J. Indian Chem. Soc.,
Vol. 84, January 2007, pp. 59-68

Volumetric and viscometric studies of binary and ternary mixtures of *o*-nitrotoluene with methyl alcohol, benzene, toluene, carbon tetrachloride and 1,4-dioxane at 298.15 K

(Ms.) Poonam Rathore and Mukhtar Singh*

Department of Chemistry, Agra College, Agra-282 002, Uttar Pradesh, India

E-mail : mukhtarsingh2003@rediffmail.com

Manuscript received 29 May 2006, accepted 7 November 2006

Abstract : Densities and viscosities of binary and ternary mixtures of *o*-nitrotoluene with methyl alcohol, benzene, toluene, carbon tetrachloride and 1,4-dioxane have been determined at 298.15 K over the whole composition range. From density and viscosity data, viscosity deviations ($\Delta\eta$) and excess thermodynamic functions, viz. the molar volume (V^E) and the excess Gibbs free energy of activation of viscous flow ($\Delta G^{\#E}$) have been calculated in respect of binary and ternary liquid mixtures at 298.15 K and fitted by Redlich-Kister and Cibulka equations respectively. From the small magnitude of the values of standard deviation it is concluded that the experimental values of $\Delta\eta$, V^E and $\Delta G^{\#E}$ compare fairly well with the corresponding theoretical values predicted by Redlich-Kister and Cibulka equations for binary and ternary mixtures respectively.

Keywords : Thermodynamic functions, ternary mixtures, binary mixtures, viscosity.

Yadava and co-workers[1,2] 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 interactions between dipoles and sterically hindered polarizable compounds. In a later publication[3], they reported 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 molar volume (V^E). It was 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.

Agarwal and Singh[4] have reported viscometric studies of molecular interactions in binary liquid mixtures of nitromethane with 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 at 298.15 K. Recently, Varshney and Singh[5] have undertaken volumetric and viscometric studies of binary and ternary mixtures of nitrobenzene with 1,4-dioxane, benzene, toluene and carbon tetrachloride at 303.15 K. Viscosity deviations ($\Delta\eta$) and excess thermodynamic properties viz. excess molar volume (V^E) and excess Gibbs free energy of activation of viscous flow ($\Delta G^{\#E}$) have been calculated from experimental data in respect of binary and ternary mixtures at 303.15 K, and fitted by Redlich-Kister[6] and Cibulka[7] equations respectively.

From the above described survey of literature it appears that volumetric and viscometric studies of ternary mixtures of *o*-nitrotoluene as the first component, methyl alcohol as the second component and a non-polar solvent (benzene/toluene/carbon tetrachloride/1,4-dioxane), as the third component and their constituent binary mixtures are still lacking. Hence the title study has been undertaken at 298.15 K in respect of the following binary and ternary mixtures :

Binary mixtures : *o*-Nitrotoluene + methyl alcohol; *o*-nitrotoluene + benzene; methyl alcohol + benzene; *o*-

*Address for correspondence : H.I.G. 142, Phase A, Shastri Puram, P.O. Sikandra, Agra-282 007. Uttar Pradesh, India.

nitrotoluene + toluene; methyl alcohol + toluene; *o*-nitrotoluene + carbon tetrachloride; methyl alcohol + carbon tetrachloride; *o*-nitrotoluene + 1,4-dioxane and methyl alcohol + 1,4-dioxane.

Ternary mixtures : *o*-Nitrotoluene + methyl alcohol + benzene; *o*-nitrotoluene + methyl alcohol + toluene; *o*-nitrotoluene + methyl alcohol + carbon tetrachloride and *o*-nitrotoluene + methyl alcohol + 1,4-dioxane.

Results and discussion

The experimentally determined densities and viscosities of the pure components at 298.15 K have been compared with the literature values and are presented in Table 1. It is seen that the experimental values compare fairly well with the literature values.

Table 1. Comparison of experimental densities and viscosities of pure liquids with literature values at 298.15 K

Pure liquid	ρ (g cm^{-3})		η (mPa.s)		
	Expt.	Lit.	Expt.	Lit.	Ref.
o-Nitrotoluene	1.1557	1.1629[a]	2.0081	2.3700[a]	20
Methyl alcohol	0.7881	0.7860	0.5482	0.5513	21
Benzene	0.8697	0.8671	0.6080	0.6048	22
Toluene	0.8605	0.8671	0.5641	0.5625	23
Carbon tetrachloride	1.5861	1.5885	0.9096	0.9082	22
1,4-Dioxane	1.0408	1.0222[b]	1.1800	1.0937[b]	24

[a]At 293.15 K, [b]at 303.15 K.

