

Refractive Indices for the Binary Mixtures of *N,N*-Dimethylformamide with 2-Butanol and 2-Pentanol at Temperatures 303.15 K, 313.15 K, and 323.15 K

Aklima Jahan¹, Md. Ashraful Alam^{2,*}, Md. Ashiqur Rahman Khan¹, Shamim Akhtar¹

¹Department of Chemistry, University of Chittagong, Chittagong, Bangladesh

²Department of Chemistry and Bioengineering, Iwate University, Morioka, Japan

Email address:

sdashraf84@yahoo.com (Md. A. Alam)

*Corresponding author

To cite this article:

Aklima Jahan, Md. Ashraful Alam, Md. Ashiqur Rahman Khan, Shamim Akhtar. Refractive Indices for the Binary Mixtures of *N,N*-Dimethylformamide with 2-Butanol and 2-Pentanol at Temperatures 303.15 K, 313.15 K, and 323.15 K. *American Journal of Physical Chemistry*. Vol. 7, No. 4 2018, pp. 55-62. doi: 10.11648/j.ajpc.20180704.11

Received: December 18, 2018; Accepted: December 20, 2018; Published: January 10, 2019

Abstract: The refractive index values have been measured as a function of composition range at temperatures 303.15 K, 313.15 K, and 323.15 K and at ambient pressure and reported here. From these data, refractive index deviations, Δn_D , excess molar refraction, R_m^E , were calculated and correlated by the Redlich-Kister-type polynomial equation to derive the coefficients and estimated the standard deviation values. For both systems, Δn_D were found to be both positive and negative. Excess molar refraction, R_m^E , versus mole fraction, x_1 , of *N,N*-dimethylformamide curves were calculated and found as sigmoid at all temperatures. The variation of these properties with composition and temperature of the binary mixtures were discussed in terms of intermolecular interactions.

Keywords: *N,N*-Dimethylformamide, 2-Butanol, 2-Pentanol, Refractive Index Deviations, Molecular Interactions

1. Introduction

Refractive index, n_D , is an important physical quantity for analysis, because many substances can be easily identified by knowing its n_D value. It is also used for theoretical purposes due to the fact that it gives information about the electronic configuration of the different ions and molecules forming the liquid [1]. The excess refractive indices (Δn_D) of the solvent-solvent interaction processes depend on the nature of the solvent and on its physical properties such as the dielectric constant, the dipole moment and the donor number [2]. Also, these properties have been used to study the structure of binary mixtures with water and aliphatic alcohols and cyclic ethers [3]. Properties such as refractive indices and their variation with temperature and composition of the binary mixtures are useful to design engineering processes and in chemical and biological industries [4].

N,N-dimethylformamide (DMF) is primarily used as an industrial solvent. Pure DMF is aprotic and unassociated [5] in its pure liquid state. It belongs to the so-called super

solvents, owing to its miscibility with almost all common polar and non-polar solvents [6], probably due to its high polarity with large dipole moment ($\mu = 3.8D$) and moderately high dielectric constant ($\epsilon = 36.76$) [7]. Several topics and examples of thermodynamic studies are depicted on the basis of the structural behavior of DMF for binary mixtures of non-electrolytes [8].

Alkanols are important compounds in both industry and science. Alkanols can also be used in the synthesis of many other organic compounds. Some industrial applications of alkanols consist of perfumes, cosmetics, paints, varnishes, drugs, fuels, explosives, fats, waxes, resins, plastics, rubber, and detergents [9-12].

In recent past, several workers [13-18] have applied various mixing rules in binary and ternary liquid mixtures. In this paper we present the results of experimental measurements of the refractive indices for binary mixtures of *N,N*-dimethylformamide with two polar solvents. Here, we reported the refractive index, n_D , refractive index deviations, Δn_D , excess molar refraction, R_m^E , as the function of

composition range at temperatures (303.15, 313.15, and 323.15) K and at ambient pressure. The findings of this study can be utilized in having a better insight into molecular interactions between the components of the systems.

2. Experimental Section

2.1. Chemicals Used

DMF (Aldrich, purity HPLC grade 99.9+%), 2-BuOH (Aldrich, purity 99+%) and 2-PnOH (Aldrich, purity 98%) were used without further treatment. The structures of the chemicals are shown in Figure 1. The densities and refractive indexes of pure chemicals were compared with literature values, which showed satisfactory agreements (Table 1).

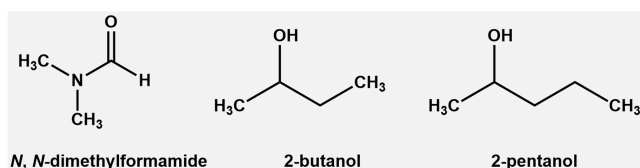


Figure 1. Chemical structures of the compounds used in the experiments.

2.2. Materials and Methods

The refractive indices of pure components and the mixtures were determined by using an Abbe refractometer (Abbe 60/ED). The samples were prepared by mixing the pure components at different proportions up to ± 0.0001 g, which was then converted into mole fraction. All the molar quantities used in the experiments are based on the IUPAC relative atomic mass table [19].

3. Results and Discussion

3.1. Refractive Index and Molecular Polarizability

Refraction index can be defined as the ratio of speed of light in vacuum to its speed in the medium, i.e.

$$n_D = \frac{c}{v}$$

Where n_D is the refractive index of the binary liquid mixture of the medium, c is the speed of the light in vacuum and v is the speed of the light in the binary liquid mixture.

