−0.0927	−0.0956	0.0012
308.15	−0.3083	−0.2822	−0.1888	−0.1365	−0.0966	0.0015
313.15	−0.3267	−0.2673	−0.2000	−0.2103	−0.0741	0.0016
318.15	−0.3491	−0.2932	−0.1331	−0.1737	−0.2382	0.0012
	Formamide + 1,3-Butanediol					
293.15	−0.4280	−0.3485	−0.2814	−0.2377	0.0246	0.0012
298.15	−0.4503	−0.3470	−0.2638	−0.2732	−0.0594	0.0012
303.15	−0.4663	−0.3466	−0.2893	−0.3081	−0.0885	0.0010
308.15	−0.4843	−0.3450	−0.3027	−0.3454	−0.1318	0.0012
313.15	−0.5042	−0.3437	−0.2833	−0.3725	−0.2730	0.0009
318.15	−0.5364	−0.3518	−0.2867	−0.4027	−0.2672	0.0010
	Formamide + 1,4-Butanediol					
293.15	−0.7445	−0.4559	−0.5058	−0.4235	0.4720	0.0018
298.15	−0.7744	−0.4480	−0.5174	−0.4734	0.3356	0.0031
303.15	−0.8041	−0.4412	−0.5265	−0.5197	0.1939	0.0045
308.15	−0.8449	−0.4347	−0.4572	−0.5585	−0.0591	0.0052
313.15	−0.8876	−0.4744	−0.3482	−0.6200	−0.3636	0.0029
318.15	−0.9482	−0.4991	−0.3233	−0.6018	−0.4886	0.0032

Results and Discussion

The experimental values of refractive index, n, of the binary mixtures of formamide with 1-butanol, 2-butanol, 1,3-butanediol, and 1,4-butanediol, as a function of mole fraction, x_1, of formamide at different temperatures are listed in Table 1. The deviations in refractive index, Δn, have been calculated by using the following relation[14]

$$\Delta n = n - (\phi_1 n_1 + \phi_2 n_2) \tag{1}$$

where ϕ is the volume fraction (calculated using the molar volumes of the pure components obtained from the density data from our earlier work[15]) and the subscripts 1 and 2 represent pure components, formamide and alkanol, respectively. The values of Δn were fitted to a Redlich–Kister type polynomial equation[16] of the form

$$\Delta n = \phi_1(1-\phi_1)\sum_{i=1}^{5} A_i(1-2\phi_1)^{i-1} \tag{2}$$

The values of coefficients A_i evaluated by the method of least-squares, together with the corresponding standard deviations σ, are listed in Table 2. The variations of Δn with volume fraction, ϕ_1, of formamide in the mixture along with smoothed values by using eq 2, at (298.15 and 318.15) K, are shown graphically in Figure 1.

Figure 1 indicates that Δn values are positive for formamide + 1-butanol and are negative for formamide + 2-butanol, + 1,3-butanediol, and + 1,4-butanediol over the entire composition range and at all temperatures investigated. The extent of deviation in Δn from linear dependence on composition follows the sequence: 1-butanol > 2-butanol > 1,3-butanediol > 1,4-butanediol. In general, the positive deviations in Δn values (on

a volume fraction dependence basis) are considered due to the presence of significant interactions in the mixtures, whereas negative deviations in Δn values indicate weak interactions between the components of the mixture.[6,14] The observed trends (Figure 1) and magnitudes of Δn values indicate the presence of significant interactions in formamide + 1-butanol mixtures, whereas weak interactions are found in formamide + 2-butanol, + 1,3-butanediol, + 1,4-butanediol mixtures, which follow the order: 1-butanol > 2-butanol > 1,3-butanediol > 1,4-butanediol. The Δn values decrease with an increase in temperature for all the four binary mixtures, indicating that the interactions between unlike molecules decrease with a rise in temperature. This further supports our earlier conclusions regarding formamide−alkanol or alkanediol interactions in these mixtures from the variations of V_m^E values[15] with composition and temperature. Also, the deviations in Δn values are found opposite to the sign of excess molar volumes for all the four binary mixtures,[15] which is in agreement with the view proposed by Brocos et al.[6,14]

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