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Density, refractive index and molar refractivity of binary liquid mixture at 293.15, 298.15, 303.15, 308.15 and 313.15 K

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Abstract Densities and refractive indices were measured for the binary liquid mixtures formed by formamide, N-methylacetamide, di-methylformamide and di-methylacetamide with acetonitrile at $T = 293.15$, 298.15, 303.15, 308.15 and 313.15 K and atmospheric pressure over the whole concentration range. Lorentz–Lorentz mixing rule, Ramaswamy and Anbananthan model and model devised by Glinski were used to study the refractive index and molar refractivity. These results have been discussed to study the type of mixing behavior between the mixing molecules. The measured data were fitted to the Redlich–Kister polynomial relation to estimate the binary coefficients and standard errors. Furthermore, McAllister multibody interaction model is used to correlate the binary refractive index with the experimental findings. It is observed that molar refractivity, molecular interaction and association constant can be better understood from these models.

1. Introduction

The knowledge of refractive index property at different temperatures of liquid mixtures is an important step for their structure and characterization. Along with other thermodynamic data, refractive index values are also useful for practical purposes in engineering calculations. Refractive index is useful to assess purity of substances, to calculate the molecular electronic polarizability (Kier and Hall, 1976) to estimate the boiling point with Meissner's method (Rechsteiner, 1990) or to estimate the other thermodynamic properties. In recent past, several work-

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ers (Sharma et al., 2007; Mehra, 2003; Fermeglia and Torriano, 1999; Nayak et al., 2003; Pandey et al., 1992) have applied various mixing rules in binary and ternary liquid mixtures to calculate the refractive index and to check the validity of these mixing rules. The mixing behavior of such liquid mixtures containing acetonitrile is interesting due to the presence of cyano group coupled with amide linkage resulting interactions in the liquid mixtures. In this work, we present the experimental data on density and refractive index of binary liquid mixtures of formamide, *N*-methyl acetamide (NMA), di-methylformamide (DMF) and di-methylacetamide (DMA) with acetonitrile at T = 293.15, 298.15, 303.15, 308.15 and 313.15 K and atmospheric pressure over the whole concentration range. These data were analyzed in terms of Lorentz–Lorentz mixing rule (Tasic et al., 1992) model of Ramaswamy and Anbananthan (1981) and Shukla et al. (2011) and model suggested by Glinski (2003). Models (Ramaswamy and Anbananthan, 1981; Shukla et al., 2011; Glinski, 2003), associated, are based on the association constant as an adjustable parameter whereas model (Tasic et al., 1992), non-associated is based on the additivity of liquids. For that purpose, we have selected the liquids having weak interacting ability but immense sense of technological significance in chemical industries. Using these experimental data, deviation in molar refraction (ΔR) has been studied and fitted to a Redlich–Kister type polynomial equation (Redlich and Kister, 1948) to derive binary coefficients and estimated standard errors. An attempt has also been made to correlate the experimental properties with the McAllister (1960) equation which is based on Eyring theory of absolute reaction rates and for liquids, the free energy of activation is additive on a number fraction.

The association phenomenon has been related usually to the deviation of different quantities from additivity and the model (Ramaswamy and Anbananthan, 1981; Shukla et al., 2011) is simple averaged geometrical derivations in terms of equilibrium. The mixing behavior of liquids and their correlation with molecular interaction have also been made using different liquid models. It is our first attempt to correlate all the models (associated and non-associated) to predict the mixing behavior of binary liquid mixtures from refractive index data.

2. Experimental section

2.1. Materials

High purity and AR grade samples of formamide, *N*-methyl acetamide (NMA), di-methylformamide (DMF) and di-methylacetamide (DMA) and acetonitrile used in this experiment were obtained from Merck Co. Inc., Germany, and purified by distillation in which the middle fraction was collected. The liquids were stored in dark bottles over 0.4 mm molecular sieves to reduce water content and were partially degassed with a vacuum pump. The purity of each compound was checked by gas chromatography and the results indicated that the mole fraction purity was higher than 0.99. All the materials were used without further purification. The purity of chemicals used was confirmed by comparing the densities and refractive indices with those reported in the literature as shown in Table 1.

2.2. Apparatus and procedure

Before each series of experiments, we calibrated the instrument at atmospheric pressure with doubly distilled water. The densities of the pure components and their mixtures were measured with the bi capillary pyknometer with an accuracy of $\pm 5.0 \times 10^{-4}$ kg m^{-3}. The liquid mixtures were prepared by mass in an air tight stopped bottle using an electronic balance model SHIMADZUAX-200 accurate to within ± 0.1 mg. The average uncertainty in the composition of the mixtures was estimated to be less than ± 0.0001. All molar quantities were based on the IUPAC relative atomic mass table.

Refractive index for sodium D-line was measured using a thermostatically controlled Abbe refractometer (Agato 3T, Japan). Calibration of the instrument was performed with double distilled water. A minimum of three readings were taken for each composition and the average value was considered in all calculations. Refractive index data are accurate to ± 0.0001 units.

3. Theoretical

Ramaswamy and Anbananthan (1981) and Shukla et al. (2011) proposed the model based on the assumption of linearity of acoustic impedance with the mole fraction of components. Further Glinski (2003) assumed that when solute is added to solvent, the molecules interact according to the equilibrium as

$$A + B = AB \tag{1}$$

and the association constant K_{as} can be defined as

$$K_{as} = \frac{[AB]}{[A][B]} \tag{2}$$

where A is the amount of solvent and B is the amount of solute in the liquid mixture.

By applying the condition of linearity with composition

$$\Delta n_{obs} = x_A n_A + x_{AB} n_{AB} \tag{3}$$

where x_A, x_{AB}, n_A and n_{AB} are the mole fraction of A, mole fraction of associate AB, refractive index of A and refractive index of associate AB, respectively. The component AB cannot be obtained in its pure form. Following simplifications have been made, firstly, concentration term should be replaced by activities for concentrated solution and second, there are also molecules of non-associated components in the liquid mixture. Eq. (3) takes the form,

$$n_{obs} = [x_A n_A + x_B n_B + x_{AB} n_{AB}]\theta \tag{4}$$

where θ is a temperature dependent adjustable parameter which changes with the changing temperature conditions.

The general idea of this model can be, however, exploited as

$$K_{as} = \frac{[AB]}{(C_A - [AB])(C_B - [AB])} \tag{5}$$

where C_A and C_B are the initial molar concentrations of the components. One can take any value of K_{as} and calculate the equilibrium value of $[AB]$ for every composition of the mixture as well as $[A] = C_A - [AB]$ and $[B] = C_B - [AB]$. Replacing molar concentration by activities for concentrated solution, Eq. (5) becomes,

Table 1 Comparison of density and refractive index with literature data for pure components at 293.15, 298.15, 303.15, 308.15 and 313.15 K.

Compound	T	V (cm^3 $mole^{-1}$)	ρ_{exp} (g cm^{-3})	ρ_{lit} (g cm^{-3})[a]	n_{exp}	n_{lit}[a]
Acetonitrile	293.15	51.5379	0.7865	0.7822	1.3409	1.34411
	298.15	52.5540	0.7811	0.77649	1.3402	1.34163
	303.15	53.0841	0.7733	0.77125	1.3392	–
	308.15	53.5551	0.7665	–	1.3283	–
	313.15	53.9776	0.7605	–	1.3260	–
Formamide	293.15	39.7879	1.1320	1.1339	1.4409	1.44754
	298.15	39.8937	1.1290	1.12915	1.4370	1.44682
	303.15	40.0355	1.1250	–	1.4359	–
	308.15	40.1784	1.1210	–	1.4280	–
	313.15	40.5145	1.1117	–	1.4250	–
NMA	293.15	76.4404	0.9563	–	1.4279	–
	298.15	76.8502	0.9512	–	1.4270	–
	303.15	76.9311	0.9502	0.9520	1.4261	–
	308.15	77.2074	0.9468	0.94604	1.4250	1.4253
	313.15	77.7246	0.9405	–	1.4230	–
N,N-DMF	293.15	76.5260	0.9551	0.94873	1.4285	1.43047
	298.15	76.9287	0.9501	0.94387	1.4267	1.42817
	303.15	77.5984	0.9419	0.9412	1.4240	–
	308.15	78.1126	0.9357	–	1.4221	–
	313.15	78.3807	0.9325	0.9310	1.4205	–
N,N-DMA	293.15	90.5331	0.9623	0.9615	1.4361	–
	298.15	91.6859	0.9502	0.97633	1.4342	1.4384
	303.15	93.0769	0.9360	0.93169	1.4320	1.4356
	308.15	94.0008	0.9268	–	1.4300	–
	313.15	94.4799	0.9221	0.9232	1.4285	–

[a] Timmermans (1950) and Riddick et al. (1986).