Assessment of the purity of substances and molecular interaction in a liquid mixture, calculation of molecular electronic polarizability, estimation of boiling point by Meissner's Method [20] and the estimation of other thermodynamic parameters can be done from the refractive index [21-24]. The detection of structural properties of liquid-liquid mixtures is possible by the use refractive index.

Refractive indices (n_D) of the two binary systems were measured in the whole range of composition, $0 \leq x_1 \leq 1$, among 303.15 K, 313.15 K and 323.15 K maintaining 10 K interval, where, x_1 represents the mole fraction of DMF. The measured refractive index, n_D , of the pure liquids are placed

(Table 1) together with a number of reported data. Their comparison also shows that there is quite satisfactory agreement between the experimental and literature values.

Table 1. Experimental and literature values of refractive index (n_D) of the pure *N,N*-dimethylformamide (DMF), 2-butanol (2-BuOH) and 2-pentanol (2-PnOH) at different temperatures.

Component	Temp. T / K	Refractive Index, n_D values	
		Experimental	Literature
2-BuOH	303.15	1.39188	
	313.15	1.38725	1.3903 [25]
	323.15	1.38333	
2-PnOH	303.15	1.40125	
	313.15	1.39649	
	323.15	1.39180	
DMF	303.15	1.42466	
	313.15	1.41998	1.4264 [26]
	323.15	1.41625	

The refractive indices, (n_D), were fitted to the polynomial equation of the following form:

$$n_D = \sum_{i=0} a_i x_1^i \quad (1)$$

Here, a_i is the i^{th} fitting coefficient and x_1 is the mole fraction of DMF. By using 'Excel', the coefficients, a_i and values of r^2 for the systems at different compositions and temperatures were computed and all of them are summarized (Table 2). The relevant r^2 values were very close to unity indicates the excellent fitting for all the experimental data.

Table 2. Fitting coefficients, a_i of polynomial Eq. (1) and the values of r^2 for the systems of DMF (x_1) + 2-BuOH (x_2) and + 2-PnOH (x_2) at different temperatures.

DMF (x_1) + 2-BuOH (x_2)

T/K	a_0	a_1	a_2	a_3	a_4	a_5	r^2
303.15 K	1.391	0.025	0.043	-0.165	0.323	-0.305	0.999
313.15 K	1.387	0.023	0.052	-0.168	0.297	-0.267	0.999
323.15 K	1.383	0.016	0.110	-0.394	0.736	-0.674	0.999

DMF (x_1) + 2-PnOH (x_2)

T/K	a_0	a_1	a_2	a_3	a_4	a_5	r^2
303.15 K	1.401	0.016	0.045	-0.158	0.286	-0.250	0.999
313.15 K	1.396	0.010	0.070	-0.247	0.442	-0.382	0.999
323.15 K	0.1391	0.011	0.069	-0.222	0.404	-0.375	0.999

3.2. Deviation in Refractive Index

For each system, the deviation in refractive index (Δn_D) of a particular composition is calculated by using the following equation:

$$\Delta n_D = n_D - \sum \phi_i n_{Di} \quad (2)$$

Here, ϕ_i and n_{Di} represent the volume fraction and the refractive index, respectively of the i^{th} component and n_D is the observed refractive index of the mixtures. All Δn_D values are listed (Table 3).

Table 3. Densities, (ρ), volume fraction of DMF (ϕ_1), refractive index, (n_D), deviations in refractive index, (Δn_D), molar refraction, (R_m), excess molar refraction (R_m^E) of the systems DMF (x_1) + 2-BuOH (x_2) and + 2-PnOH (x_2) for different molar ratios at 303.15K, 313.15K and 323.15K.

T=303.15K

DMF+2-BuOH

3	ρ /kg m ⁻³	ϕ_1	n_D	Δn_D	$R_m \times 10^6 / \text{m}^3 \text{mol}^{-1}$	$R_m^E \times 10^6 / \text{m}^3 \text{mol}^{-1}$
0.0000	798.683	0.000000	1.39188	0.00000	22.09285	0.00000
0.0506	804.205	0.042348	1.39341	0.00014	22.00189	0.01206
0.0997	810.160	0.085046	1.39467	0.00000	21.88714	0.01346
0.1515	815.793	0.128358	1.39631	0.00022	21.80106	0.02575
0.2000	821.967	0.172031	1.39790	0.00038	21.69937	0.02479
0.2497	828.575	0.219703	1.39966	0.00058	21.59475	0.02720
0.2909	834.597	0.263784	1.40094	0.00041	21.48535	0.03162
0.3510	841.410	0.310189	1.40261	0.00056	21.37507	0.02415
0.3999	848.374	0.358350	1.40421	0.00058	21.25903	0.01926
0.4494	855.730	0.406386	1.40586	0.00066	21.13760	0.00438
0.5003	863.058	0.456253	1.40742	0.00058	21.01436	-0.00313
0.5491	871.791	0.505906	1.40894	0.00048	20.85786	-0.04483
0.6002	880.089	0.556955	1.41068	0.00054	20.72416	-0.07040
0.6500	888.162	0.611440	1.41236	0.00044	20.59465	-0.07868
0.7000	895.575	0.661847	1.41399	0.00041	20.48156	-0.08486
0.7499	902.987	0.715092	1.41555	0.00023	20.36665	-0.08174
0.7999	910.279	0.770199	1.41699	-0.00014	20.25077	-0.07014
0.8500	917.420	0.826344	1.41878	-0.00019	20.15468	-0.05236
0.9000	924.083	0.882983	1.42066	-0.00016	20.07416	-0.02315
0.9500	931.500	0.941050	1.42236	-0.00037	19.97085	-0.00654
1.0000	939.496	1.000000	1.42466	0.00000	19.88139	0.00000