The viscosity deviations ($\Delta\eta$), excess molar volumes (V^E) and excess molar Gibbs free energies of activation of viscous flow ($\Delta G^{\#E}$) for binary and ternary mixtures were determined using the following equation[8].

$$\Delta\eta = \eta - \sum_{i=1}^{n} x_i\eta_i \quad (1)$$

where x_i, is the mole fraction of the i-the component and η_i and η refer to the viscosities of i-th pure components and of the mixtures

$$V^E = V - \sum_{i=1}^{n} x_iV_i \quad (2)$$

where V_i represents the molar volume and x_i the mole fraction of the i-th component. The quantity V refers to the molar volume of the mixture which can be calculated from the mixture density (ρ), and the component molecular weight M_i as below :

$$V = \sum_{i=1}^{n} x_iM_i / \rho \quad (3)$$

$$\Delta G^{\#E} = RT\left[\ln \eta V - \left[\sum_{i=1}^{n} x_i \ln \eta_i V_i\right]\right] \quad (4)$$

where the letters have their usual significance.

The values of densities (ρ), viscosities (η), viscosity deviations ($\Delta\eta$) and excess thermodynamic properties viz. the excess molar volumes (V^E) and the excess molar Gibbs free energies of activation of viscous flow ($\Delta G^{\#E}$) at 298.15 K in respect of binary and ternary mixtures have been presented in Tables 2 and 3 respectively.

Table 2. Densities, viscosities, viscosity deviations and excess properties of binary liquid mixtures at 298.15 K

x_1	x_2	ρ (g cm^{-3})	η (mPa.s)	Δη (mPa.s)	V (cm^3 mol^{-1})	V^E (cm^3 mol^{-1})	$\Delta G^{\#E}$ (J mol^{-1})
			o-Nitrotoluene + methyl alcohol				
0.0000	1.0000	0.7881	0.5482	0.0000	40.655	0.0000	0.00
0.0366	0.9634	0.8903	0.6659	0.0642	40.310	−3.2000	250.00
0.0791	0.9209	0.9602	0.8743	0.2106	42.025	−4.8000	787.55
0.1281	0.8719	1.0382	1.0518	0.3166	43.830	−6.8175	1066.87
0.1859	0.8141	1.1514	1.3786	0.5590	44.795	−10.3615	1458.50
0.2550	0.7450	1.2097	1.6589	0.7384	48.639	−11.9081	1719.82
0.3396	0.6604	1.2719	1.9265	0.8825	53.251	−13.8960	1819.82
0.4443	0.5557	1.3468	2.4395	1.2427	58.461	−16.8533	2024.86
0.5780	0.4220	1.3342	2.9003	1.5083	69.544	−16.2003	2100.00
0.7550	0.2450	1.2767	2.8156	1.1652	87.252	−12.3000	1540.00
1.0000	0.0000	1.1557	2.0081	0.0000	118.664	0.0000	0.00

Table-2 (contd.)

