

## Viscometric studies of molecular interactions in binary liquid mixtures of nitromethane with some polar and non-polar solvents at 298.15 K

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Densities and viscosities of binary liquid mixtures of nitromethane with some polar and non-polar solvents viz. methyl alcohol, ethyl alcohol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol, acetone, methyl ethyl ketone, methyl acetate, ethyl acetate, carbon tetrachloride, benzene and toluene, have been measured at 298.15 K. From the density and viscosity data the values of various excess properties, viz. excess viscosity ( $\eta^E$ ), excess molar volume ( $V^E$ ) and excess Gibbs free energy of activation of flow ( $\Delta G^{#E}$ ) have been determined. Further, the viscosities of binary liquid mixtures have been correlated to various viscosity models. On the basis of the values of interaction parameters of these viscosity models and also on the basis of the values of various excess properties, the nature and strength of molecular interactions between the mixing components of the binary liquid mixtures have been explained.

Various excess properties<sup>1</sup> like the excess Gibbs free energy, excess enthalpy, excess volume etc. have been helpful in the study of molecular interactions in binary liquid mixtures. Yadava and co-workers<sup>2</sup> measured dielectric constants and viscosities of binary mixtures of nitroalkanes with non-polar aromatic hydrocarbons and observed that the nitroalkane series show a distinct trend of their dipole moments. Aromatic hydrocarbons with different polarizabilities and progressively overcrowded steric environments were chosen as the second component to study the effect of the interactions between dipoles and sterically hindered polarizable compounds. Recently, they have reported<sup>3</sup> a study on the measurement of densities of binary mixtures of some nitroalkanes, viz. nitromethane, nitroethane and 2-nitropropane with symmetrical aromatic hydrocarbons (benzene, *p*-xylene and mesitylene) at 298.15 K with a view to determining the excess volume of mixing ( $V^E$ ). It has been found that  $V^E$  values are positive over the whole mole fraction range except those for the mixtures of nitroethane and 2-nitropropane with benzene and *p*-xylene where they are negative at lower and positive at higher mole fractions of nitroalkanes.

From the above survey of literature, it is seen that viscometric studies of binary mixtures of nitromethane with polar and non-polar solvents in regard to molecular interactions between the mixing components are still scanty. With this aim in view, comprehensive viscometric studies

of the following binary liquid mixtures of nitromethane with some polar and non-polar solvents vis-a-vis molecular interactions have been undertaken :

(1) Nitromethane + methyl alcohol, (2) nitromethane + ethyl alcohol, (3) nitromethane + *n*-propyl alcohol, (4) nitromethane + isopropyl alcohol, (5) nitromethane + *n*-butyl alcohol, (6) nitromethane + isobutyl alcohol, (7) nitromethane + acetone, (8) nitromethane + methyl ethyl ketone, (9) nitromethane + methyl acetate, (10) nitromethane + ethyl acetate, (11) nitromethane + carbon tetrachloride, (12) nitromethane + benzene, (13) nitromethane + toluene.

### Results and discussion

The experimental values of densities and viscosities of the pure components have been compared with the literature values and presented in Table 1. It is seen that the experimental values compare fairly well with the literature values.

The excess viscosity ( $\eta^E$ ) of a given binary liquid mixture was evaluated from the observed viscosity of mixture and that of its pure components using the following equation<sup>4</sup> :

$$\eta^E = \eta - (x_1\eta_1 + x_2\eta_2) \quad (1)$$

where  $\eta$  is viscosity of binary liquid mixture,  $\eta_1$  and  $\eta_2$  are the viscosities of pure components 1 and 2, respectively;

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**Table 1.** Comparison of experimental density ( $\rho$ ) and viscosity ( $\eta$ ) of pure liquids with literature values at 298.15 K

Pure liquid	$\rho$ g cm <sup>-3</sup>		$\eta$ mPa.s	
	Expt.	Lit. <sup>23</sup>	Expt.	Lit. <sup>24</sup>
Nitromethane	1.1317	1.1342	0.6313	0.6304
Methyl alcohol	0.7881	0.7863	0.5482	0.5441
Ethyl alcohol	0.7874	0.7854	1.1120	1.0784
<i>n</i> -Propyl alcohol	0.8000	0.7996	1.9544	1.9554
Isopropyl alcohol	0.7843	0.7812	2.0443	2.0462
<i>n</i> -Butyl alcohol	0.8063	0.8058	2.5383	2.5402
Isobutyl alcohol	0.8048	0.8024	3.1028	3.1012
Acetone	0.7808	0.7816	0.3121	0.3060
Methyl ethyl ketone	0.7974	0.7999	0.4011	0.4053
Methyl acetate	0.9239	0.9261	0.3711	0.3647
Ethyl acetate	0.8919	0.8953	0.4274	0.4239
Carbon tetrachloride	1.5861	1.5885	0.9096	0.9082
Benzene	0.8697	0.8671	0.6080	0.6048
Toluene	0.8605	0.8671	0.5641	0.5625

and  $x_1$  and  $x_2$  are the mole fractions of the components 1 and 2, respectively.

The excess molar volume ( $V^E$ ) of binary liquid mixtures was evaluated from the molar volume of the mixtures ( $V$ ) and that of the pure components ( $V_1$  and  $V_2$ ) using the following equation<sup>5</sup> :

$$V^E = V - (x_1 V_1 + x_2 V_2) \quad (2)$$

The molar volume  $V$  of binary liquid mixture was calculated from the measured density ( $\rho$ ) of mixtures using the following equation<sup>6</sup> :

$$V = \frac{x_1 M_1 + x_2 M_2}{\rho} \quad (3)$$

where  $x_1$  and  $x_2$  are the mole fractions of components 1 and 2 of the binary liquid mixtures, respectively;  $V_1$  is  $M_1/\rho_1$  and  $V_2$  is  $M_2/\rho_2$ ;  $\rho_1$  and  $\rho_2$  are the densities of components 1 and 2 of binary liquid mixtures, respectively.

The excess Gibbs free energy of activation of flow ( $\Delta G^{\#E}$ ) for the binary liquid mixture was computed from the Eyring's equation<sup>7</sup> :

$$\eta = \frac{Nh}{V} \exp\left[\frac{-\Delta S^{\#}}{R}\right] \exp\left[\frac{-\Delta H^{\#}}{RT}\right]$$

$$\text{or } \ln \eta V = \ln (Nh) - \frac{\Delta S^{\#}}{R} + \frac{\Delta H^{\#}}{RT}$$

and for the components 1 and 2

$$\ln \eta_1 V_1 = \ln (Nh) - \frac{\Delta S_1^{\#}}{R} + \frac{\Delta H_1^{\#}}{RT}$$

$$\ln \eta_2 V_2 = \ln (Nh) - \frac{\Delta S_2^{\#}}{R} + \frac{\Delta H_2^{\#}}{RT}$$

From the above

$$RT (\ln \eta V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2) = (\Delta H^{\#} - T\Delta S^{\#}) - (x_1 \Delta H_1^{\#} - x_1 T\Delta S_1^{\#}) - (x_2 \Delta H_2^{\#} - x_2 T\Delta S_2^{\#})$$

Since  $\Delta G = \Delta H - T\Delta S$ , we have

$$\Delta G^{\#} - x_1 \Delta G_1^{\#} - x_2 \Delta G_2^{\#} = RT (\ln \eta V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2)$$

$$\text{or } \Delta G^{\#E} = RT (\ln \eta V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2) \quad (4)$$

where the symbols have their usual significance.