Table 2 Coefficients of the Redlich–Kister equation and standard deviations (σ) for molar refractivity of binary liquid mixtures at various temperatures.

	T	A0	A1	A2	A3	σ
Acetonitrile + formamide						
ΔR	293.15	−2.0315	−0.1889	−0.9531	−2.8605	0.0904
	298.15	−1.9217	0.3225	0.0652	−7.7578	0.0981
	303.15	−1.6476	−0.1599	−0.5022	−6.6511	0.1121
	308.15	−0.8264	−1.3079	2.7451	4.8070	0.0903
	313.15	−0.4447	1.9884	−2.7031	−4.8913	0.0705
Acetonitrile + NMA						
ΔR	293.15	1.2501	−0.4386	−2.3835	5.4272	0.1704
	298.15	0.7610	1.5891	−4.3049	−1.8726	0.1178
	303.15	1.5405	−0.9992	−4.7506	−0.2562	0.1422
	308.15	1.7268	−2.6296	−6.4052	3.2337	0.1500
	313.15	2.2992	−7.9806	−5.3893	17.5480	0.1800
Acetonitrile + DMF						
ΔR	293.15	0.4292	−4.0572	0.5360	13.8886	0.1243
	298.15	0.5172	−1.3493	2.6418	3.3518	0.1205
	303.15	−0.3637	−3.3653	−0.7733	5.8006	0.2001
	308.15	−1.1838	−0.4123	−6.8095	2.7590	0.0882
	313.15	−22.5512	21.7620	71.9787	−81.9660	4.2072
Acetonitrile + DMA						
ΔR	293.15	−0.7744	0.8444	2.0731	0.0058	0.0775
	298.15	−1.3985	1.1097	7.6152	−6.6792	0.1061
	303.15	0.0721	−6.2540	−0.9942	20.2712	0.1930
	308.15	0.4789	−1.0475	4.0208	3.8755	0.0789
	313.15	−1.0524	7.1479	1.5652	−11.4325	0.2420

Table 3 Parameters of McAllister three body and four body interaction models and standard deviations (σ) for refractive index of binary liquid mixtures at various temperatures.

Component	Temperature	McAllister three body (n)			McAllister four body (n)			
		a	b	σ	a	b	c	σ
Acetonitrile + Formamide	293.15	1.3844	1.4289	0.0029	0.3515	3.1291	0.5709	0.0546
	298.15	1.3829	1.4324	0.0032	1.3811	1.3899	1.4440	0.0028
	303.15	1.3827	1.4326	0.0032	1.3814	1.3885	1.4448	0.0028
	308.15	1.3889	1.4019	0.0048	1.3935	1.3577	1.4312	0.0037
	313.15	1.3720	1.3980	0.0026	1.3510	1.4023	1.3941	0.0022
Acetonitrile + NMA	293.15	1.4300	1.4562	0.0473	1.3487	1.5770	1.3435	0.0447
	298.15	1.4498	1.4261	0.0022	1.4050	1.4563	1.4040	0.0015
	303.15	1.4364	1.4355	0.0042	1.3834	1.4847	1.3881	0.0025
	308.15	1.4296	1.4300	0.0042	1.3805	1.4721	1.3884	0.0030
	313.15	1.4281	1.4223	0.0008	1.3969	1.4160	1.4213	0.0008
Acetonitrile + DMF	293.15	1.4537	1.4300	0.0033	1.4301	1.4081	1.4456	0.0027
	298.15	1.4661	1.4342	0.0023	1.4389	1.4166	1.4480	0.0013
	303.15	1.4389	1.4405	0.0018	1.4066	1.4338	1.4326	0.0046
	308.15	1.4242	1.4218	0.0045	1.3726	1.4710	1.3808	0.0026
	313.15	1.4306	1.4257	0.0018	1.3994	1.4176	1.4240	0.0018
Acetonitrile + DMA	293.15	1.4634	1.4365	0.0021	1.4648	1.4366	1.4500	0.0020
	298.15	1.4572	1.4264	0.0032	1.4714	1.3989	1.4662	0.0015
	303.15	1.4868	1.3932	0.0496	1.5610	1.2492	1.5670	0.0479
	308.15	1.4609	1.4318	0.0035	1.4778	1.3959	1.4743	0.0008
	313.15	1.4452	1.4032	0.0039	1.4322	1.4451	1.3982	0.0035

Table 4 Comparison of average and average percent deviation values obtained from various liquid state models.

Temperature	$K_{as} \times 10^4$	$\%\Delta R_{LL}$ Eq. (10)	$\%\Delta R_{RS}$ Eq. (4)	$\%\Delta R_{GLI}$ Eq. (9)	n_{LL} Eq. (10)	n_{RS} Eq. (4)	n_{GLI} Eq. (9)	n_{McA} Eq. (15)	n_{McA} Eq. (16)
Acetonitrile + formamide									
293.15	1.3000	2.97	1.79	3.11	0.0180	0.0081	0.0140	0.0021	0.3865
298.15	1.0000	3.41	2.20	3.54	0.0169	0.0099	0.0159	0.0023	0.0019
303.15	1.2000	3.57	2.34	3.70	0.0152	0.0105	0.0166	0.0024	0.0020
308.15	1.1200	3.71	8.72	3.86	0.0056	0.0370	0.0164	0.0042	0.0029
313.15	1.1100	2.44	1.24	2.58	0.0075	0.0051	0.0108	0.0020	0.0018
Acetonitrile + NMA									
293.15	1.4000	2.91	3.20	3.02	0.0063	0.0137	0.0288	0.0212	0.0242
298.15	1.5000	2.14	2.42	2.24	0.0043	0.0105	0.0097	0.0018	0.0012
303.15	1.6000	1.90	2.18	1.96	0.0066	0.0095	0.0085	0.0036	0.0022
308.15	1.7000	1.37	1.69	1.43	0.0077	0.0073	0.0061	0.0032	0.0023
313.15	1.8000	1.61	2.03	1.74	0.0061	0.0084	0.0072	0.0006	0.0006
Acetonitrile + DMF									
293.15	1.1800	2.68	3.95	2.79	0.0059	0.0172	0.0121	0.0028	0.0020
298.15	1.1900	3.81	5.00	3.92	0.0061	0.0221	0.0173	0.0020	0.0011
303.15	1.2100	2.41	3.59	2.51	0.0050	0.0157	0.0110	0.0017	0.0032
308.15	1.3200	1.24	1.94	1.30	0.0129	0.0083	0.0055	0.0036	0.0023
313.15	1.3300	2.07	3.32	2.19	0.0058	0.0141	0.0091	0.0016	0.0014
Acetonitrile + DMA									
293.15	1.3400	3.03	4.98	3.16	0.0035	0.0220	0.0139	0.0019	0.0016
298.15	1.3500	2.42	4.33	2.55	0.0042	0.0189	0.0111	0.0025	0.0014
303.15	1.3600	2.23	4.14	2.36	0.0204	0.0333	0.0255	0.0240	0.0265
308.15	1.3700	3.28	5.16	3.40	0.0074	0.0226	0.0149	0.0030	0.0006
313.15	1.3800	1.80	3.46	1.92	0.0053	0.0145	0.0080	0.0033	0.0030

$$K_{as} = \frac{a_{AB}}{(a_A - a_{AB})(a_B - a_{AB})} \tag{6}$$

where a_A, a_B and a_{AB} are the activities of components A, B and associate AB, respectively. Taking equimolar activities which are equal to

$$a'_A = a_A - a_{AB} \quad \text{and} \quad a'_B = a_B - a_{AB}$$

where a'_A and a'_B are the activities of $[A]$ and $[B]$ in equimolar quantities, respectively.