			o-Nitrotoluene + benzene				
0.0000	1.0000	0.8650	0.5640	0.0000	90.301	0.0000	0.00
0.0777	0.9223	0.9376	0.7188	0.0426	88.204	−4.3000	250.00
0.1602	0.8398	1.0428	0.9971	0.2017	83.976	−10.8684	630.00
0.2461	0.7539	1.0991	1.2094	0.2900	84.281	−12.9999	791.55
0.3367	0.6633	1.1728	1.4822	0.4320	83.551	−16.3000	930.00
0.4318	0.5682	1.2400	1.7165	0.5290	83.548	−19.0000	930.00
0.5332	0.4668	1.2535	1.9489	0.6149	87.424	−18.0000	970.00
0.6399	0.3601	1.2481	2.0384	0.5504	92.851	−15.5993	820.00
0.7531	0.2469	1.2298	2.1210	0.4694	99.661	−12.0000	658.21
0.8723	0.1277	1.2199	2.1844	0.3607	106.242	−8.7999	430.00
1.0000	0.0000	1.1557	2.0081	0.0000	118.664	0.0000	0.00
			Methyl alcohol + benzene				
0.0000	1.0000	0.8650	0.5640	0.0000	90.301	0.0000	0.00
0.1979	0.8021	0.9493	0.7278	0.1669	72.676	−7.8000	507.54
0.3570	0.6430	0.9933	0.8351	0.2767	62.077	−10.5002	788.31
0.4878	0.5122	1.0342	0.8502	0.2939	53.798	−12.2853	745.09
0.5971	0.4029	1.0258	0.8567	0.3021	49.328	−11.3286	773.27
0.6895	0.3105	1.0166	0.8151	0.2620	45.586	−10.4836	641.47
0.7692	0.2308	1.0106	0.7810	0.2292	42.227	−9.8859	507.00
0.8384	0.1616	0.9707	0.7175	0.1667	40.677	−8.0007	343.07
0.8990	0.1010	0.9250	0.6896	0.1398	39.669	−6.0003	306.22
0.9523	0.0477	0.8346	0.6003	0.0513	41.023	−2.0000	152.00
1.0000	0.0000	0.7881	0.5482	0.0000	40.655	0.0000	0.00
			o-Nitrotoluene + toluene				
0.0000	1.0000	0.8582	0.5229	0.0000	107.364	0.0000	0.00
0.0911	0.9089	1.0682	1.2082	0.5500	90.093	−18.3007	1336.85
0.1849	0.8151	1.2333	1.1874	0.3899	81.454	−28.0000	697.34
0.2796	0.7204	1.5648	1.7981	0.8599	66.924	−43.6000	902.88
0.3761	0.6239	1.7011	2.3316	1.2501	64.114	−47.4999	1098.04
0.4746	0.5254	1.9326	2.9962	1.7684	58.727	−54.0003	1150.01
0.5757	0.4243	1.9080	2.8578	1.4799	61.870	−52.0000	793.84
0.6789	0.3211	1.6617	2.4712	0.9400	73.836	−41.2000	497.11
0.7837	0.2163	1.5328	2.5469	0.8600	83.120	−33.1000	489.85
0.8907	0.1093	1.3712	2.4757	0.6300	96.429	−21.0003	402.92
1.0000	0.0000	1.1557	2.0081	0.0000	118.664	0.0000	0.00
			Methyl alcohol + toluene				
0.0000	1.0000	0.8582	0.5229	0.0000	107.3643	0.0000	0.00
0.2269	0.7731	0.8455	0.4483	−0.0804	92.8476	0.6197	−226.00
0.3977	0.6023	0.8357	0.4159	−0.1170	81.6539	0.8200	−340.78
0.5309	0.4691	0.8275	0.4113	−0.1250	72.7882	0.8400	−348.31
0.6377	0.3623	0.8201	0.4185	−0.1205	65.6227	0.7991	−317.00
0.7252	0.2748	0.8130	0.4363	−0.1050	59.7256	0.7391	−246.05
0.7983	0.2017	0.8084	0.4562	−0.0869	54.6300	0.5200	−188.00
0.8606	0.1394	0.8025	0.4771	−0.0676	50.3631	0.4091	−135.00
0.9136	0.0864	0.7973	0.4928	−0.0532	46.6975	0.2791	−120.57

Table-2 (contd.)