T=313.15K

DMF+2-BuOH

x_1	ρ /kg m ⁻³	ϕ_1	n_D	Δn_D	$R_m \times 10^6 / \text{m}^3 \text{mol}^{-1}$	$R_m^E \times 10^6 / \text{m}^3 \text{mol}^{-1}$
0.0000	789.992	0.000000	1.38725	0.00000	22.10151	0.00000
0.0506	795.526	0.042320	1.38834	-0.00030	21.98745	0.01069
0.0997	801.469	0.084993	1.39003	0.00000	21.89371	0.01132
0.1515	807.356	0.128282	1.39153	0.00008	21.79330	0.01577
0.2000	813.213	0.171934	1.39279	-0.00009	21.68335	0.02224
0.2497	819.776	0.219587	1.39477	0.00033	21.59006	0.02471
0.2909	825.751	0.263652	1.39600	0.00012	21.47872	0.02934
0.3510	832.513	0.310044	1.39800	0.00060	21.38475	0.02203
0.3999	839.423	0.358193	1.39914	0.00017	21.24752	0.01733
0.4494	846.723	0.406221	1.40104	0.00049	21.13838	0.00262
0.5003	854.077	0.456084	1.40254	0.00036	21.01082	-0.00670
0.5491	862.573	0.505736	1.40426	0.00046	20.86796	-0.04416
0.6002	870.920	0.556787	1.40601	0.00054	20.73244	-0.07228
0.6500	878.920	0.611278	1.40730	0.00004	20.58624	-0.07998
0.7000	886.292	0.661695	1.40906	0.00015	20.47912	-0.08631
0.7499	893.641	0.714953	1.41051	-0.00014	20.36006	-0.08274
0.7999	900.874	0.770078	1.41213	-0.00032	20.25252	-0.07078
0.8500	907.973	0.826246	1.41402	-0.00027	20.16104	-0.05293
0.9000	914.536	0.882913	1.41599	-0.00016	20.08605	-0.02225
0.9500	922.000	0.941012	1.41723	-0.00082	19.96163	-0.00752
1.0000	929.906	1.000000	1.41998	0.00000	19.89243	0.00000

T=323.15K

DMF+2-BuOH

x_1	ρ /kg m ⁻³	ϕ_1	n_D	Δn_D	$R_m \times 10^6 / \text{m}^3 \text{mol}^{-1}$	$R_m^E \times 10^6 / \text{m}^3 \text{mol}^{-1}$
0.0000	780.886	0.000000	1.38333	0.00000	22.15788	0.00000
0.0506	786.481	0.042272	1.38419	-0.00053	22.02895	0.00833
0.0997	792.462	0.084901	1.38579	-0.00033	21.92862	0.00715
0.1515	798.271	0.128150	1.38730	-0.00025	21.82982	0.01306
0.2000	804.217	0.171765	1.38871	-0.00027	21.72372	0.01651
0.2497	810.763	0.219384	1.39036	-0.00019	21.61374	0.01873
0.2909	816.723	0.263422	1.39201	0.00001	21.52217	0.02321
0.3510	823.461	0.309790	1.39339	-0.00014	21.39795	0.01576
0.3999	830.349	0.357921	1.39519	0.00008	21.29151	0.01097

x_1	$\rho / \text{kg m}^{-3}$	ϕ_1	n_D	Δn_D	$R_m \times 10^6 / \text{m}^3 \text{ mol}^{-1}$	$R_m^E \times 10^6 / \text{m}^3 \text{ mol}^{-1}$
0.4494	837.585	0.405935	1.39687	0.00018	21.17242	-0.00291
0.5003	844.925	0.455790	1.39851	0.00018	21.05041	-0.01261
0.5491	853.420	0.505440	1.39984	-0.00013	20.88799	-0.05104
0.6002	861.642	0.556494	1.40179	0.00014	20.76336	-0.07705
0.6500	869.598	0.610997	1.40328	-0.00016	20.62571	-0.08442
0.7000	876.922	0.661430	1.40503	-0.00007	20.51813	-0.09021
0.7499	884.201	0.714711	1.40659	-0.00027	20.40427	-0.08552
0.7999	891.412	0.769868	1.40816	-0.00051	20.29386	-0.07342
0.8500	898.461	0.826076	1.40976	-0.00076	20.18998	-0.05470
0.9000	905.015	0.882790	1.41153	-0.00086	20.10599	-0.02393
0.9500	912.100	0.940947	1.41358	-0.00073	20.02318	-0.00119
1.0000	920.277	1.000000	1.41625	0.00000	19.94388	0.00000