From Eq. (6) one can obtain the value of K_{as} as

Table 5 Experimental densities (ρ), experimental refractive index (n_{exp}), experimental molar refractivity (R_{exp}), theoretical molar refractivity from Ramaswamy and Anbananthan (Eq. (4)), Lorentz–Lorentz relation (Eq. (10)), model devised by Glinski (Eq. (9)), experimental refractive indices, theoretical refractive indices from Ramaswamy and Anbananthan (Eq. (4)), Lorenz–Lorenz relation (Eq. (10)), model devised by Glinski (Eq. (9)) of binary liquid mixtures at various temperatures.

Φ_1	ρ_{mix} (g cm^3)	R_{LL} Eq. (10)	R_{exp}	R_{RS} Eq. (4)	R_{GLI} Eq. (9)	$\%\Delta R_{LL}$	$\%\Delta R_{RS}$	$\%\Delta R_{GLI}$	n_{exp}	n_{LL} (Eq. (10))	n_{RS} (Eq. (4))	n_{GLI} (Eq. (9))
Acetonitrile + formamide												
T = 293.15 K												
0.1531	1.1258	10.1213	10.4027	10.1943	10.1116	2.70	2.00	2.80	1.4387	1.4455	1.4286	1.4246
0.2892	1.0992	9.9640	10.3566	10.0854	9.9483	3.79	2.62	3.94	1.4298	1.4405	1.4169	1.4105
0.4108	1.0835	9.7429	9.9907	9.8913	9.7243	2.48	0.99	2.67	1.4105	1.4401	1.4058	1.3981
0.5203	1.0405	9.8022	10.1990	9.9651	9.7824	3.89	2.29	4.08	1.4058	1.4264	1.3952	1.3871
0.6193	1.0102	9.7758	10.2255	9.9374	9.7568	4.40	2.82	4.58	1.3978	1.4181	1.3851	1.3773
0.7094	0.9705	9.8718	10.2417	10.0215	9.8546	3.61	2.15	3.78	1.3848	1.4050	1.3755	1.3685
0.7915	0.9403	9.9024	10.2041	10.0281	9.8883	2.96	1.72	3.10	1.3735	1.3958	1.3663	1.3606
0.8668	0.9015	10.0541	10.2753	10.1473	10.0440	2.15	1.25	2.25	1.3625	1.3822	1.3574	1.3534
0.9361	0.8503	10.3916	10.4727	10.4435	10.3860	0.78	0.28	0.83	1.3501	1.3623	1.3490	1.3468
T = 298.15 K												
0.1553	1.1015	10.2680	10.6322	10.3447	10.2583	3.43	2.70	3.52	1.4387	1.4334	1.4251	1.4210
0.2927	1.0825	10.0469	10.4993	10.1735	10.0316	4.31	3.10	4.45	1.4290	1.4331	1.4138	1.4072
0.4149	1.0657	9.8412	10.1554	9.9960	9.8232	3.09	1.57	3.27	1.4104	1.4333	1.4030	1.3952
0.5245	1.0345	9.8007	10.2492	9.9683	9.7818	4.38	2.74	4.56	1.4054	1.4262	1.3928	1.3845
0.6233	0.9985	9.8379	10.3384	10.0049	9.8197	4.84	3.23	5.02	1.3975	1.4163	1.3830	1.3751
0.7128	0.9624	9.9087	10.3231	10.0626	9.8923	4.01	2.52	4.17	1.3846	1.4057	1.3737	1.3666
0.7943	0.9351	9.9180	10.2511	10.0467	9.9046	3.25	1.99	3.38	1.3731	1.3988	1.3648	1.3590
0.8687	0.8792	10.2755	10.5281	10.3726	10.2656	2.40	1.48	2.49	1.3622	1.3775	1.3562	1.3521
0.9371	0.8492	10.3783	10.4809	10.4312	10.3731	0.98	0.47	1.03	1.3499	1.3683	1.3480	1.3459
T = 303.15 K												
0.1562	1.0998	10.2589	10.6338	10.3374	10.2493	3.53	2.79	3.62	1.4380	1.4337	1.4240	1.4199
0.2940	1.0735	10.1048	10.5852	10.2353	10.0895	4.54	3.31	4.68	1.4289	1.4304	1.4127	1.4060
0.4164	1.0538	9.9254	10.2635	10.0851	9.9073	3.29	1.74	3.47	1.4101	1.4295	1.4020	1.3940
0.5261	1.0258	9.8564	10.3271	10.0287	9.8375	4.56	2.89	4.74	1.4050	1.4242	1.3917	1.3833
0.6248	0.9802	9.9935	10.5197	10.1668	9.9750	5.00	3.35	5.18	1.3970	1.4098	1.3820	1.3739
0.7142	0.9594	9.9117	10.3410	10.0690	9.8954	4.15	2.63	4.31	1.3840	1.4067	1.3726	1.3655
0.7953	0.9256	9.9917	10.3513	10.1241	9.9784	3.47	2.19	3.60	1.3729	1.3968	1.3637	1.3579
0.8695	0.8728	10.3222	10.5974	10.4217	10.3124	2.60	1.66	2.69	1.3619	1.3772	1.3552	1.3510
0.9374	0.8402	10.4610	10.5658	10.5153	10.4558	0.99	0.48	1.04	1.3489	1.3667	1.3470	1.3448
T = 308.15 K												
0.1569	1.0856	10.2091	10.3831	9.9464	10.1983	1.68	4.21	1.78	1.4199	1.4208	1.3998	1.4114
0.2951	1.0568	10.0653	10.3470	9.6011	10.0481	2.72	7.21	2.89	1.4105	1.4158	1.3772	1.3970
0.4177	1.0215	10.0245	10.5834	9.4163	10.0039	5.28	11.03	5.48	1.4099	1.4073	1.3594	1.3846
0.5274	0.9856	10.0284	10.4048	9.3348	10.0067	3.62	10.28	3.83	1.3904	1.3979	1.3458	1.3736
0.6260	0.9508	10.0577	10.4341	9.3380	10.0368	3.61	10.50	3.81	1.3801	1.3883	1.3359	1.3639
0.7152	0.9256	10.0168	10.3693	9.3357	9.9983	3.40	9.97	3.58	1.3700	1.3827	1.3293	1.3552
0.7962	0.8809	10.2241	10.7356	9.6238	10.2088	4.76	10.36	4.91	1.3675	1.3675	1.3255	1.3474
0.8701	0.8405	10.4269	10.9501	9.9677	10.4158	4.78	8.97	4.88	1.3599	1.3538	1.3243	1.3404
0.9377	0.8028	10.6390	11.0323	10.3800	10.6330	3.57	5.91	3.62	1.3480	1.3409	1.3253	1.3341
T = 313.15 K												
0.1568	1.0807	10.1923	10.2642	10.2764	10.1816	0.70	−0.12	0.81	1.4123	1.4196	1.4128	1.4085
0.2950	1.0559	10.0117	10.2513	10.1511	9.9946	2.34	0.98	2.50	1.4058	1.4163	1.4013	1.3943
0.4176	1.0158	10.0183	10.2889	10.1924	9.9978	2.63	0.94	2.83	1.3945	1.4056	1.3903	1.3819
0.5273	0.9758	10.0661	10.3897	10.2564	10.0444	3.11	1.28	3.32	1.3854	1.3942	1.3798	1.3710
0.6259	0.9365	10.1475	10.5636	10.3379	10.1265	3.94	2.14	4.14	1.3789	1.3825	1.3698	1.3614
0.7151	0.8905	10.3463	10.7441	10.5241	10.3272	3.70	2.05	3.88	1.3687	1.3672	1.3602	1.3528
0.7961	0.8726	10.2564	10.5195	10.4037	10.2410	2.50	1.10	2.65	1.3555	1.3643	1.3511	1.3450
0.8700	0.8405	10.3610	10.6291	10.4694	10.3499	2.52	1.50	2.63	1.3482	1.3545	1.3424	1.3380
0.9377	0.7992	10.6191	10.5675	10.6789	10.6131	0.49	-1.05	0.43	1.3302	1.3398	1.3340	1.3317
Acetonitrile + NMA												
T = 303.15 K												
0.2023	0.9357	17.0320	17.3975	17.0260	17.0160	2.10	2.14	2.19	1.4157	1.4199	1.4097	1.4094
0.3538	0.9235	15.3004	15.7587	15.2539	15.2795	2.91	3.20	3.04	1.4083	1.4100	1.3951	1.3959
0.4778	0.8895	14.4204	14.9367	14.3497	14.3984	3.46	3.93	3.60	1.3903	1.4013	1.3835	1.3850