0.9597	0.0403	0.7922	0.5171	–0.0300	43.5023	0.1592	–70.18
1.0000	0.0000	0.7881	0.5482	0.0000	40.6547	0.0000	0.00
			o-Nitrotoluene + carbon tetrachloride				
0.0000	1.0000	1.5775	0.8300	0.0000	97.509	0.000	0.00
0.0834	0.9166	1.3873	0.7357	–0.1925	109.874	10.601	–230.00
0.1709	0.8291	1.1737	0.6586	–0.3727	128.624	27.500	–350.00
0.2606	0.7394	1.1070	0.6591	–0.4779	135.022	32.001	–470.00
0.3540	0.6460	1.0315	0.6571	–0.5899	143.398	38.400	–580.00
0.4507	0.5493	0.9978	0.7078	–0.6532	146.625	39.582	–600.00
0.5524	0.4476	0.9853	0.7646	–0.7162	146.758	37.563	–680.00
0.6570	0.3430	0.9859	0.8878	–0.7162	144.908	33.500	–620.00
0.7668	0.2332	1.0093	1.0574	–0.6760	139.730	25.999	–570.00
0.8804	0.1196	1.0459	1.4312	–0.4360	133.034	16.900	–240.00
1.0000	0.0000	1.1557	2.0081	0.0000	118.664	0.000	0.00
			Methyl alcohol + carbon tetrachloride				
0.0000	1.0000	1.5775	0.8300	0.0000	97.509	0.000	0.00
0.2104	0.7896	1.6363	0.8395	0.0688	78.347	–7.200	161.00
0.3750	0.6250	1.6365	0.8288	0.1045	66.089	–10.100	235.00
0.5069	0.4931	1.6103	0.8105	0.1234	57.189	–11.500	243.00
0.6154	0.3846	1.5075	0.7666	0.1100	52.321	–10.200	231.01
0.7057	0.2943	1.4297	0.7387	0.1075	47.477	–9.910	186.00
0.7826	0.2174	1.3205	0.7057	0.0962	44.314	–8.701	147.00
0.8483	0.1517	1.2271	0.6886	0.0976	41.166	–8.114	113.00
0.9057	0.0943	1.0877	0.6477	0.0729	40.016	–6.000	74.00
0.9555	0.0445	0.9051	0.5806	0.0199	41.385	–1.800	45.00
1.0000	0.0000	0.7881	0.5482	0.0000	40.655	0.000	0.00
			o-Nitrotoluene + 1,4-dioxane				
0.0000	1.0000	1.0195	1.0500	0.0000	86.425	0.000	0.00
0.0747	0.9253	1.0209	1.1607	0.0391	89.891	1.058	170.00
0.1543	0.8457	1.0273	1.3254	0.1276	93.131	1.732	400.00
0.2380	0.7620	1.0385	1.3984	0.1204	96.080	1.983	410.00
0.3269	0.6731	1.0518	1.5023	0.1391	99.007	2.043	450.00
0.4210	0.5790	1.0621	1.6227	0.1693	102.393	2.396	500.00
0.5222	0.4778	1.0799	1.7572	0.2069	105.298	2.038	525.02
0.6297	0.3703	1.0953	1.8813	0.2280	108.636	1.910	514.12
0.7448	0.2552	1.1189	1.9919	0.2284	111.387	0.950	441.09
0.8673	0.1327	1.1386	2.0507	0.1697	114.736	0.350	290.90
1.0000	0.0000	1.1557	2.0081	0.0000	118.664	0.000	0.00
			Methyl alcohol + 1,4-dioxane				
0.0000	1.0000	1.0195	1.0500	0.0000	86.425	0.000	0.00
0.1911	0.8089	1.0843	1.0269	0.0728	71.377	–6.301	138.10
0.3470	0.6530	1.1228	0.9980	0.1221	61.142	–9.400	227.69
0.4767	0.5233	1.1324	0.9857	0.1749	54.206	–10.400	352.02
0.5864	0.4136	1.1049	0.9327	0.1770	49.986	–9.600	396.60
0.6799	0.3201	1.0703	0.8558	0.1470	46.706	–8.600	339.54
0.7612	0.2388	1.0569	0.8084	0.1404	42.984	–8.600	274.30

Table-2 (contd.)

0.8323	0.1677	0.9860	0.7304	0.0980	42.030	−6.300	213.57
0.8950	0.1050	0.9351	0.6788	0.0779	40.561	−4.900	161.16
0.9502	0.0498	0.8468	0.5806	0.0074	41.134	−1.800	51.20
1.0000	0.0000	0.7881	0.5482	0.0000	40.655	0.000	0.00