The first component of the binary liquid mixtures, nitromethane, under discussion is a polar liquid with a dipole moment,  $\mu = 3.46$  D. The second component of the mixtures is either a polar solvent or a non-polar solvent. The dipole moments of the polar and non-polar solvents are as under :

Methyl alcohol,  $\mu = 1.70$  D; ethyl alcohol,  $\mu = 1.69$  D; *n*-propyl alcohol,  $\mu = 1.55$  D; isopropyl alcohol,  $\mu = 1.56$  D; *n*-butyl alcohol,  $\mu = 1.66$  D; isobutyl alcohol,  $\mu = 1.8$  D; acetone,  $\mu = 2.88$  D; methyl ethyl ketone,  $\mu = 2.78$  D; methyl acetate,  $\mu = 1.72$  D; ethyl acetate,  $\mu = 1.78$  D; carbon tetrachloride,  $\mu = 0.0$  D; benzene,  $\mu = 0.0$  D; toluene,  $\mu = 0.375$  D.

The values of density ( $\rho$ ), viscosity ( $\eta$ ), molar volume ( $V$ ) and excess thermodynamic properties, viz. the excess viscosity ( $\eta^E$ ), the excess molar volume ( $V^E$ ), the excess Gibbs free energy of activation of flow ( $\Delta G^{\#E}$ ), at a constant temperature 298.15 K and as a function of the composition of the binary mixtures have been presented in Table 2. The results of the study are discussed below.

(i) *Excess viscosity ( $\eta^E$ )* :

A perusal of Table 2 shows that the values of  $\eta^E$  are negative over the entire range of composition for all the binary liquid mixtures except for the ones involving acetone and methyl acetate where the values are positive. The negative values suggest that dispersion type<sup>8</sup> of forces are predominant in these mixtures while the positive values may be attributed to the presence of strong interactions<sup>9</sup>.

The plots of  $\eta^E$  versus  $x_1$  (the mole fraction of nitromethane) for the binary mixtures have been presented

**Table 2.** Densities, viscosities, excess properties and interaction parameters ( $d_{12}$ ,  $T_{12}$  and  $H_{12}$ ) of binary liquid mixtures of nitromethane with polar and non-polar solvents at 298.15 K

Sl. no.	$\phi$	$x_1$	$\rho$ g cm <sup>-3</sup>	$\eta$ mPa.s	$\eta^E$ mPa.s	$V$ cm <sup>3</sup> mol <sup>-1</sup>	$V^E$ cm <sup>3</sup> mol <sup>-1</sup>	$\Delta G^{#E}$ J mol <sup>-1</sup>	$d_{12}$	$T_{12}$	$H_{12}$
Nitromethane + methyl alcohol system											
1.	0.0	0.0000	0.7881	0.5482	0.0000	40.655	0.0000	0.00	-	-	-
2.	0.1	0.0771	0.8207	0.5277	-0.0269	41.764	0.0855	-108.73	-0.0041	0.4217	0.4007
3.	0.2	0.1586	0.8538	0.5151	-0.0463	42.913	0.1521	-186.98	-0.0160	0.4314	0.4163
4.	0.3	0.2441	0.8874	0.5082	-0.0596	44.083	0.1858	-240.19	-0.0351	0.4384	0.4283
5.	0.4	0.3345	0.9213	0.5081	-0.0679	45.306	0.2086	-271.20	-0.0619	0.4429	0.4372
6.	0.5	0.4298	0.9554	0.5102	-0.0737	46.582	0.2184	-292.27	-0.0999	0.4409	0.4394
7.	0.6	0.5305	0.9897	0.5169	-0.0754	47.918	0.2174	-295.62	-0.1510	0.4356	0.4384
8.	0.7	0.6375	1.0244	0.5265	-0.0747	49.324	0.2021	-290.74	-0.2293	0.4203	0.4282
9.	0.8	0.7509	1.0595	0.5426	-0.0680	50.794	0.1658	-262.42	-0.3504	0.3932	0.4080
10.	0.9	0.8715	1.0953	0.5721	-0.0485	52.327	0.0969	-184.19	-0.5448	0.3481	0.3731
11.	1.0	1.0000	1.1317	0.6313	0.0000	53.937	0.0000	0.00	-	-	-
Nitromethane + ethyl alcohol system											
1.	0.0	0.0000	0.7874	1.1120	0.0000	58.509	0.0000	0.00	-	-	-
2.	0.1	0.1074	0.8199	0.9963	-0.0641	58.151	0.1328	-115.18	-0.0059	0.5179	0.5375
3.	0.2	0.2135	0.8533	0.9148	-0.0946	57.736	0.2032	-174.18	-0.0202	0.5740	0.5901
4.	0.3	0.3174	0.8868	0.8400	-0.1194	57.309	0.2511	-237.28	-0.0469	0.5826	0.5960
5.	0.4	0.4199	0.9207	0.7770	-0.1332	56.865	0.2763	-285.27	-0.0874	0.5871	0.5983
6.	0.5	0.5202	0.9546	0.7236	-0.1383	56.419	0.2884	-320.32	-0.1466	0.5857	0.5945
7.	0.6	0.6192	0.9888	0.6847	-0.1297	55.966	0.2884	-318.36	-0.2185	0.5902	0.5967
8.	0.7	0.7167	1.0233	0.6557	-0.1118	55.506	0.2737	-289.62	-0.3098	0.5920	0.5964
9.	0.8	0.8126	1.0583	0.6418	-0.0796	55.027	0.2331	-210.30	-0.3885	0.6077	0.6103
10.	0.9	0.9071	1.0941	0.6370	-0.0390	54.519	0.1576	-100.21	-0.4258	0.6389	0.6405
11.	1.0	1.0000	1.1317	0.6313	0.0000	53.937	0.0000	0.00	-	-	-
Nitromethane + <i>n</i> -propyl alcohol system											
1.	0.0	0.0000	0.8000	1.9544	0.0000	75.125	0.0000	0.00	-	-	-
2.	0.1	0.1338	0.8307	1.5504	-0.2270	72.500	0.2100	-177.49	-0.0124	0.8980	0.3137
3.	0.2	0.2584	0.8618	1.2400	-0.3725	70.020	0.3697	-366.18	-0.0568	0.1367	0.3209
4.	0.3	0.3737	0.8930	1.01104	0.4496	67.695	0.4877	-539.78	-0.1417	0.1867	0.3225
5.	0.4	0.4815	0.9247	0.8394	-0.4779	65.484	0.5607	-691.20	-0.2795	0.2243	0.3357
6.	0.5	0.5819	0.9568	0.7389	-0.4456	63.385	0.5897	-724.33	-0.4385	0.2973	0.3771
7.	0.6	0.6764	0.9893	0.6772	-0.3823	61.393	0.5995	-677.32	-0.6177	0.3665	0.4197
8.	0.7	0.7649	1.0224	0.6555	-0.2869	59.487	0.5685	-515.64	-0.7420	0.4622	0.4953
9.	0.8	0.8479	1.0564	0.6441	-0.1884	57.646	0.4864	-336.37	-0.8463	0.5445	0.5623
10.	0.9	0.9262	1.0919	0.6388	-0.0901	55.839	0.3387	-152.14	-0.8984	0.6256	0.6334
11.	1.0	1.0000	1.1317	0.6313	0.0000	53.937	0.0000	0.00	-	-	-
Nitromethane + isopropyl alcohol system											
1.	0.0	0.0000	0.7843	2.0443	0.0000	76.629	0.0000	0.00	-	-	-
2.	0.1	0.1361	0.8166	1.5990	-0.2530	73.755	0.2141	-188.87	0.0022	-0.0016	0.0141
3.	0.2	0.2622	0.8493	1.2667	-0.4071	71.054	0.3755	-381.74	-0.0135	0.0046	0.2619
4.	0.3	0.3785	0.8819	1.0255	-0.4840	68.552	0.5120	-554.25	-0.0606	0.0766	0.2856
5.	0.4	0.4866	0.9146	0.8807	-0.4760	66.212	0.6251	-608.70	-0.1493	0.1450	0.3091
6.	0.5	0.5871	0.9479	0.7784	-0.4363	63.986	0.6793	-619.35	-0.2562	0.2616	0.3850
7.	0.6	0.6805	0.9817	0.7133	-0.3695	61.872	0.6851	-565.77	-0.3920	0.3474	0.4378