(*continued on next page*)

Table 5 (*continued*).

Φ_1	ρ_{mix} (g cm^3)	R_{LL} Eq. (10)	R_{exp}	R_{RS} Eq. (4)	R_{GLI} Eq. (9)	$\%\Delta R_{LL}$	$\%\Delta R_{RS}$	$\%\Delta R_{GLI}$	n_{exp}	n_{LL} (Eq. (10))	n_{RS} (Eq. (4))	n_{GLI} (Eq. (9))
0.5898	0.8764	13.4249	14.1096	13.3656	13.4045	4.85	5.27	5.00	1.3829	1.3976	1.3740	1.3753
0.6827	0.8658	12.6586	13.1657	12.6060	12.6411	3.85	4.25	3.98	1.3769	1.3845	1.3662	1.3673
0.7647	0.8465	12.1655	12.6080	12.1257	12.1513	3.51	3.82	3.62	1.3668	1.3756	1.3595	1.3604
0.8346	0.8351	11.6974	11.8827	11.6667	11.6867	1.56	1.82	1.65	1.3607	1.3612	1.3539	1.3545
0.8982	0.8252	11.2834	11.5844	11.2678	11.2765	2.60	2.73	2.66	1.3554	1.3599	1.3489	1.3492
0.9540	0.8051	11.0899	11.2439	11.0562	11.0866	1.37	1.67	1.40	1.3453	1.3501	1.3446	1.4974
T = 303.15 K												
0.2046	0.9305	17.0905	17.2604	17.0659	17.0746	0.98	1.13	1.08	1.4160	1.4135	1.4082	1.4084
0.3570	0.9197	15.3294	15.7864	15.2734	15.3086	2.90	3.25	3.03	1.4102	1.4089	1.3938	1.3949
0.4813	0.8807	14.5323	15.0495	14.4567	14.5104	3.44	3.94	3.58	1.3903	1.4002	1.3824	1.3840
0.5933	0.8704	13.4888	14.0326	13.4279	13.4687	3.88	4.31	4.02	1.3850	1.3921	1.3731	1.3744
0.6858	0.8595	12.7262	13.1270	12.6733	12.7089	3.05	3.46	3.19	1.3794	1.3801	1.3654	1.3665
0.7673	0.8405	12.2301	12.5317	12.1910	12.2161	2.41	2.72	2.52	1.3698	1.3701	1.3588	1.3597
0.8365	0.8305	11.7430	11.8801	11.7132	11.7325	1.15	1.41	1.24	1.3648	1.3589	1.3532	1.3539
0.8995	0.8205	11.3317	11.3620	11.3169	11.3250	0.27	0.40	0.33	1.3598	1.3500	1.3484	1.3487
0.9546	0.8015	11.1259	11.2594	11.1232	11.1226	1.19	1.21	1.22	1.3504	1.3489	1.3442	1.3442
T = 303.15 K												
0.2060	0.9108	17.4263	17.6150	17.3527	17.4103	1.07	1.49	1.16	1.4064	1.4130	1.4060	1.4075
0.3591	0.8998	15.6384	16.0869	15.5483	15.6175	2.79	3.35	2.92	1.4012	1.4075	1.3921	1.3940
0.4835	0.8712	14.6638	15.1900	14.5643	14.6420	3.46	4.12	3.61	1.3871	1.3995	1.3810	1.3832
0.5954	0.8652	13.5466	14.0467	13.4694	13.5268	3.56	4.11	3.70	1.3844	1.3899	1.3719	1.3737
0.6877	0.8501	12.8466	13.2317	12.7821	12.8295	2.91	3.40	3.04	1.3771	1.3788	1.3644	1.3659
0.7689	0.8357	12.2830	12.4633	12.2360	12.2692	1.45	1.82	1.56	1.3702	1.3655	1.3580	1.3591
0.8377	0.8256	11.7978	11.6866	11.7630	11.7875	−0.95	−0.65	−0.86	1.3654	1.3501	1.3526	1.3534
0.9003	0.7958	11.6706	11.6179	11.6523	11.6638	−0.45	−0.30	−0.39	1.3509	1.3468	1.3479	1.3483
0.9550	0.7853	11.3447	11.2952	11.3406	11.3415	−0.44	−0.40	−0.41	1.3459	1.3423	1.3438	1.3438
T = 308.15 K												
0.2069	0.9007	17.5779	17.6987	17.4821	17.5617	0.68	1.22	0.77	1.4023	1.4100	1.4043	1.4063
0.3603	0.8795	15.9574	16.2728	15.8510	15.9361	1.94	2.59	2.07	1.3923	1.4023	1.3905	1.3929
0.4848	0.8654	14.7223	15.0544	14.6124	14.7005	2.21	2.94	2.35	1.3857	1.3925	1.3795	1.3821
0.5967	0.8556	13.6611	14.2043	13.5764	13.6412	3.82	4.42	3.96	1.3813	1.3899	1.3706	1.3725
0.6888	0.8456	12.8795	13.1076	12.8102	12.8624	1.74	2.27	1.87	1.3768	1.3726	1.3631	1.3648
0.7698	0.8298	12.3363	12.3823	12.2860	12.3225	0.37	0.78	0.48	1.3693	1.3600	1.3568	1.3580
0.8384	0.8198	11.8487	11.7359	11.8118	11.8385	−0.96	−0.65	−0.87	1.3646	1.3490	1.3515	1.3523
0.9008	0.7902	11.7214	11.6759	11.7019	11.7146	−0.39	−0.22	−0.33	1.3503	1.3460	1.3468	1.3472
0.9552	0.7805	11.3838	11.3616	11.3791	11.3806	−0.19	−0.15	−0.17	1.3458	1.3422	1.3427	1.3428
T = 313.15 K												
0.2071	0.8798	17.8412	18.0763	17.7570	17.8203	1.30	1.77	1.42	1.3910	1.4089	1.4007	1.4023
0.3606	0.8697	15.9421	16.3079	15.8422	15.9150	2.24	2.86	2.41	1.3851	1.3982	1.3854	1.3873
0.4851	0.8556	14.6661	15.0200	14.5584	14.6383	2.36	3.07	2.54	1.3774	1.3865	1.3731	1.3754
0.5970	0.8425	13.6249	13.9268	13.5416	13.5994	2.17	2.77	2.35	1.3703	1.3748	1.3632	1.3649
0.6891	0.8346	12.7838	13.0216	12.7152	12.7621	1.83	2.35	1.99	1.3659	1.3645	1.3549	1.3564
0.7700	0.8194	12.2113	12.4016	12.1617	12.1938	1.53	1.93	1.68	1.3580	1.3556	1.3479	1.3489
0.8386	0.8008	11.8332	12.0112	11.7961	11.8200	1.48	1.79	1.59	1.3485	1.3489	1.3419	1.3427
0.9009	0.7824	11.5275	11.6073	11.5087	11.5189	0.69	0.85	0.76	1.3393	1.3400	1.3368	1.3371
0.9553	0.7615	11.3428	11.4415	11.3389	11.3387	0.86	0.90	0.90	1.3290	1.3356	1.3322	1.3322
Acetonitrile + DMF												
T = 293.15 K												
0.1551	0.9391	17.6433	17.8874	17.4617	17.6297	1.36	2.38	1.44	1.4189	1.4211	1.4097	1.4141
0.2923	0.9297	15.9640	16.5653	15.7119	15.9441	3.63	5.15	3.75	1.4128	1.4196	1.3951	1.4017
0.4146	0.9158	14.7188	15.1063	14.4522	14.6967	2.56	4.33	2.71	1.4047	1.4032	1.3835	1.3908
0.5242	0.8957	13.8215	14.2602	13.5687	13.7996	3.08	4.85	3.23	1.3936	1.3956	1.3740	1.3812
0.6229	0.8748	13.1170	13.4980	12.8943	13.0971	2.82	4.47	2.97	1.3823	1.3855	1.3662	1.3726
0.7125	0.8569	12.5066	12.9444	12.3235	12.4897	3.38	4.80	3.51	1.3727	1.3799	1.3595	1.3649
0.7941	0.8354	12.0585	12.4043	11.9190	12.0453	2.79	3.91	2.89	1.3615	1.3700	1.3539	1.3580
0.8685	0.8253	11.5379	11.9253	11.4454	11.5289	3.25	4.02	3.32	1.3559	1.3653	1.3489	1.3518
0.9370	0.7902	11.4444	11.5915	11.3973	11.4397	1.27	1.68	1.31	1.3385	1.3512	1.3446	1.3461
T = 298.15 K												
0.1570	0.9342	17.6705	18.1493	17.4967	17.6571	2.64	3.60	2.71	1.4182	1.4256	1.4082	1.4124
0.2953	0.9272	15.9498	16.6204	15.7095	15.9302	4.03	5.48	4.15	1.4143	1.4199	1.3938	1.4001