 $T=303.15\text{K}$

DMF+2-PnOH

x_1	$\rho / \text{kg m}^{-3}$	ϕ_1	n_D	Δn_D	$R_m \times 10^6 / \text{m}^3 \text{ mol}^{-1}$	$R_m^E \times 10^6 / \text{m}^3 \text{ mol}^{-1}$
0.0000	801.295	0.000000	1.40125	0.00000	26.7426	0.00000
0.0506	805.702	0.036327	1.40215	0.00005	26.4188	0.02010
0.0997	810.540	0.072636	1.40310	0.00015	26.0933	0.02551
0.1515	816.272	0.112126	1.40442	0.00055	25.7512	0.01636
0.2000	821.868	0.150253	1.40546	0.00069	25.4159	0.00594
0.2497	828.337	0.190535	1.40644	0.00073	25.0491	-0.02149
0.2909	833.318	0.224899	1.40751	0.00100	24.7738	-0.02803
0.3510	841.237	0.276684	1.40879	0.00106	24.3428	-0.04941
0.3999	847.995	0.320340	1.40985	0.00110	23.9890	-0.06890
0.4494	854.694	0.365999	1.41120	0.00138	23.6534	-0.07823
0.5003	861.886	0.414565	1.41217	0.00122	23.2835	-0.08943
0.5491	868.917	0.462746	1.41350	0.00142	22.9496	-0.09734
0.6002	876.136	0.514989	1.41449	0.00118	22.5888	-0.09499
0.6500	883.479	0.567791	1.41590	0.00136	22.2550	-0.09397
0.7000	890.808	0.622665	1.41692	0.00109	21.9072	-0.08542
0.7499	898.243	0.679607	1.41798	0.00082	21.5634	-0.07288
0.7999	905.546	0.738772	1.41940	0.00086	21.2432	-0.05060
0.8500	913.278	0.800317	1.42080	0.00081	20.9158	-0.03162
0.9000	921.494	0.864233	1.42172	0.00024	20.5618	-0.01712
0.9500	929.400	0.930740	1.42306	0.00002	20.2373	0.01141
1.0000	939.496	1.000000	1.42466	0.00000	19.8814	0.00000

 $T=313.15\text{K}$

DMF+2-PnOH

x_1	$\rho / \text{kg m}^{-3}$	ϕ_1	n_D	Δn_D	$R_m \times 10^6 / \text{m}^3 \text{ mol}^{-1}$	$R_m^E \times 10^6 / \text{m}^3 \text{ mol}^{-1}$
0.0000	792.841	0.000000	1.39649	0.00000	26.7440	0.00000
0.0506	797.301	0.036314	1.39736	0.00002	26.4159	0.01713
0.0997	802.145	0.072612	1.39834	0.00014	26.0911	0.02108
0.1515	807.889	0.112091	1.39950	0.00038	25.7386	0.01006
0.2000	813.304	0.150208	1.40051	0.00049	25.4066	0.00391
0.2497	819.826	0.190481	1.40166	0.00070	25.0464	-0.02681
0.2909	824.859	0.224838	1.40272	0.00095	24.7682	-0.03610
0.3510	832.691	0.276614	1.40399	0.00100	24.3379	-0.05671
0.3999	839.281	0.320265	1.40519	0.00118	23.9950	-0.07292
0.4494	845.990	0.365918	1.40645	0.00136	23.6535	-0.08402
0.5003	853.098	0.414481	1.40740	0.00117	23.2835	-0.09444
0.5491	859.934	0.462660	1.40872	0.00136	22.9533	-0.09861
0.6002	867.282	0.514902	1.40982	0.00123	22.5931	-0.10116
0.6500	874.535	0.567706	1.41096	0.00113	22.2477	-0.09918
0.7000	881.790	0.622584	1.41237	0.00126	21.9189	-0.09022
0.7499	889.234	0.679532	1.41354	0.00109	21.5786	-0.07923
0.7999	896.660	0.738705	1.41477	0.00093	21.2457	-0.06103
0.8500	904.314	0.800261	1.41595	0.00066	20.9095	-0.04136
0.9000	912.550	0.864192	1.41710	0.00031	20.5637	-0.02852
0.9500	920.623	0.930718	1.41834	-0.00001	20.2303	-0.00469
1.0000	929.906	1.000000	1.41998	0.00000	19.8924	0.00000

$T=323.15K$
DMF+2-PnOH

x_1	$\rho / \text{kg m}^{-3}$	ϕ_1	n_D	Δn_D	$R_m \times 10^6 / \text{m}^3 \text{ mol}^{-1}$	$R_m^E \times 10^6 / \text{m}^3 \text{ mol}^{-1}$
0.0000	784.055	0.000000	1.39180	0.00000	26.7601	0.00000
0.0506	788.606	0.036289	1.39260	-0.00009	26.4236	0.01314
0.0997	793.497	0.072563	1.39341	-0.00016	26.0863	0.01454
0.1515	799.188	0.112018	1.39459	0.00005	25.7357	0.00407
0.2000	804.939	0.150115	1.39567	0.00020	25.3960	-0.01373
0.2497	810.993	0.190368	1.39678	0.00033	25.0470	-0.03110
0.2909	816.199	0.224710	1.39766	0.00037	24.7529	-0.04659
0.3510	823.970	0.276467	1.39909	0.00053	24.3318	-0.06675
0.3999	830.635	0.320105	1.40058	0.00095	24.0011	-0.08626
0.4494	837.197	0.365748	1.40160	0.00086	23.6501	-0.09413
0.5003	844.144	0.414302	1.40275	0.00082	23.2934	-0.10121
0.5491	850.907	0.462478	1.40399	0.00088	22.9600	-0.10442
0.6002	858.055	0.514719	1.40530	0.00092	22.6140	-0.10283
0.6500	865.240	0.567526	1.40658	0.00090	22.2755	-0.10022
0.7000	872.564	0.622411	1.40769	0.00067	21.9293	-0.09396
0.7499	880.001	0.679372	1.40891	0.00050	21.5900	-0.08376
0.7999	887.533	0.738563	1.40999	0.00013	21.2465	-0.06892
0.8500	895.210	0.800144	1.41150	0.00014	20.9234	-0.05056
0.9000	903.473	0.864106	1.41277	-0.00016	20.5808	-0.03910
0.9500	911.572	0.930670	1.41399	-0.00056	20.2446	-0.01643
1.0000	920.277	1.000000	1.41625	0.00000	19.9439	0.00000