8.	0.7	0.7685	1.0172	0.6771	-0.2813	59.794	0.6041	-466.64	-0.5395	0.4252	0.4882
9.	0.8	0.8503	1.0542	0.6562	-0.1866	57.768	0.4346	-300.33	-0.6705	0.5058	0.5472
10.	0.9	0.9277	1.0922	0.6386	-0.0949	55.825	0.2478	-159.72	-0.7794	0.5800	0.6047
11.	1.0	1.0000	1.1317	0.6313	0.0000	53.937	0.0000	0.00	-	-	-
Nitromethane + <i>n</i> -butyl alcohol system											
1.	0.0	0.0000	0.8063	2.5383	0.0000	91.926	0.0000	0.00	-	-	-
2.	0.1	0.1589	0.8355	1.9297	-0.3056	86.226	0.3361	-80.12	-0.0100	0.0082	0.4416
3.	0.2	0.2990	0.8665	1.4989	-0.4692	81.026	0.4589	-192.13	-0.0472	0.1029	0.4655
4.	0.3	0.4222	0.8979	1.1719	-0.5613	76.398	0.5109	-360.21	-0.1355	0.1443	0.4344
5.	0.4	0.5319	0.9296	0.9681	-0.5559	72.249	0.5296	-448.82	-0.2543	0.2472	0.4685
6.	0.5	0.6302	0.9616	0.8288	-0.5077	68.508	0.5226	-496.75	-0.4130	0.3326	0.4955
7.	0.6	0.7188	0.9937	0.7435	-0.4240	65.128	0.5092	-468.67	-0.5820	0.4216	0.5358
8.	0.7	0.7993	1.0262	0.6894	-0.3246	62.040	0.4786	-392.32	-0.7616	0.4995	0.5730
9.	0.8	0.8718	1.0589	0.6557	-0.2201	59.228	0.4214	-285.63	-0.9552	0.5621	0.6002
10.	0.9	0.9387	1.0931	0.6378	-0.1104	56.575	0.3093	-148.69	-1.1493	0.6177	0.6255
11.	1.0	1.0000	1.1317	0.6313	0.0000	53.937	0.0000	0.00	-	-	-
Nitromethane + isobutyl alcohol system											
1.	0.0	0.0000	0.8048	3.1028	0.0000	92.097	0.0000	0.00	-	-	-
2.	0.1	0.1592	0.8349	2.3039	-0.4054	86.283	0.2608	-60.10	-0.0084	0.2465	0.3526
3.	0.2	0.2992	0.8654	1.7787	-0.5846	81.126	0.4463	-115.94	-0.0342	0.0037	0.4730
4.	0.3	0.4225	0.8963	1.3819	-0.6767	76.530	0.5553	-236.04	-0.0996	0.1051	0.4804
5.	0.4	0.5327	0.9278	1.1078	-0.6784	72.378	0.6089	-341.21	-0.2072	0.2114	0.5044
6.	0.5	0.6306	0.9594	0.9667	-0.6176	68.659	0.6261	-398.18	-0.3488	0.3202	0.5415
7.	0.6	0.7193	0.9915	0.8220	-0.5031	65.266	0.6180	-353.26	-0.4689	0.4569	0.6213
8.	0.7	0.7993	1.0238	0.7537	-0.3736	62.185	0.5896	-266.31	-0.5669	0.5820	0.7025
9.	0.8	0.8724	1.0574	0.7066	-0.2401	59.305	0.4990	-158.35	-0.6187	0.6999	0.7888
10.	0.9	0.9387	1.0927	0.6682	-0.1146	56.595	0.3195	-63.16	-0.6248	0.8048	0.8712
11.	1.0	1.0000	1.1317	0.6313	0.0000	53.937	0.0000	0.00	-	-	-
Nitromethane + acetone system											
1.	0.0	0.0000	0.7808	0.3121	0.0000	74.385	0.0000	0.00	-	-	-
2.	0.1	0.1326	0.8145	0.3560	0.0016	71.789	0.1157	112.29	0.0058	0.5110	0.4785
3.	0.2	0.2566	0.8489	0.3972	0.0032	69.313	0.1746	178.99	0.0208	0.5128	0.4801
4.	0.3	0.3714	0.8833	0.4352	0.0045	66.998	0.2074	212.28	0.0419	0.5138	0.4814
5.	0.4	0.4790	0.9179	0.4701	0.0051	64.820	0.2292	219.40	0.0664	0.5140	0.4819
6.	0.5	0.5797	0.9526	0.5032	0.0061	62.771	0.2402	212.87	0.0956	0.5159	0.4841
7.	0.6	0.6739	0.9874	0.5325	0.0053	60.841	0.2364	186.31	0.1230	0.5150	0.4837
8.	0.7	0.7631	1.0227	0.5603	0.0046	59.000	0.2186	151.57	0.1533	0.5155	0.4845
9.	0.8	0.8465	1.0582	0.5855	0.0032	57.254	0.1780	106.98	0.1810	0.5146	0.4840
10.	0.9	0.9257	1.0946	0.6101	0.0025	55.564	0.1078	59.54	0.2265	0.5200	0.4900
11.	1.0	1.0000	1.1317	0.6313	0.0000	53.937	0.0000	0.00	-	-	-
Nitromethane + methyl ethyl ketone system											
1.	0.0	0.0000	0.7974	0.4011	0.0000	90.431	0.0000	0.00	-	-	-
2.	0.1	0.1563	0.8273	0.4237	-0.0135	85.065	0.3559	8.80	-0.0030	0.5051	0.4652
3.	0.2	0.2954	0.8588	0.4466	-0.0255	80.158	0.5075	13.73	-0.0111	0.5020	0.4621
4.	0.3	0.4180	0.8910	0.4694	-0.0279	75.738	0.5616	15.76	-0.0232	0.5018	0.4588
5.	0.4	0.5281	0.9238	0.4923	-0.0304	71.730	0.5712	16.29	-0.0388	0.5017	0.4553
6.	0.5	0.6264	0.9567	0.5150	-0.0303	68.126	0.5545	15.65	-0.0573	0.5010	0.4515