Table 5 (*continued*).

Φ_1	ρ_{mix} (g cm^3)	R_{LL} Eq. (10)	R_{exp}	R_{RS} Eq. (4)	R_{GLI} Eq. (9)	$\%\Delta R_{LL}$	$\%\Delta R_{RS}$	$\%\Delta R_{GLI}$	n_{exp}	n_{LL} (Eq. (10))	n_{RS} (Eq. (4))	n_{GLI} (Eq. (9))
0.4181	0.9215	14.5781	15.2423	14.3267	14.5567	4.36	6.01	4.50	1.4112	1.4102	1.3824	1.3893
0.5277	0.8901	13.8646	14.6061	13.6237	13.8433	5.08	6.73	5.22	1.3951	1.4036	1.3731	1.3799
0.6263	0.8721	13.1200	13.7547	12.9087	13.1007	4.61	6.15	4.75	1.3859	1.3924	1.3654	1.3715
0.7154	0.8504	12.5702	13.1198	12.3960	12.5539	4.19	5.52	4.31	1.3749	1.3824	1.3588	1.3639
0.7964	0.8344	12.0466	12.5870	11.9148	12.0338	4.29	5.34	4.39	1.3668	1.3756	1.3532	1.3572
0.8702	0.8248	11.5239	11.9355	11.4367	11.5153	3.45	4.18	3.52	1.3620	1.3654	1.3484	1.3511
0.9379	0.7899	11.4322	11.6256	11.3879	11.4278	1.66	2.05	1.70	1.3448	1.3522	1.3442	1.3455
T = 303.15 K												
0.1572	0.9304	17.6550	18.0095	17.4852	17.6423	1.97	2.91	2.04	1.4181	1.4199	1.4060	1.4101
0.2956	0.9255	15.9091	16.5326	15.6750	15.8906	3.77	5.19	3.88	1.4157	1.4165	1.3921	1.3981
0.4184	0.9192	14.5584	15.0537	14.3133	14.5381	3.29	4.92	3.42	1.4125	1.4033	1.3810	1.3877
0.5281	0.8892	13.8323	14.3290	13.5979	13.8122	3.47	5.10	3.61	1.3973	1.3945	1.3719	1.3785
0.6266	0.8706	13.1050	13.4597	12.8994	13.0867	2.64	4.16	2.77	1.3880	1.3822	1.3644	1.3703
0.7157	0.8584	12.4231	12.7882	12.2555	12.4078	2.85	4.17	2.97	1.3819	1.3755	1.3580	1.3630
0.7966	0.8261	12.1436	12.4042	12.0143	12.1315	2.10	3.14	2.20	1.3659	1.3654	1.3526	1.3564
0.8703	0.8259	11.4906	11.5378	11.4060	11.4825	0.41	1.14	0.48	1.3659	1.3524	1.3479	1.3505
0.9379	0.7853	11.4858	11.6249	11.4424	11.4815	1.20	1.57	1.23	1.3460	1.3499	1.3438	1.3451
T = 308.15 K												
0.1575	0.9280	17.6332	17.3847	17.4653	17.6207	−1.43	−0.46	−1.36	1.4184	1.4022	1.4043	1.4083
0.2961	0.9234	15.8865	16.2197	15.6552	15.8684	2.05	3.48	2.17	1.4163	1.4065	1.3905	1.3965
0.4190	0.9065	14.7098	15.0335	14.4649	14.6897	2.15	3.78	2.29	1.4079	1.3964	1.3795	1.3861
0.5286	0.8801	13.9274	14.0855	13.6941	13.9076	1.12	2.78	1.26	1.3947	1.3825	1.3706	1.3770
0.6271	0.8647	13.1509	13.3713	12.9470	13.1330	1.65	3.17	1.78	1.3871	1.3765	1.3631	1.3689
0.7161	0.8561	12.4171	12.5136	12.2515	12.4021	0.77	2.09	0.89	1.3830	1.3654	1.3568	1.3617
0.7970	0.8248	12.1258	12.0259	11.9983	12.1140	−0.83	0.23	−0.73	1.3675	1.3524	1.3515	1.3552
0.8706	0.8234	11.4920	11.4988	11.4084	11.4840	0.06	0.79	0.13	1.3669	1.3499	1.3468	1.3494
0.9381	0.7805	11.5242	11.4000	11.4813	11.5201	−1.09	−0.71	−1.05	1.3459	1.3401	1.3427	1.3440
T = 313.15 K												
0.1581	0.9255	17.5590	17.8738	17.3750	17.5430	1.76	2.79	1.85	1.4158	1.4138	1.4007	1.4051
0.2970	0.9199	15.7847	16.1754	15.5310	15.7615	2.41	3.98	2.56	1.4119	1.4035	1.3854	1.3918
0.4200	0.9002	14.6181	15.0482	14.3487	14.5923	2.86	4.65	3.03	1.4010	1.3937	1.3731	1.3803
0.5297	0.8751	13.7831	14.1264	13.5267	13.7576	2.43	4.24	2.61	1.3876	1.3813	1.3632	1.3701
0.6282	0.8615	12.9546	13.4178	12.7309	12.9316	3.45	5.12	3.62	1.3801	1.3764	1.3549	1.3611
0.7170	0.8502	12.2408	12.5634	12.0587	12.2215	2.57	4.02	2.72	1.3738	1.3642	1.3479	1.3531
0.7977	0.8227	11.8741	12.0473	11.7345	11.8590	1.44	2.60	1.56	1.3597	1.3521	1.3419	1.3460
0.8711	0.8207	11.2374	11.4086	11.1459	11.2272	1.50	2.30	1.59	1.3582	1.3456	1.3368	1.3395
0.9383	0.7798	11.2192	11.1941	11.1723	11.2139	−0.22	0.19	−0.18	1.3379	1.3330	1.3322	1.3336
Acetonitrile + DMA												
T = 293.15 K												
0.1561	0.9591	20.0390	20.4129	19.7001	20.0211	1.83	3.49	1.92	1.4324	1.4298	1.4127	1.4203
0.2939	0.9512	17.5288	18.0019	17.0868	17.5033	2.63	5.08	2.77	1.4266	1.4200	1.3958	1.4067
0.4164	0.9421	15.6735	16.3668	15.2301	15.6461	4.24	6.95	4.40	1.4203	1.4156	1.3831	1.3949
0.5261	0.9159	14.5072	15.0818	14.1002	14.4806	3.81	6.51	3.99	1.4055	1.4025	1.3731	1.3844
0.6248	0.8856	13.6742	14.2744	13.3232	13.6500	4.21	6.66	4.37	1.3891	1.3945	1.3651	1.3751
0.7141	0.8653	12.8865	13.2809	12.6048	12.8662	2.97	5.09	3.12	1.3779	1.3801	1.3585	1.3668
0.7953	0.8529	12.1423	12.5919	11.9345	12.1268	3.57	5.22	3.69	1.3707	1.3748	1.3530	1.3593
0.8694	0.8355	11.5954	11.8436	11.4591	11.5849	2.10	3.25	2.18	1.3613	1.3614	1.3483	1.3526
0.9374	0.8159	11.1740	11.3953	11.1070	11.1687	1.94	2.53	1.99	1.3509	1.3543	1.3443	1.3464
T = 298.15 K												
0.1570	0.9358	20.4636	20.8744	20.1247	20.4456	1.97	3.59	2.05	1.4253	1.4287	1.4111	1.4186
0.2953	0.9256	17.9523	18.2016	17.5096	17.9268	1.37	3.80	1.51	1.4189	1.4123	1.3945	1.4052
0.4181	0.9145	16.0956	16.5355	15.6509	16.0682	2.66	5.35	2.83	1.4121	1.4065	1.3820	1.3935
0.5278	0.8995	14.7292	15.0866	14.3260	14.7029	2.37	5.04	2.54	1.4034	1.3945	1.3722	1.3832
0.6264	0.8755	13.7961	14.2897	13.4510	13.7725	3.45	5.87	3.62	1.3904	1.3899	1.3643	1.3740
0.7155	0.8504	13.0823	13.5105	12.8038	13.0624	3.17	5.23	3.32	1.3770	1.3800	1.3578	1.3659
0.7964	0.8348	12.3810	12.8466	12.1748	12.3657	3.62	5.23	3.74	1.3685	1.3742	1.3524	1.3585
0.8701	0.8119	11.9125	12.1818	11.7764	11.9021	2.21	3.33	2.30	1.3566	1.3612	1.3478	1.3519
0.9378	0.7999	11.3821	11.4962	11.3158	11.3769	0.99	1.57	1.04	1.3501	1.3500	1.3439	1.3459