3.3. Molar Refraction

The presence of short range interaction between similar and dissimilar molecules can be known from the molar refraction. The following equation is used to calculate the molar polarization. The calculation of the molar refraction, R_m , was carried out by using the following equation:

$$R_m^E = \{ (n_D^2 - 1) / (n_D^2 + 2) \} [\{ (x_1 M_1 + x_2 M_2) / \rho_{\text{mix}} \} - \{ x_1 M_1 / \rho_1 + x_2 M_2 / \rho_2 \}] \quad (3)$$

3.4. Excess Properties

The variation of excess parameters like excess molar refraction with mole fractions is also studied. The excess molar refractions (R_m^E) are estimated as the following equation:

The excess values were fitted by the Redlich-Kister type [27] polynomial equation as shown below:

$$\Delta n_D = x_1 x_2 \sum_{i=0} A_i (2x_2 - 1)^i \quad (5)$$

Where, A_i is the relevant i^{th} fitting coefficient of the Redlich-Kister polynomial equation and all the other terms have their usual significance.

The relevant standard deviations, σ , were calculated by using the following relation:

$$\sigma = \left[\frac{\sum \left(Y_{\text{exp}}^E - Y_{\text{cal}}^E \right)^2}{n - p - 2} \right]^{1/2} \quad (6)$$

Where, n and p are the number of experimental points and number of parameters retained respectively.

All the coefficients, A_i , of Eq. 5 and their relevant σ values by using Eq. 6 are listed (Table 4 and Table 5).

Table 4. Fitting coefficients, A_i , of Redlich-Kister polynomial Eq. (5) and the values of standard deviation, σ , (Δn_D) for the systems DMF (x_1) + 2-BuOH (x_2), + 2-PnOH (x_2) at different temperatures.

DMF (x_1) + 2-BuOH (x_2)

T/K	A_0	A_1	A_2	A_3	A_4	A_5	σ
303.15 K	0.0024	-0.0006	-0.0009	-0.0031	-0.0067	-0.008	0.00010
313.15 K	0.0017	-0.0009	-0.0029	-0.0003	-0.9978	-0.0037	0.00022
323.15 K	0.0003	0.0003	-0.0017	-0.0049	-0.0136	-0.0003	0.00012

DMF (x_1) + 2-PnOH (x_2)

T/K	A_0	A_1	A_2	A_3	A_4	A_5	σ
303.15 K	0.0051	0.0009	0.0005	0.0006	-0.0058	-0.0017	0.00013
313.15 K	0.0050	0.0003	0.0015	0.0101	-0.0085	-0.0137	0.00007
323.15 K	0.0036	0.0011	-0.0029	0.0031	-0.0093	-0.0108	0.00012

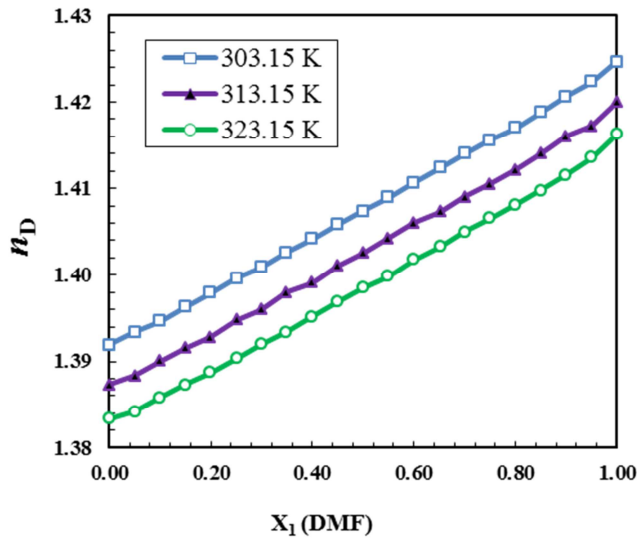
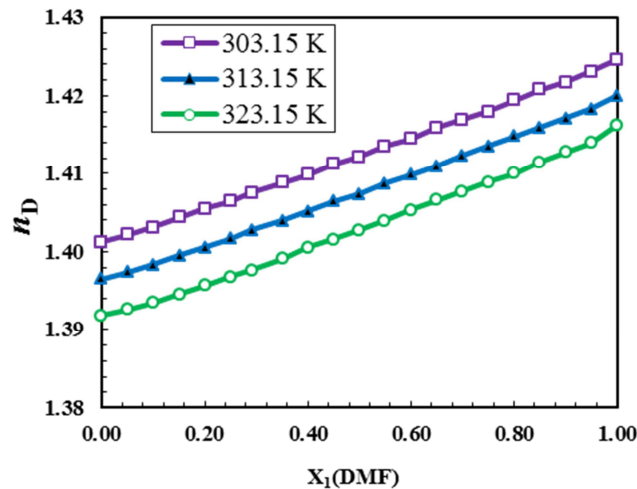
Table 5. Fitting coefficients, A_i , of Redlich-Kister polynomial Eq. (5) and the values of standard deviation, σ , (R_m^E) for the systems DMF (x_1) + 2-BuOH (x_2), + 2-PnOH (x_2) at different temperatures.DMF (x_1) + 2-BuOH (x_2)