Table-2 (contd.)

7.	0.6	0.7156	0.9899	0.5377	-0.0281	64.843	0.5275	14.14	-0.0792	0.5000	0.4471
8.	0.7	0.7963	1.0234	0.5604	-0.0240	61.848	0.4771	12.04	-0.1045	0.4985	0.4422
9.	0.8	0.8703	1.0578	0.5834	-0.0180	59.062	0.3920	9.10	-0.1347	0.4965	0.4363
10.	0.9	0.9376	1.0934	0.6067	-0.0102	56.458	0.2437	4.93	-0.1720	0.4925	0.4287
11.	1.0	1.0000	1.1317	0.6313	0.0000	53.937	0.0000	0.00	-	-	-
Nitromethane + methyl acetate system											
1.	0.0	0.0000	0.9239	0.3711	0.0000	80.182	0.0000	0.00	-	-	-
2.	0.1	0.1415	0.9421	0.4094	0.0015	76.674	0.2062	85.31	0.0038	-	-
3.	0.2	0.2710	0.9614	0.4445	0.0029	73.379	0.3092	137.02	0.0136	0.5439	0.5073
4.	0.3	0.3891	0.9813	0.4757	0.0034	70.321	0.3513	160.21	0.0265	0.5452	0.5085
5.	0.4	0.4980	1.0015	0.5048	0.0041	67.485	0.3732	168.95	0.0428	0.5445	0.5083
6.	0.5	0.5977	1.0218	0.5313	0.0047	64.872	0.3768	164.56	0.0613	0.5456	0.5094
7.	0.6	0.6903	1.0424	0.5553	0.0046	62.431	0.3667	148.09	0.0809	0.5465	0.5109
8.	0.7	0.7763	1.0633	0.5776	0.0045	60.150	0.3419	124.65	0.1039	0.5471	0.5119
9.	0.8	0.8562	1.0851	0.5968	0.0029	57.981	0.2703	87.98	0.1203	0.5489	0.5142
10.	0.9	0.9303	1.1077	0.6147	0.0015	55.926	0.1598	47.01	0.1386	0.5476	0.5130
11.	1.0	1.0000	1.1317	0.6313	0.0000	53.937	0.0000	0.00	-	0.5468	0.5130
Nitromethane + ethyl acetate system											
1.	0.0	0.0000	0.8919	0.4274	0.0000	98.789	0.0000	0.00	-	-	-
2.	0.1	0.1688	0.9114	0.4555	-0.0063	91.662	0.4438	62.23	-0.0004	-	-
3.	0.2	0.3141	0.9332	0.4808	-0.0106	85.306	0.6048	95.57	-0.0022	0.5567	0.5068
4.	0.3	0.4395	0.9556	0.5046	-0.0124	79.754	0.6774	115.38	-0.0042	0.5564	0.5046
5.	0.4	0.5500	0.9788	0.5260	-0.0135	74.807	0.6872	118.55	-0.0085	0.5577	0.5042
6.	0.5	0.6469	1.0023	0.5465	-0.0128	70.436	0.6624	115.75	-0.0119	0.5574	0.5020
7.	0.6	0.7330	1.0264	0.5651	-0.0118	66.512	0.5996	102.51	-0.0182	0.5583	0.5013
8.	0.7	0.8102	1.0508	0.5828	-0.0098	62.979	0.5290	84.82	-0.0252	0.5579	0.4993
9.	0.8	0.8801	1.0762	0.5995	-0.0074	59.734	0.4196	61.01	-0.0361	0.5577	0.4975
10.	0.9	0.9429	1.1026	0.6154	-0.0043	56.762	0.2642	32.88	-0.0534	0.5571	0.4945
11.	1.0	1.0000	1.1317	0.6313	0.0000	53.937	0.0000	0.00	-	0.5547	0.4898
Nitromethane + carbon tetrachloride system											
1.	0.0	0.0000	1.5861	0.9096	0.0000	96.980	0.0000	0.00	-	-	-
2.	0.1	0.1662	1.5258	0.8265	-0.0368	90.707	0.8803	-11.08	-0.0070	-	-
3.	0.2	0.3102	1.4747	0.7692	-0.0541	84.790	1.1620	-16.60	-0.0244	0.5974	0.6375
4.	0.3	0.4351	1.4270	0.7285	-0.0607	79.503	1.2516	-18.60	-0.0497	0.6163	0.6441
5.	0.4	0.5452	1.3809	0.6969	-0.0610	74.760	1.2475	-18.83	-0.0806	0.6288	0.6469
6.	0.5	0.6424	1.3357	0.6735	-0.0573	70.538	1.2095	-18.22	-0.1184	0.6375	0.6475
7.	0.6	0.7297	1.2907	0.6556	-0.0509	66.722	1.1511	-16.87	-0.1645	0.6428	0.6457
8.	0.7	0.8077	1.2473	0.6427	-0.0421	63.242	1.0281	-14.87	-0.2198	0.6454	0.6414
9.	0.8	0.8780	1.2051	0.6339	-0.0314	60.044	0.8562	-11.78	-0.2911	0.6459	0.6349
10.	0.9	0.9419	1.1652	0.6295	-0.0180	57.012	0.5747	-6.71	-0.3903	0.6427	0.6241
11.	1.0	1.0000	1.1317	0.6313	0.0000	53.937	0.0000	0.00	-	0.6345	0.6063
Nitromethane + benzene system											
1.	0.0	0.0000	0.8697	0.6080	0.0000	89.813	0.0000	0.00	-	-	-
2.	0.1	0.1559	0.8911	0.5732	-0.0384	84.669	0.4498	-109.76	-0.0120	0.4662	0.4736
3.	0.2	0.2940	0.9146	0.5584	-0.0565	79.916	0.6512	-156.13	-0.0400	0.4880	0.4837
4.	0.3	0.4165	0.9390	0.5532	-0.0645	75.613	0.7425	-173.12	-0.0786	0.5002	0.4869
5.	0.4	0.5262	0.9638	0.5534	-0.0669	71.724	0.7896	-174.66	-0.1265	0.5063	0.4856