(*continued on next page*)

Table 5 (*continued*).

Φ_1	ρ_{mix} (g cm^3)	R_{LL} Eq. (10)	R_{exp}	R_{RS} Eq. (4)	R_{GLI} Eq. (9)	$\%\Delta R_{LL}$	$\%\Delta R_{RS}$	$\%\Delta R_{GLI}$	n_{exp}	n_{LL} (Eq. (10))	n_{RS} (Eq. (4))	n_{GLI} (Eq. (9))
T = 303.15 K												
0.1564	0.9248	20.6280	21.0667	20.2885	20.6106	2.08	3.69	2.17	1.4247	1.4274	1.4094	1.4168
0.2942	0.9016	18.3694	18.6463	17.9193	18.3444	1.48	3.90	1.62	1.4113	1.4113	1.3931	1.4037
0.4168	0.8908	16.4770	16.7356	16.0244	16.4500	1.55	4.25	1.71	1.4046	1.4000	1.3808	1.3922
0.5265	0.8705	15.1828	15.5576	14.7697	15.1567	2.41	5.06	2.58	1.3931	1.3936	1.3712	1.3821
0.6252	0.8559	14.0827	14.4035	13.7324	14.0594	2.23	4.66	2.39	1.3848	1.3835	1.3635	1.3732
0.7145	0.8391	13.2350	13.5058	12.9549	13.2156	2.01	4.08	2.15	1.3754	1.3742	1.3572	1.3652
0.7956	0.8069	12.7900	13.1542	12.5783	12.7748	2.77	4.38	2.88	1.3586	1.3699	1.3519	1.3580
0.8696	0.7909	12.2137	12.4679	12.0749	12.2034	2.04	3.15	2.12	1.3500	1.3600	1.3474	1.3515
0.9375	0.7854	11.5804	12.0059	11.5134	11.5753	3.54	4.10	3.59	1.3467	1.4990	1.3435	1.3455
T = 308.15 K												
0.1562	0.9158	20.7508	21.3781	20.4105	20.7336	2.93	4.53	3.01	1.4228	1.4298	1.4076	1.4150
0.2940	0.9016	18.3024	18.8255	17.8555	18.2778	2.78	5.15	2.91	1.4141	1.4158	1.3916	1.4020
0.4166	0.8759	16.6989	17.2305	16.2419	16.6719	3.09	5.74	3.24	1.3996	1.4056	1.3794	1.3907
0.5263	0.8669	15.1951	15.8398	14.7832	15.1694	4.07	6.67	4.23	1.3939	1.3998	1.3699	1.3807
0.6249	0.8498	14.1384	14.7286	13.7882	14.1154	4.01	6.38	4.16	1.3843	1.3901	1.3623	1.3719
0.7143	0.8257	13.4085	13.9863	13.1259	13.3891	4.13	6.15	4.27	1.3712	1.3822	1.3560	1.3639
0.7954	0.8067	12.7554	13.2274	12.5451	12.7404	3.57	5.16	3.68	1.3610	1.3721	1.3507	1.3568
0.8695	0.7895	12.2005	12.6176	12.0624	12.1903	3.31	4.40	3.39	1.3517	1.3641	1.3463	1.3504
0.9375	0.7759	11.6899	11.8883	11.6226	11.6848	1.67	2.23	1.71	1.3444	1.3512	1.3425	1.3445
T = 313.15 K												
0.1566	0.9098	20.7511	20.4521	20.3759	20.7293	−1.46	0.37	−1.36	1.4191	1.4056	1.4038	1.4118
0.2946	0.8890	18.3804	18.5576	17.8839	18.3491	0.95	3.63	1.12	1.4057	1.4026	1.3861	1.3974
0.4173	0.8654	16.4854	16.6883	15.9847	16.4516	1.22	4.22	1.42	1.3966	1.3912	1.3727	1.3849
0.5270	0.8566	15.1380	15.5174	14.6811	15.1053	2.45	5.39	2.66	1.3847	1.3854	1.3622	1.3739
0.6256	0.8442	13.9728	14.4572	13.5864	13.9438	3.35	6.02	3.55	1.3765	1.3792	1.3537	1.3641
0.7148	0.8198	13.2255	13.6420	12.9136	13.2011	3.05	5.34	3.23	1.3626	1.3687	1.3468	1.3554
0.7959	0.7908	12.7124	12.7749	12.4773	12.6933	0.49	2.33	0.64	1.3468	1.3501	1.3410	1.3476
0.8698	0.7828	11.9949	12.2468	11.8423	11.9821	2.06	3.30	2.16	1.3415	1.3489	1.3361	1.3405
0.9376	0.7742	11.3963	11.2615	11.3223	11.3899	−1.20	-0.54	−1.14	1.3360	1.3300	1.3319	1.3341

$$K_{as} = \frac{a_{AB}}{a_A a_B - a_A a_{AB} - a_B a_{AB} + a_{AB}^2} = \frac{a_{AB}}{a'_A \cdot a'_B} \tag{7}$$

Now, assuming any value of refractive index in the pure component, it is possible to compare the refractive indices calculated using Eq. (4) with the experimental values. On changing both the adjustable parameters K_{as} and n_{AB} gradually, one can get different values of the sum of squares of deviations,

$$S = \sum (n_{obs} - n_{cal})^2 \tag{8}$$

The minimum value of S can be obtained theoretically by a pair of the fitted parameters. But we found that for some K_{as} and n_{as}, the value of S is high and changes rapidly, and for others, it is low and changes slowly when changing the fitted parameters. In such cases, the value of n_{AB} should not be much lower than the lowest observed refractive index of the system or much higher than the highest one. Quantitatively, it should be reasonable to accept the pair of adjustable parameters K_{as} and n_{AB} which have the physical sense and which reproduce the experimental refractive indices satisfactorily.