T/K	A_0	A_1	A_2	A_3	A_4	A_5	σ
303.15 K	-0.0675	-0.9053	-0.5423	1.3707	0.9010	-0.6445	0.00547
313.15 K	-0.0734	-0.9138	-0.5661	1.4967	0.8948	-0.7561	0.00470
323.15 K	-0.0962	-0.8874	-0.5945	1.3668	0.9655	-0.5342	0.00479

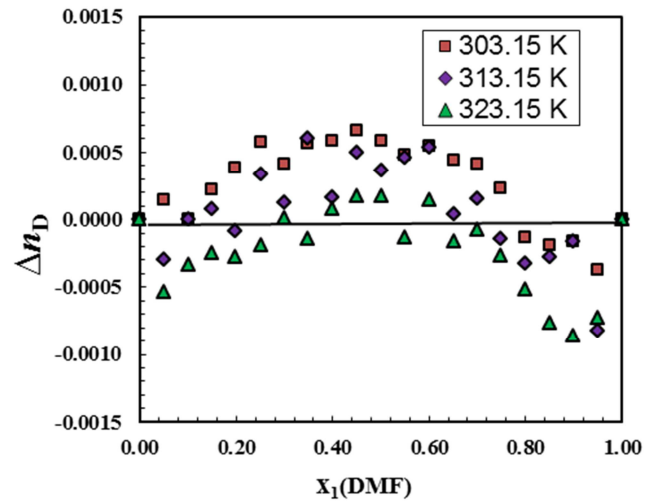
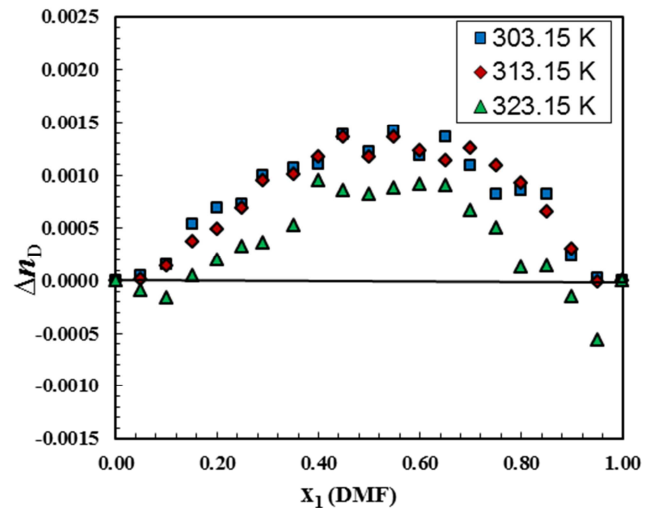
DMF (x_1) + 2-PnOH (x_2)

T/K	A_0	A_1	A_2	A_3	A_4	A_5	σ
303.15 K	-0.3565	-0.2987	0.3685	-0.1047	0.4969	0.3099	0.00380
313.15 K	-0.3770	-0.2872	0.3778	-0.1161	0.2842	0.1308	0.00313
323.15 K	-0.4062	-0.2054	0.3914	-0.3044	-0.0787	0.1334	0.00182

The refractive indices, (n_D), of the systems DMF + 2-BuOH and DMF + 2-PnOH in the whole range of composition at three different temperatures (303.15 K, 313.15 K and 323.15 K) are displayed (Table 2) and presented graphically in Figure 2 and 3.

**Figure 2.** Refractive index, n_D of DMF (x_1) + 2-BuOH (x_2) system for different molar ratios at different temperatures.**Figure 3.** Refractive index, n_D of DMF (x_1) + 2-PnOH (x_2) system for different molar ratios at different temperatures.

The variations of Δn_D with mole fraction x_1 , of DMF at three temperatures, along with the smoothed Δn_D values by using Eq. 5, are presented graphically in Figure 4 and 5.

**Figure 4.** Deviation in refractive index (Δn_D) of DMF (x_1) + 2-BuOH (x_2) system for different molar ratios at different temperatures.**Figure 5.** Deviation in refractive index (Δn_D) of DMF (x_1) + 2-PnOH (x_2) system for different molar ratios at different temperatures.

The calculated values of Δn_D are presented (Table 2) and Figure 6 and 7 also.