Table-2 (contd.)

6.	0.5	0.6247	0.9888	0.5571	-0.0655	68.210	0.8094	-167.34	-0.1846	0.5077	0.4801
7.	0.6	0.7142	1.0146	0.5652	-0.0594	64.970	0.7800	-147.42	-0.2495	0.5087	0.4740
8.	0.7	0.7953	1.0408	0.5770	-0.0495	62.004	0.7240	-117.06	-0.3195	0.5090	0.4675
9.	0.8	0.8693	1.0679	0.5909	-0.0374	59.248	0.6225	-84.13	-0.4072	0.5043	0.4553
10.	0.9	0.9376	1.0966	0.6098	-0.0209	56.634	0.4590	-41.63	-0.5076	0.4988	0.4406
11.	1.0	1.0000	1.1317	0.6313	0.0000	53.937	0.0000	0.00	-	-	-
Nitromethane + toluene system											
1.	0.0	0.0000	0.8605	0.5614	0.0000	107.077	0.0000	0.00	-	-	-
2.	0.1	0.1803	0.8855	0.5448	-0.0314	97.722	0.2258	-56.75	-0.0121	0.5084	0.4914
3.	0.2	0.3318	0.9114	0.5368	-0.0496	89.775	0.3299	-88.41	-0.0432	0.5133	0.4858
4.	0.3	0.4595	0.9375	0.5331	-0.0619	83.040	0.3804	-117.44	-0.0920	0.5094	0.4731
5.	0.4	0.5699	0.9640	0.5340	-0.0684	77.195	0.4027	-137.30	-0.1577	0.5041	0.4582
6.	0.5	0.6650	0.9905	0.5420	-0.0668	72.144	0.4052	-133.07	-0.2279	0.5034	0.4478
7.	0.6	0.7483	1.0171	0.5534	-0.0610	67.710	0.3979	-120.34	-0.3073	0.5013	0.4358
8.	0.7	0.8226	1.0443	0.5683	-0.0511	63.734	0.3699	-98.93	-0.3949	0.4992	0.4227
9.	0.8	0.8880	1.0719	0.5861	-0.0377	60.195	0.3068	-71.15	-0.4891	0.4954	0.4083
10.	0.9	0.9472	1.1009	0.6066	-0.0212	56.937	0.1947	-39.76	-0.6094	0.4878	0.3862
11.	1.0	1.0000	1.1317	0.6313	0.0000	53.937	0.0000	0.00	-	-	-

in the representative Fig. 1. It is seen that in each case the plots are of parabolic shape and are characterized by the presence of well-defined minima which occur at  $x_1 \approx 0.5$  except for the plots in the case of binary mixtures of nitromethane with acetone and methyl acetate where maxima occur at  $x_1 \approx 0.6$ . These minima/maxima indicate the presence of complex formation<sup>9,10</sup>. According to Fort and Moore<sup>4</sup>,  $\eta^E$  is approximately proportional to the strength of interaction. Therefore, on comparing the values of  $\eta^E$  corresponding to minima/maxima in the plots of  $\eta^E$  versus  $x_1$ , it is seen that the strength of interaction between binary mixtures of nitromethane with polar and non-polar solvents follows the following order : acetone > methyl acetate > ethyl acetate > methyl ethyl ketone > carbonyl tetrachloride > benzene ~ toluene > methyl alcohol > ethyl alcohol > isopropyl alcohol > *n*-propyl alcohol > *n*-butyl alcohol > isobutyl alcohol.

(ii) Excess molar volume ( $V^E$ ) :

A perusal of Table 2 shows that the values of  $V^E$  are positive over the entire range of composition for all the binary liquid mixtures under discussion. The positive values of  $V^E$  in these mixtures may be attributed to the dominance of dispersion forces<sup>11</sup>.

The plots of  $V^E$  versus  $x_1$  are of parabolic shape (vide representative Fig. 2) with well-defined maxima which indicate the presence of complex formation<sup>10</sup>.

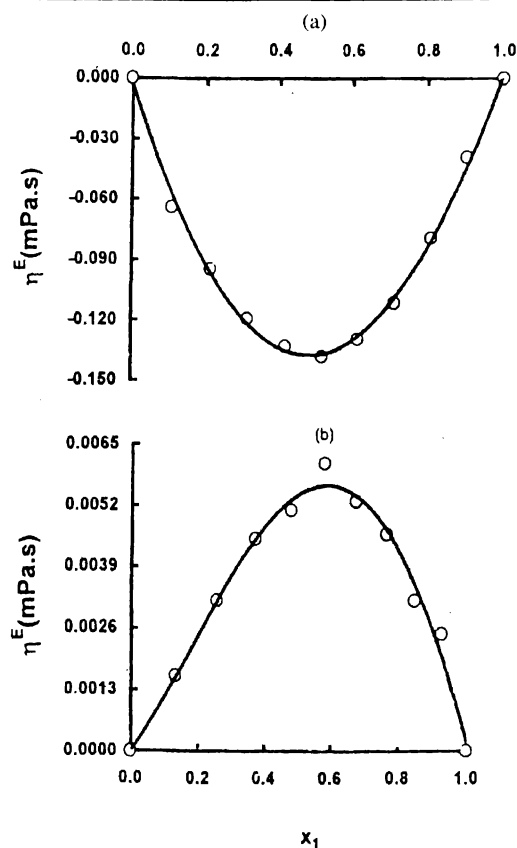


Fig. 1. (a) Variation of excess viscosity ( $\eta^E$ ) with mole fraction ( $x_1$ ) of nitromethane in binary liquid mixture of nitromethane + ethyl alcohol at 298.15 K. (b) Variation of excess viscosity ( $\eta^E$ ) with mole fraction ( $x_1$ ) of nitromethane in binary liquid mixture of nitromethane + acetone at 298.15 K.