Glinski (2003) suggested that experimental results with significantly well accuracy can be produced from the following equation as

$$n_{cal} = \frac{n_1 n_2}{\phi_1 n_2 + \phi_2 n_1} \tag{9}$$

where n_{cal} is the calculated refractive index, ϕ_1, ϕ_2 are the volume fractions of components 1 and 2 and n_1, n_2 are the refractive indices of pure components.

Lorentz–Lorentz (L–L) relation (Tasic et al., 1992) has a widest application during the evaluation of refractive indices of mixture and density of pure components as well as density of the mixture and represented in terms of specific refraction as

$$\left[\frac{n_m^2 - 1}{n_m^2 + 2}\right] = \left[\frac{n_1^2 - 1}{n_1^2 + 2}\right]\phi_1 + \left[\frac{n_2^2 - 1}{n_2^2 + 2}\right]\phi_2 \tag{10}$$

here n_m, n_1, n_2 are the refractive indices of mixture and pure components, 1 and 2, respectively, and ϕ_1, ϕ_2 are the volume fractions of pure components.

4. Results and discussion

Table 1 presents the comparison of experimental densities and refractive indices of acetonitrile, formamide, NMA, DMF and DMA with literature values (Timmermans, 1950; Riddick et al., 1986) at 293.15, 298.15, 303.15, 308.15 and 313.15 K. Coefficients of the Redlich–Kister polynomials and their standard deviations (σ) are presented in Table 2. Parameters of McAllister three body and four body interaction models and standard deviations for refractive indices are presented in Table 3. Table 4 presents the comparison of average percent molar refractivity deviation ($\%\Delta R$), average molar refractivity deviation (ΔR),

average refractive index deviation (Δn) obtained from Lorentz–Lorentz mixing rule, Ramaswamy and Anbananthan model, model devised by Glinski and MacAllister three body and four body models. Values of volume fraction (Φ_1), density of the mixture (ρ), experimental refractive index (n_{exp}), experimental molar refractivity (R_{exp}), theoretical molar refractivity (R_{theo}), percent deviation in molar refractivity values (%ΔR) and theoretical refractive index (n_{theo}) obtained from various models (Eqs. (4), (9), and (10)) for acetonitrile + formamide, acetonitrile + NMA, acetonitrile + DMF and acetonitrile + DMA over the whole composition range at five temperatures were recorded in Table 5.

Ramaswamy and Anbananthan model has been extended and corrected for the prediction of refractive index and molar refractivity of binary mixtures which was originally derived for the prediction of acoustical impedance. The results of fittings obtained from the model were utilized properly. The basic doubt regarding this model except the assumption of linearity of refractive index with mole fraction is that these liquids have poor tendency to form dimmers. Calculations were performed using a computer program which allows easily both the adjustable parameters simultaneously or the parameters were changed, manually.

We constructed the data sheet in a computer program, with association constant K_{as} and C_{AB} as the fitted parameters (C_{AB} is the refractive index in the pure component AB means a hypothetical liquid having only the associate A–B. On changing these parameters, the equilibrium concentrations of species [A], [B] and [AB] will change and the refractive index can be computed. The difference between experimental and theoretical refractive indices is used to obtain the sum of squares of deviations. It is assumed that in solution three associates are formed instead of two (pure A, pure B and AB). The values of refractive index in pure associate can be treated as a fitted one with the value of K_{as}. The mixing function, ΔR was represented mathematically by the Redlich–Kister equation (Redlich and Kister, 1948) for correlating the experimental data as

$$y = x_1(1 - x_1)\sum_{i=0}^{p} A_i(2x_1 - 1)^i \tag{11}$$

where y refers to ΔR, x_1 is the mole fraction and A_i is the coefficient. The values of coefficients A_i were determined by a multiple regression analysis based on the least squares method and are summarized along with the standard deviations between the experimental and fitted values of the respective function in Table 2. The standard deviation is defined by

$$\sigma = \left[\sum_{i=1}^{m}(y_{exp_i} - y_{cal_i})^2/(m - p)\right]^{1/2} \tag{12}$$

where m is the number of experimental points and p is the number of adjustable parameters. For the case the σ values lie between 0.07 and 4.20 and the largest σ value corresponds to acetonitrile + DMF mixture at 313.15 K.

Molar refractivity was obtained from refractive index data according to the following expression:

$$R = [n^2 - 1/n^2 + 2]M/\rho \tag{13}$$

where M is the mean molecular weight of the mixture and ρ is the mixture density.

The molar refractivity deviation function shown in Figs. 1 and 2 has been calculated by the following expression:

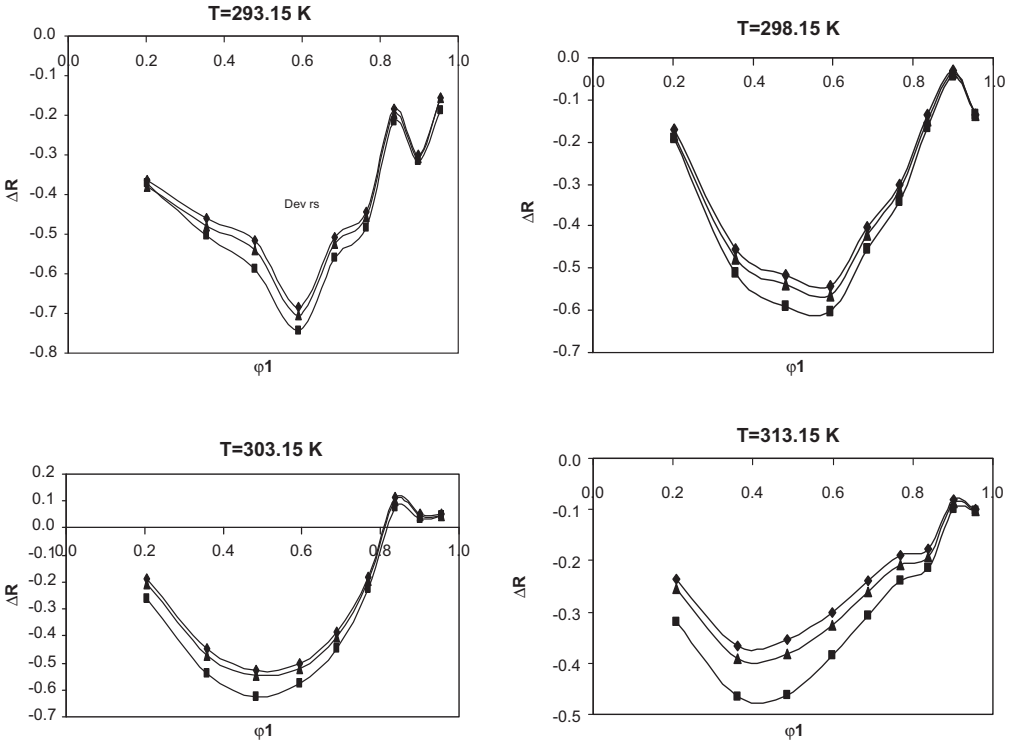

Figure 1 Plot of molar refractivity deviation, ΔR, with volume fraction, Φ_1, for Φ acetonitrile + (1−Φ) DMA at 293.15, 298.15, 303.15 and 313.15 K: ♦, Lorenz–Lorenz mixing rule (Eq. (10)), ■, Ramaswamy and Anbananthan model (Eq. (4)), ▲, model devised by Glinski (Eq. (9)).