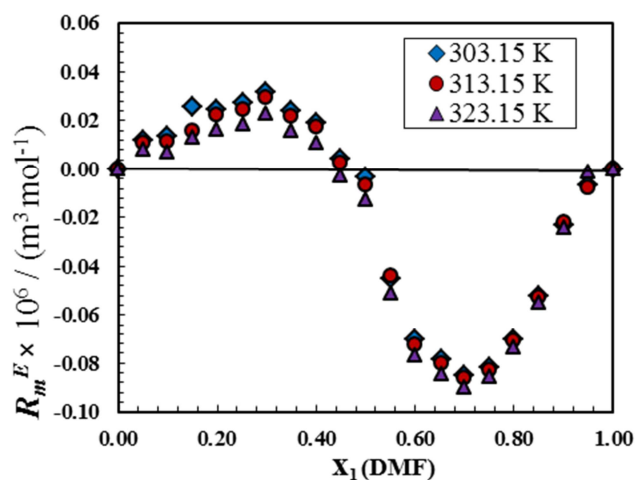


Figure 6. Excess molar refraction (R_m^E) of DMF (x_1) + 2-BuOH (x_2) system for different molar ratios at different temperatures.

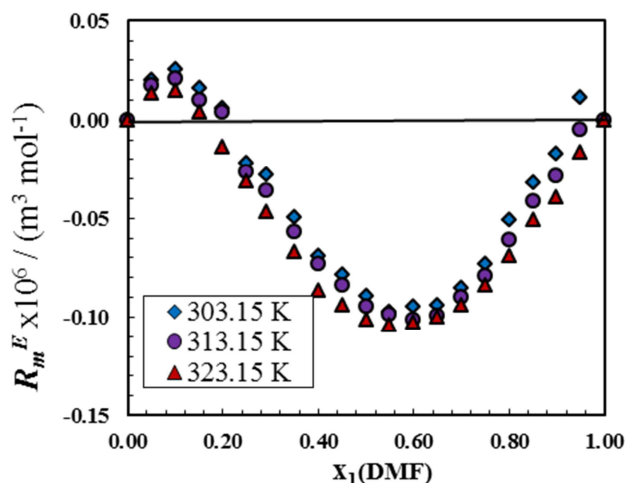


Figure 7. Excess molar refraction (R_m^E) of DMF (x_1) + 2-PnOH (x_2) system for different molar ratios at different temperatures.

The n_D versus x_1 curves for both systems followed a similar trend. The refractive index values, n_D increased almost linearly with the concentration of the DMF. The increment of n_D with respect to x_1 follows the order: 2-PnOH + DMF > 2-BuOH + DMF. Effect of temperature on n_D values is large, but with the rise of temperature, n_D values decreased. For 2-PnOH + DMF system, the Δn_D values were positive except only the small negative values of $x_1 = 0.05\text{--}0.10$ & $0.90\text{--}0.95$ at lower temperatures, whereas, for 2-BuOH + DMF, Δn_D were found to be both positive and negative. For both systems R_m^E versus x_1 curves were found to be sigmoid at all temperatures. The magnitude of negative R_m^E follows the order: 2-PnOH + DMF > 2-BuOH + DMF. The refractive index, (n_D) is a parameter which also depends on the nature of incident light, density and molecular polarizability of the substance. Therefore, at a fixed frequency (Na D-line), n_D or any deviation of n_D is expected to have close similarity to the respective ρ . Moreover, positive excess refractive indices were obtained which indicates the presence of specific molecular interactions between the unlike components. The sign of R_m^E of solutions

depends upon the relative magnitude of expansion and contraction on mixing up of the components. If the factors causing expansion out to weigh the factors causing contraction, the values of R_m^E becomes positive. But when the contractive factors are dominant over the expansive factors, the overall R_m^E becomes negative.

4. Conclusions

In the present study, the refractive indices, n_D , of the binary mixtures of *N,N*-dimethylformamide with 2-butanol and 2-pentanol have been experimentally measured at $T = (303.15, 313.15, 323.15)$ K. From the values of refractive index, deviations in refractive index, Δn_D , excess molar refraction, R_m^E , were determined. The Redlich-Kister polynomial equation was used to correlate the results. The deviations in refractive index, Δn_D , were found to be both positive and negative. Excess molar refraction, R_m^E versus mole fraction, x_1 , of *N,N*-dimethylformamide curves were calculated and found as sigmoid at all temperatures. The variation pattern of n_D , Δn_D and R_m^E were due to respective density and molecular polarizability.

Acknowledgments

The authors are grateful to Prof. Dr. M. A. Saleh laboratory, Department of Chemistry, University of Chittagong, Chittagong, Bangladesh.

References

- [1] Rogers, R. D., Seddon, K. N. (2005): *Ionic Liquids IIIA: Fundamentals, Progress, Challenges and Opportunities*, American Chemical Society, Washington.
- [2] Farid, I., Dossaki, E. I. (2007): Refractive Index and Density Measurements for Selected Binary Protic-Protic, Aprotic-Aprotic, and Aprotic-Protic Systems at Temperatures from 298.15 K to 308.15 K. *Journal of Chinese Chemical Society*. 54, 1129-1137.
- [3] Gascom, I., Artigas, H., Lafunte, C., Lopez, M. C. (2002): Excess properties of the ternary system cyclohexane + 1,3-dioxolane + 1-butanol at 298.15 and 313.15 K, *Fluid Phase Equilib.* 202, 385-397.
- [4] Gupta, M. M., Vibhu, I., Shukla, J. P. (2010): Refractive index, molar refraction deviation and excess molar volume of binary mixtures of 1,4-dioxane with carboxylic acids, *Physics and Chemistry of Liquids*. 48, 415-427.
- [5] Shuqin, L., Xingen, H., Ruisen, L. (1999): Apparent Molar Volumes of Sodium Chlorobenzoates in *N,N*-dimethylformamide-Water Mixtures at 298.15 K. *J. Chem. Eng. Data*. 44, 353-356.
- [6] Krestov, G. A. (1991): *Thermodynamics of Solvation*; Eills Harwood: England.
- [7] Marcus, Y. (1977): *Introduction to Liquid-State Chemistry*, Wiley-Inter-science: London.
- [8] Venkatesu, P. (2010): Thermophysical contribution of *N,N*-dimethylformamide in the molecular interactions with other solvents. *Fluid Phase Equilib.* 298, 173-191.