(iii) Excess Gibbs free energy of activation of flow ( $\Delta G^{\#E}$ ):

The values of  $\Delta G^{\#E}$  for the binary mixtures have been presented in Table 2. It is seen that the values of  $\Delta G^{\#E}$  for the mixtures of nitromethane with aliphatic alcohols and with non-polar solvents namely carbon tetrachloride, benzene and toluene are negative over the entire range of composition. On the other hand, the values of  $\Delta G^{\#E}$  are positive over the entire range of composition for the binary mixtures of nitromethane with acetone, methyl ethyl ketone, methyl acetate and ethyl acetate.

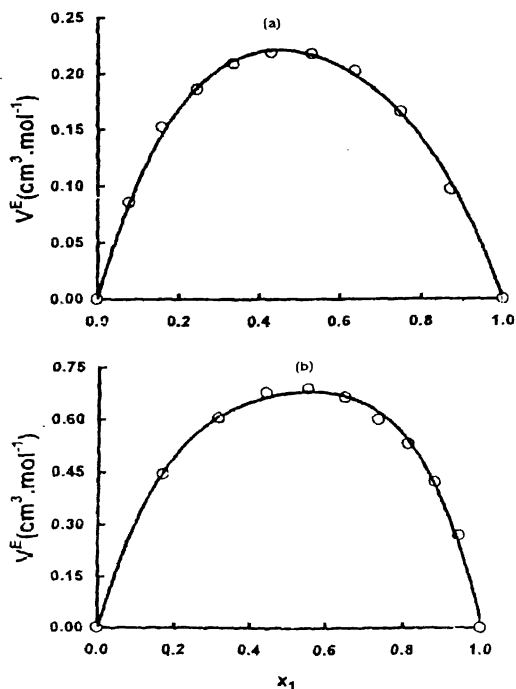


Fig. 2. (a) Variation of excess molar volume ( $V^E$ ) with mole fraction ( $x_1$ ) of nitromethane in binary liquid mixture of nitromethane + methyl alcohol at 298.15 K. (b) Variation of excess molar volume ( $V^E$ ) with molar fraction ( $x_1$ ) of nitromethane in binary liquid mixture of nitromethane + ethyl acetate at 298.15 K.

The values of  $\Delta G^{\#E}$  for the above binary mixtures have been plotted against  $x_1$  and the plots have been presented in representative Fig. 3. It is seen that all the plots are of parabolic shape and are characterized by the presence of well-defined minima/maxima which give the composition at which maximum interactions are expected to occur between the mixing components<sup>9</sup>.

The negative values of  $\Delta G^{\#E}$  may be attributed to the dominance of dispersion forces, while the positive ones to the size effect of the mixing components<sup>12</sup>.

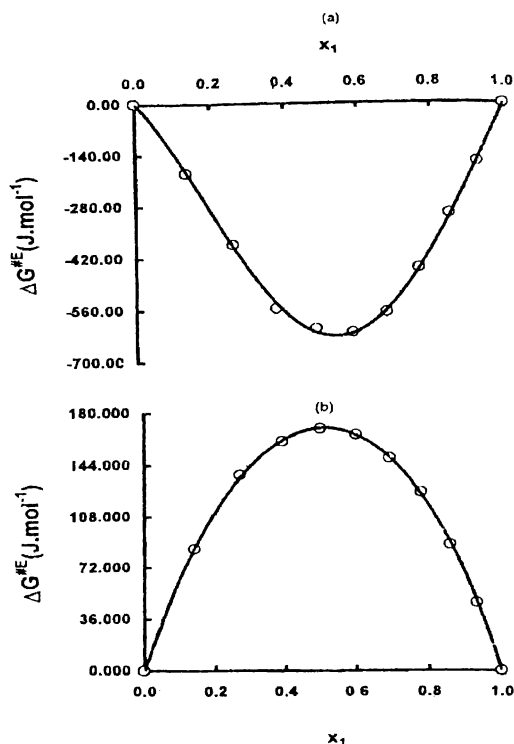


Fig. 3. (a) Variation of excess Gibbs free energy of activation of flow ( $\Delta G^{\#E}$ ) with mole fraction ( $x_1$ ) of nitromethane in binary liquid mixture of nitromethane + isopropyl alcohol at 298.15 K. (b) Variation of excess Gibbs free energy of activation of flow ( $\Delta G^{\#E}$ ) with molar fraction ( $x_1$ ) of nitromethane in binary liquid mixture of nitromethane + methyl acetate at 298.15 K.

The polynomial function of the Redlich-Kister polynomial equation<sup>13</sup> of the type;

$$X^E = x_1 x_2 [\sum_{i=0}^k A_i (x_1 - x_2)^i] \quad (5)$$

is fitted to each set of the experimental excess properties for the binary mixtures to evaluate the  $A_i$  coefficients by the least-square method<sup>14</sup> with all points weighed equally, using a computer [Pentium III system], where  $X^E$  is  $\eta^E$ /mPa.s or  $V^E$ /cm<sup>3</sup> mol<sup>-1</sup> or  $\Delta G^{\#E}$ /J mol<sup>-1</sup>. The  $A_i$  coefficients are then used to evaluate  $X^E$  (calcd.) values from the equation (5). The standard deviation  $\sigma(X^E)$  is defined by the equation<sup>15</sup>,

$$\sigma(X^E) = [\sum (X_{obs.}^E - X_{calcd.}^E)^2 / (n - p)]^{0.5} \quad (6)$$

where  $n$  is the number of data points and  $p$  is the number of coefficients  $A_i$  is ascertained from an examination of the variation of the standard deviation  $\sigma(X^E)$  with  $K$ .

From the binary mixtures under discussion, the coefficients  $A_i$  and the standard deviation  $\sigma(\eta^E)$  have been evaluated from the experimental values of  $\eta^E$ . The results have been presented in Table 3. It is seen that for all the binary

**Table 3.** Coefficients of eq. (5) and standard deviation ( $\sigma$ ) in respect of excess properties ( $X^E$ ) of binary liquid mixtures of nitromethane with some polar and non-polar solvents at 298.15 K