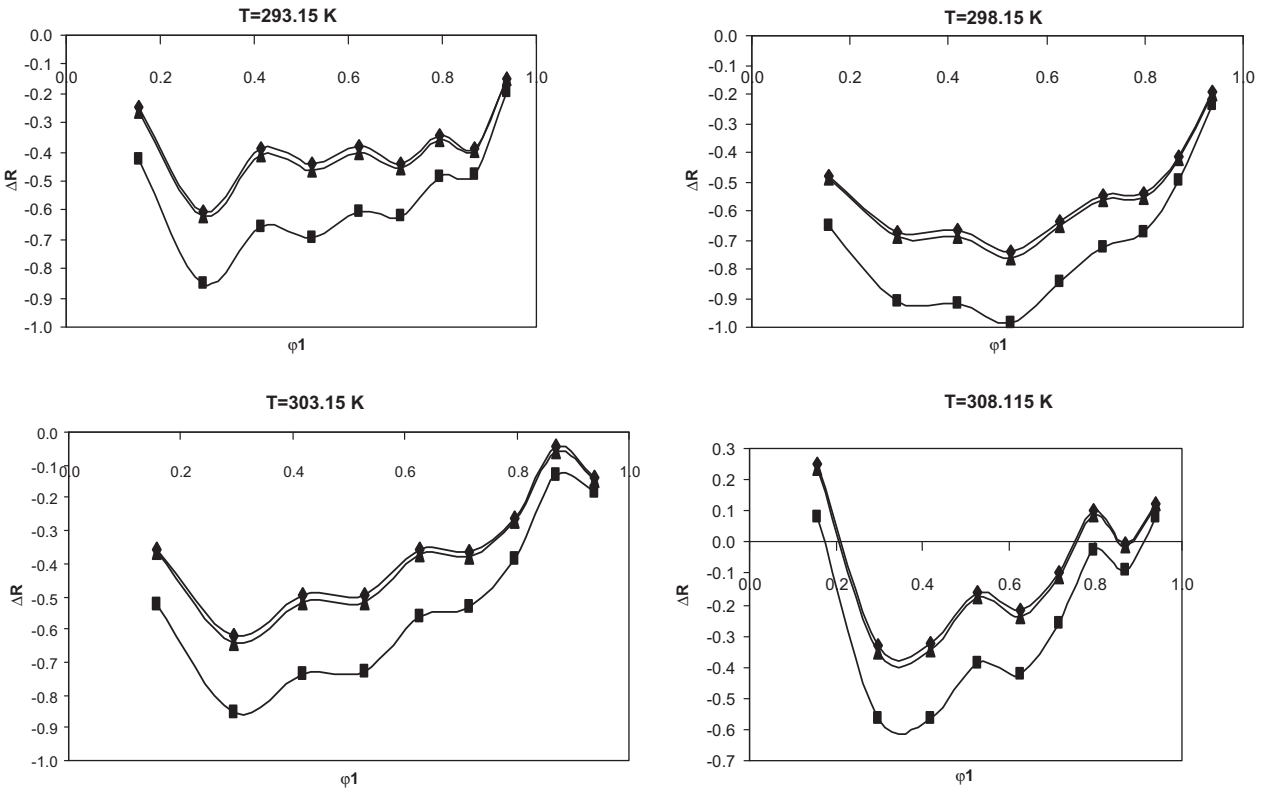

Figure 2 Plot of molar refractivity deviation, ΔR, with volume fraction, Φ_1, for Φ acetonitrile + $(1-\Phi)$ DMF at 293.15, 298.15, 303.15 and 308.15 K: ♦, Lorenz–Lorenz mixing rule (Eq. (10)), ■, Ramaswamy and Anbananthan model (Eq. (4)), ▲, model devised by Glinski (Eq. (9)).

$$\Delta R = R - \Phi_1 R_1 - \Phi_2 R_2 \tag{14}$$

where Φ_1 and Φ_2 are volume fractions which are obtained by the relation (Araguppi et al., 1999; Aralaguppi et al., 1990; Aralaguppi et al., 1999) as $\Phi_i = (\sum x_i v_i / \sum^2 x_i v_i)$. There is no general rule that states how to calculate a refractivity function. Konti et al. (1997) reported deviations in molar refractivity with volume fraction referring to the Lorentz–Lorentz mixing rules.

McAllister (1960) multibody interaction model which is based on the Eyring's theory of absolute reaction rates and for liquids the free energy of activation for viscosity is additive on a number fractions and that interactions of like and unlike molecules must be considered hence it can be applied to refractive index data. The three body model is defined as

$$\ln n = x_1^3 \ln n_1 + 3x_1^2 x_2 \ln a + 3x_1 x_2^2 \ln b + x_2^3 \ln n_2 - \ln(x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln(2 + M_2/M_1)/3] + 3x_1 x_2^2 \times \ln[(1 + 2M_2/M_1)/3] + x_2^3 \ln(M_2/M_1)] \tag{15}$$

and the four body model is given by

$$\ln n = x_1^4 \ln n_1 + 4x_1^3 x_2 \ln a + 6x_1^2 x_2^2 \ln b 4x_1 x_2^3 \ln c + x_2^4 \times \ln \eta_2 - \ln(x_1 + x_2 M_2/M_1)] + 4x_1^3 x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^2 x_2^2 \ln(1 + M_2/M_1)/2] + 4x_1 x_2^3 \times \ln[(1 + 3M_2/M_1)/4] + x_2^4 \ln(M_2/M_1)] \tag{16}$$

where n is the refractive index of the mixture and x_1, n_1, M_1, x_2, n_2 and M_2 are the mole fractions, refractive indices, and molecular weights of pure components 1 and 2, respectively; a, b and c are adjustable parameters that are characteristic of the system. In the above Eqs. (15) and (16) the coefficients a, b and c have been calculated using the least squares procedure. The estimated parameters of the refractive index equations and the standard deviations, σ, between the calculated and experimental values are given in Table 3. It is observed that the four body model of the McAllister equation correlated the refractive index of the mixture to a significantly higher degree of accuracy for all of the systems than does the three body model. Furthermore, the values of the McAllister parameters have shown a decreasing tendency with rise in temperature. Generally, McAllister's models are adequate in correlation for those systems as evidenced by small deviations.

The minimum and maximum average percent deviation ($\%\Delta R$) in molar refractivity and average deviation in refractive index for all the systems are found to be 1.24 & 8.72 and 0.0006 & 0.38 at 308.15 K, 313.15 & 293.15 K, respectively, as indicated in Table 4. With the increase of volume fraction (Φ), the values of refractive index obtained from all the models decrease at all temperatures except in few places. Results of molar refractivity computed from Eq. (13) for the entire systems show regular trend except in few places as shown in Table 5. The minimum and maximum percent deviation ($\%\Delta R$) in molar refractivity are 0.12 at 313.15 K for acetonitrile + formamide and 11.03 at 308.15 K for acetonitrile + formamide system, respectively.

The results of deviation in molar refraction, ΔR, plotted as a function of Φ_i for acetonitrile + DMA mixtures at 298.15, 303.15, 308.15 and 313.15 K are displayed in the Figs. 1 and 2 which indicate negative values for all the mixtures. In all

the cases, theoretical molar refractivity computed from all the models agree well within the experimental precision. The trend in all the figures is almost similar and negative. Molar refraction increases with molecular weight for all the systems. Density and refractive index depend on molecular weight and nature of solution and values decrease with the increase of temperature as evidenced in Table 5. Very close values of McAllister three and four body interaction models with the experimental data confirm the success of our experimental findings as evidenced in Table 4.

Finally, it can be concluded that the expressions used for interpolating the experimental data measured in this work provide good results as can be seen by inspecting the σ values obtained. All the models based on associated processes and non-associated processes give more reliable results and are helpful in deducing the internal structure of associates through the fitted values of refractive index in a hypothetical pure associate and observed dependence of concentration on the composition of a mixture.

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