- [9] Krishna, T. V., Mohan, T. M. (2012): Study of molecular interactions in the polar binary mixtures of *N*-methyl aniline and alcohols, using excess dielectric and thermodynamic parameters. *J. Chem. Thermodyn.* 47, 267–275.
- [10] Singh, S., Parveen, S., Shukla, D., Gupta, M., Shukla, J. P. (2007): Volumetric, Optical, Acoustical and Viscometric Study of Molecular Association in Binary Mixtures of Butylamine with 1-Butanol and Tert-Butanol. *Acta Phys. Pol.* 68, 847–858.
- [11] Bai, T. C., Yao, J., Han, S. J. (1998): Excess molar volumes for ternary mixture *N*, *N*-dimethylformamide + 1-propanol + water at the temperature 298.15 K. *Fluid Phase Equilib.* 152, 283–298.
- [12] Serbanovic, S. P., Kijevcanin, M. L., Radovic, I. R., Djordjevic, B. (2006): Effect of temperature on the excess molar volumes of some alcohol + aromatic mixtures and modelling by cubic EOS mixing rules. *Fluid Phase Equilib.* 239, 69–82.
- [13] Bhatia, S. C., Tripathi, N., Dubey, G. P. (2002): Refractive indices of binary liquid mixtures of (decane + benzene) and (hexadecane + benzene, or + hexane) at 303.15, 308.15 and 313.15 K. *Ind. J. Chem.* 41, 266–269.
- [14] Sharma, S., Patel, P. B., Patel, R. S., Vora, J. J. E.: (2007): *J. Chem.* 4, 343–349.
- [15] Mehra, R. (2003): *Proc. Indian Acad. Sci.* 115, 147–1547.
- [16] Fermeiglia, M., Torriano, G. (1999): Density, Viscosity, and Refractive Index for Binary Systems of *n*-C16 and Four Nonlinear Alkanes at 298.15 K. *J. Chem. Eng. Data.* 44, 965–969.
- [17] Naya, K. J. N., Aralaguppi, M. I., Toti, U. S., Bhavi, T. M. A. (2003): Density, Viscosity, Refractive Index, and Speed of Sound in the Binary Mixtures of Tri-*n*-butylamine + Triethylamine, + Tetrahydrofuran, + Tetradecane, + Tetrachloroethylene, + Pyridine, or + Trichloroethylene at (298.15, 303.15, and 308.15) K. *J. Chem. Eng. Data.* 48, 1483–1488.
- [18] Pandey, J. D., Shukla, R. K., Rai, R. D., Shukla, A. K. (1992): *Indian J. Pure & Appl. Phys.* 30, 94–97.
- [19] International Union of Pure and Applied Chemistry. (1986): Inorganic Chemistry Division, Commission on Atomic Weights and Isotopic Abundances. *Pure appl. Chem.* 58, 1677–1692.
- [20] Jorgensen, S. E., Sorensen, B. H., Mahler, H. (1998): *Handbook of estimation methods in ecotoxicology and environmental chemistry.* Washington (DC): Lewis Publishers, p. 14.
- [21] Leron, R. B., Soriano, N., Li, M. H. (2012): Densities and refractive indices of the deep eutectic solvents (choline chloride + ethylene glycol or glycerol) and their aqueous mixtures at the temperature ranging from 298.15 to 333.15 K. *J Taiwan Inst Chem Eng.* 43, 551–557.
- [22] Rilo, E., Domínguez-Pérez, M., Vila, J. et al. (2012): Easy prediction of the refractive index for binary mixtures of ionic liquids with water or ethanol. *J Chem Thermodyn.* 47, 219–222.
- [23] Kier, L. B., Hall, L. H. (1976): *Molecular connectivity in chemistry and drug research.* Sand Diego (CA): Academic Press.
- [24] Rechsteiner, C. E. Lyman, W. J., Reehl, W. F., Rosenblatt, D. H. (1990): *Hand book of chemical property estimation.* Washington (DC): American Chemical Society. 12, 8–16.
- [25] Ali, A., Nain, A. K., Lal, B., Chand, D. (2004): Densities, Viscosities, and Refractive Indices of Binary Mixtures of Benzene with Isomeric Butanols at 30°C. *International Journal of Thermophysics.* 25, 1835–1847.
- [26] Baragi, J. G., Aralaguppi, M. I., Aminabhavi, T. M., Kariduraganavar, M. Y., Kittur, A. S. (2005): Density, Viscosity, Refractive Index, and Speed of Sound for Binary Mixtures of Anisole with 2- Chloroethanol, 1,4-Dioxane, Tetrachloroethylene, Tetrachloroethane, DMF, DMSO, and Diethyl Oxalate at (298.15, 303.15, and 308.15) K. *J. Chem. Eng. Data.* 50, 910–916.
- [27] Redlich, O., Kister, A. T. (1948): Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* 44, 345–348.