( $X^E$ )	$A_0$	$A_1$	$A_2$	$\sigma$
Nitromethane + methyl alcohol				
$\eta^E$ (mPa.s)	-0.3006	-0.0440	-0.1683	0.0006
$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	0.8760	-0.1419	0.2694	0.0044
$\Delta G^{#E}$ (J mol <sup>-1</sup> )	-1184.01	-61.28	-652.80	0.7250
Nitromethane + ethyl alcohol				
$\eta^E$ (mPa.s)	-0.9440	0.2101	-0.2964	0.0025
$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	1.1397	0.2246	0.6824	0.0045
$\Delta G^{#E}$ (J mol <sup>-1</sup> )	-1253.43	-461.23	-17.90	1.4551
Nitromethane + <i>n</i> -propyl alcohol				
$\eta^E$ (mPa.s)	-1.8908	0.3222	0.3968	0.0042
$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	2.2254	1.2556	1.3202	0.0272
$\Delta G^{#E}$ (J mol <sup>-1</sup> )	-2811.61	-1597.40	2171.18	4.3681
Nitromethane + isopropyl alcohol				
$\eta^E$ (mPa.s)	-1.9060	0.5081	0.1702	0.0048
$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	2.5549	1.3404	0.1874	0.0164
$\Delta G^{#E}$ (J mol <sup>-1</sup> )	-2450.69	-468.27	-942.38	0.5413
Nitromethane + <i>n</i> -butyl alcohol				
$\eta^E$ (mPa.s)	-2.2475	0.1838	0.2891	0.0050
$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	2.0194	0.5219	2.2202	0.0368
$\Delta G^{#E}$ (J mol <sup>-1</sup> )	-1703.60	-1538.05	-855.45	0.8098
Nitromethane + isobutyl alcohol				
$\eta^E$ (mPa.s)	-2.6827	0.4365	-0.3047	0.0187
$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	2.3193	1.3329	1.6946	0.0331
$\Delta G^{#E}$ (J mol <sup>-1</sup> )	-1248.14	-1951.20	-451.63	1.8579
Nitromethane + acetone				
$\eta^E$ (mPa.s)	-0.0876	-0.0001	-0.0119	0.0003
$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	0.9248	0.2735	0.5266	0.0013
$\Delta G^{#E}$ (J mol <sup>-1</sup> )	878.74	-73.82	127.99	0.6687
Nitromethane + methyl ethyl ketone				
$\eta^E$ (mPa.s)	-0.1194	-0.0370	-0.0207	0.0002
$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	2.2469	0.2812	1.6329	0.0178
$\Delta G^{#E}$ (J mol <sup>-1</sup> )	65.10	4.37	12.36	0.0002
Nitromethane + methyl acetate				
$\eta^E$ (mPa.s)	-0.0632	-0.0155	0.0081	0.0001
$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	1.4882	0.3075	0.9360	0.0048
$\Delta G^{#E}$ (J mol <sup>-1</sup> )	677.37	15.45	-26.37	0.3853
Nitromethane + ethyl acetate				
$\eta^E$ (mPa.s)	-0.0521	-0.0144	-0.0096	0.0003
$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	2.6971	0.2846	1.6403	0.0206
$\Delta G^{#E}$ (J mol <sup>-1</sup> )	471.89	53.42	244.44	0.2840
Nitromethane + carbon tetrachloride				
$\eta^E$ (mPa.s)	-0.2440	-0.0064	-0.0686	0.0008
$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	4.9028	0.4083	4.4394	0.0525

Table-3 (contd.)

$\Delta G^{#E}$ (J mol <sup>-1</sup> )	-75.36	-2.59	-41.67	0.0017
Nitromethane + benzene				
$\eta^E$ (mPa.s)	-0.2671	-0.0211	-0.0823	0.0004
$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	3.0388	1.0557	2.8664	0.0499
$\Delta G^{#E}$ (J mol <sup>-1</sup> )	-698.38	-2.46	-494.67	0.2470
Nitromethane + toluene				
$\eta^E$ (mPa.s)	-0.1556	-0.0505	-0.0338	0.0004
$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	1.5097	0.6971	1.4347	0.0209
$\Delta G^{#E}$ (J mol <sup>-1</sup> )	-511.33	-438.26	575.85	0.1143

mixtures the fit is good as evident by very small values of the standard deviation  $\sigma(\eta^E)$ .

The coefficients  $A_i$  and the standard deviation,  $\sigma(V^E)$  have been evaluated from the experimental values of  $V^E$ . The results have been presented in Table 3. It is seen that the fit is good as revealed by small values of  $\sigma(V^E)$ .

The coefficients  $A_i$  and the standard deviation,  $\sigma(\Delta G^{#E})$  have also been computed from the experimental values of  $\Delta G^{#E}$ . The results have been summarized in Table 3. It is found that the fit is quite satisfactory as revealed by the values of  $\sigma(\Delta G^{#E})$ .

#### Viscosity models and interaction parameters :

The several models (equations) have been put forward from time to time for correlating the viscosity of binary liquid mixtures with those of the component liquids with a view to interpreting the molecular interactions in the liquid mixtures in terms of interaction parameters of the viscosity models. These are detailed as under :

(i) Grunberg and Nissan<sup>16</sup> have suggested the following logarithmic relation between the viscosity of the binary liquid mixture and pure components :

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12} \quad (7)$$

where  $d_{12}$  is a constant, proportional to interchange energy ( $w$ ). It may be regarded as an approximate measure of strength of molecular interaction between the mixing components<sup>4</sup>.

(ii) Tamura and Kurata<sup>17</sup> developed the following equation for the viscosity of binary liquid mixtures :

$$\eta = x_1 \phi_1 \eta_1 + x_2 \phi_2 \eta_2 + 2(x_1 x_2 \phi_1 \phi_2)^{0.5} T_{12} \quad (8)$$

where  $T_{12}$  is interaction parameter which depends on temperature and composition of the mixtures;  $\phi_1$  and  $\phi_2$  are the volume fractions; and  $x_1$  and  $x_2$  are the mole fractions and  $\eta_1$  and  $\eta_2$  are the viscosities of pure components 1 and 2, respectively.

(iii) Hind *et al.*<sup>18</sup> suggested the following equation for



the viscosity of binary liquid mixtures :

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2 x_1 x_2 H_{12} \quad (9)$$

where  $x_1$  and  $x_2$  are the mole fractions,  $\eta_1$  and  $\eta_2$  are the viscosities of liquid components 1 and 2, respectively;  $\eta$  is the viscosity of binary liquid mixture and  $H_{12}$  is Hind interaction parameter and is attributed to unlike pair interactions.

(iv) McAllister<sup>19</sup> two-parameter equation based on Eyring's theory of absolute reaction rates, takes into account interactions of both like and unlike molecules by a two-dimensional three-body model. The equation is :

$$\begin{aligned} \ln \eta = & x_1^3 \ln \eta_1 + 3 x_1^2 x_2 \ln Z_{12} + 3 x_1 x_2^2 \ln Z_{21} + x_2^3 \ln \eta_2 \\ & + \ln (x_1 + x_2 M_2/M_1) + 3 x_1^2 x_2 \ln [(2 + M_2/M_1)/3] \\ & + 3 x_1 x_2^2 \ln [(1 + 2 M_2/M_1)/3] + x_2^3 \ln (M_2/M_1) \quad (10) \end{aligned}$$

where  $\eta$  is the viscosity of binary liquid mixture,  $x_1$  and  $x_2$  are the mole fractions,  $\eta_1$  and  $\eta_2$  are the viscosities,  $M_1$  and  $M_2$  are the molecular weights of components 1 and 2, respectively.  $Z_{12}$  and  $Z_{21}$  are the McAllister interaction parameters.

(v) Heric and Brewer<sup>20</sup> proposed the following equation for the kinematic viscosity  $\lambda$  ( $\eta/\rho$ ) of the binary liquid mixtures :

$$\lambda = x_1 \lambda_1 + x_2 \lambda_2 + x_1 x_2 [a + b(x_1 - x_2) + c(x_1 - x_2)^2] \quad (11)$$

where  $\lambda_1$  and  $\lambda_2$  are the kinematic viscosities of components 1 and 2, respectively and  $a$ ,  $b$  and  $c$  are the Heric and Brewer interaction parameters.

It would not be out of place to give here a passing comment as to the relative merits of the above mentioned interaction parameters in ascertaining the strength of molecular interactions in binary liquid mixtures. According to Fort and Moore<sup>4</sup> the values of  $T_{12}$  and  $H_{12}$  (vide eqs. 8 and 9, respectively) for a given mixture are not very different except where the molar volumes of the components differ considerably. Further,  $T_{12}$  and  $H_{12}$  show some variation with composition although this is only large for systems in which there is a strong specific interaction between the components. There is tendency of  $T_{12}$  and  $H_{12}$  at a certain composition, to increase with the strength of interaction between the components but this is not well defined and  $T_{12}$  and  $H_{12}$  cannot generally be regarded as a measure of the strength of interaction. The values of  $d_{12}$  (vide eq. 7), on the other hand, provide better measure of the strength of interaction. Their variation with composition is not large except where strong specific interaction might be expected to vary with the composition. At any given composition the variation of  $d_{12}$  with strength of interaction is similar to that of  $\eta^E$  being negative for systems in which dispersion

forces are dominant, becoming less negative and then increasingly positive as the strength of interaction increases.

Kalra *et al.*<sup>21</sup> have reported that interaction parameters  $Z_{12}$  and  $Z_{21}$  (vide eq. 10) act in reverse directions in regard to the variation in the strength of interaction. So for as the interaction parameters  $a$ ,  $b$  and  $c$  (vide eq. 11) are concerned, it is reported<sup>21</sup> that while  $a$  shows a gradation in its values with the strength of interaction,  $b$  and  $c$  do not exhibit such a trend.

The values of various interaction parameters viz.  $d_{12}$ ,  $T_{12}$ ,  $H_{12}$ ,  $Z_{12}$ ,  $Z_{21}$ ,  $a$ ,  $b$  and  $c$  have been obtained from eqs. 7, 8, 9, 10 and 11, respectively as a function of the composition of the binary mixtures and listed in Tables 2 and 4. A perusal of these Tables shows that the values of  $d_{12}$  are negative for all the binary mixtures except for the two binary mixtures involving acetone and methyl acetate as the second component where the values of  $d_{12}$  are positive.

The negative values of  $d_{12}$  indicate the dominance of dispersion forces<sup>4</sup>. On the other hand, the positive values of  $d_{12}$  may be attributed to the presence of strong interactions<sup>4-6</sup>.

**Table 4.** Values of McAllister parameters ( $Z_{12}$  and  $Z_{21}$ ) and Brewer parameters ( $a$ ,  $b$ ,  $c$ ) at 298.15 K

System	$Z_{12}$	$Z_{21}$	$a \times 10^2$ cm <sup>2</sup> s <sup>-1</sup>	$b \times 10^2$ cm <sup>2</sup> s <sup>-1</sup>	$c \times 10^2$ cm <sup>2</sup> s <sup>-1</sup>
Nitromethane + Methyl alcohol	0.4964	0.1626	-0.4049	0.0492	-0.1925
Ethyl alcohol	0.5006	0.2164	-1.2572	0.4558	-0.3723
<i>n</i> -Propyl alcohol	0.5876	0.3438	-2.4744	0.6643	0.3756
Isopropyl alcohol	0.6218	0.3525	-2.5800	0.9091	0.0980
<i>n</i> -Butyl alcohol	0.6235	0.4964	-2.9643	0.5009	0.3500
Isobutyl alcohol	0.6598	0.6088	-3.6133	0.8775	0.3455
Acetone	0.5108	0.1337	0.0301	0.0185	0.0172
Methyl ethyl ketone	0.5109	0.1506	0.0037	0.0013	0.0036
Methyl acetate	0.5295	0.1498	0.0188	0.0046	0.0198
Ethyl acetate	0.5502	0.1629	0.0590	0.0197	0.0132
Carbon tetrachloride	0.6814	0.2555	-0.2368	-0.0649	-0.0453
Benzene	0.5231	0.1783	-0.2056	0.0359	-0.0453
Toluene	0.5454	0.1849	-0.0667	-0.0035	-0.0028

A perusal of the values of  $T_{12}$  and  $H_{12}$  shows that these are positive for all the binary mixtures and are almost identical and do not change appreciably with the change in the composition of the binary mixtures. The values of the parameters  $Z_{12}$  and  $Z_{21}$  are positive for all the binary mixtures and that for each mixture the value of  $Z_{21}$  is smaller than that of  $Z_{12}$ .

A perusal of values of parameters  $a$ ,  $b$  and  $c$  shows that the values of  $a$  are negative for the binary mixtures of nitromethane with aliphatic alcohols and the non-polar solvents while the values are positive in the case of mixtures involving aliphatic ketones and esters as the second component. The values of  $b$  are positive for all the binary mixtures except the ones involving non-polar solvents as the second component. The values of  $c$  are positive for all the mixtures except the ones involving methyl and ethyl alcohols and non-polar solvents as the second component.

### Experimental

Nitromethane and all the polar and non-polar solvents were of A.R. grade and were further purified according to standard procedures<sup>22</sup>. Their purities were checked by comparing their densities and viscosities with the values reported in literature<sup>23,24</sup> at 298.15 K, which almost agreed within the accuracy  $\pm 1 \times 10^{-4}$  g cm<sup>-3</sup> and  $\pm 3 \times 10^{-3}$  mPa.s, respectively and are given in Table I. All the binary mixtures were prepared gravimetrically in stoppered bottles. We charged the heavier components first to minimize the errors in composition due to evaporation during the solution preparation. This led to an accuracy of the order of  $3 \times 10^{-4}$  in the mole fraction. Viscosities of the systems were determined with an accuracy of  $\pm 3 \times 10^{-3}$  mPa.s using an Oswald viscometer, which was suspended in a thermostat maintained at  $298.15 \pm 0.01$  K. The experimental details have been described in our earlier publication<sup>25</sup>.

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