Table 3. Densities, viscosities, viscosity deviations and thermodynamic excess properties of ternary liquid mixtures at 298.15 K

x_1	x_2	x_3	ρ (g cm^{-3})	η (mPa.s)	Δη (mPa.s)	V (cm^3 mol^{-1})	V^E (cm^3 mol^{-1})	$\Delta G^{\#E}$ (J mol^{-1})
			o-Nitrotoluene + methyl alcohol + benzene					
0.2373	0.6932	0.0695	1.2914	1.6519	0.7562	46.603	−16.014	1562.314
0.0691	0.2023	0.7286	1.9042	1.4030	0.7424	38.268	−43.949	285.677
0.0992	0.2906	0.6102	1.8315	1.3870	0.6843	38.535	−40.152	341.190
0.1275	0.3713	0.5011	1.7169	1.4231	0.6809	39.912	−35.563	553.415
0.1529	0.4457	0.4014	1.6596	1.4776	0.6998	40.131	−32.380	717.126
0.1764	0.5146	0.3089	1.5521	1.5883	0.7777	41.755	−27.992	1052.358
0.1983	0.5786	0.2231	1.4652	1.5894	0.7482	43.105	−24.095	1181.437
0.2185	0.6381	0.1433	1.3966	1.6721	0.8027	44.111	−20.699	1413.759
0.2373	0.6932	0.0695	1.2914	1.6519	0.7562	46.603	−16.014	1562.314
0.2660	0.6993	0.0347	1.2632	1.7193	0.7822	48.762	−14.366	1678.362
0.3083	0.6551	0.0366	1.2756	1.9190	0.9201	51.840	−14.682	1852.991
0.3734	0.5446	0.0819	1.3984	2.2610	1.1664	53.673	−20.172	1871.600
0.4301	0.4827	0.0871	1.4091	2.4226	1.2452	57.662	−20.864	1876.824
0.4946	0.4124	0.0930	1.4507	2.6277	1.3560	60.872	−22.983	1819.928
0.6054	0.2356	0.1590	1.4905	2.8980	1.4635	69.101	−26.674	1587.087
0.6537	0.2386	0.1077	1.5173	3.2297	1.7255	69 668	−27.329	1699.210
0.7537	0.1295	0.1168	1.5357	3.4261	1.7757	75.948	−29.301	1449.373
0.8098	0.1314	0.0588	1.5378	3.9029	2.1715	77.941	−28.805	1628.844
0.8098	0.1314	0.0588	1.5378	3.9029	2.1715	77.941	−28.805	1628.844
			o-Nitrotoluene + methyl alcohol + toulene					
0.0781	0.2288	0.6930	1.4062	1.0361	0.3915	58.237	−34.736	430.99
0.1099	0.3217	0.5684	1.6323	1.2361	0.5418	47.632	−39.513	468.65
0.1385	0.4033	0.4582	1.8584	1.5405	0.8017	39.891	−42.134	662.28
0.1633	0.4760	0.3607	2.0844	1.8558	1.0783	34.005	−43.451	808.17
0.1855	0.5411	0.2735	2.3105	2.3645	1.5524	29.421	−43.954	1123.42
0.2056	0.6000	0.1944	2.5366	2.7516	1.9082	25.756	−43.906	1235.17
0.2236	0.6530	0.1234	2.7626	3.3078	2.4363	22.789	−43.541	1448.56
0.2400	0.7011	0.0589	2.9887	3.8232	2.9261	20.345	−42.962	1579.81
0.2673	0.7029	0.0298	3.2148	4.3756	3.4379	19.262	−44.232	1686.88
0.3099	0.6586	0.0315	3.4408	5.1761	4.1763	19.328	−47.603	1860.55
0.3785	0.5520	0.0696	3.6669	5.9290	4.8299	20.728	−54.101	1879.87
0.4363	0.4896	0.0740	3.8930	6.6930	5.5098	21.151	−58.472	1882.40
0.5021	0.4187	0.0791	4.1190	7.4609	6.1817	21.744	−63.352	1820.99
0.6208	0.2417	0.1375	4.3451	8.4485	6.9975	24.292	−73.964	1567.99
0.6654	0.2428	0.0918	4.5712	9.7302	8.2129	23.515	−75.171	1682.10
0.8682	0.1320	0.0998	4.7972	0.7022	9.0350	24.760	−82.480	1419.53
0.8168	0.1325	0.0506	5.0233	2.7488	0.2013	24.073	−83.672	1614.76

Table-3 (contd.)

0.8168	0.1325	0.0506	5.0233	12.7488	0.2013	24.073	−83.672	1614.76
			o-Nitrotoluene + methyl alcohol + carbon tetrachloride					
0.0730	0.2139	0.7130	1.9042	1.4030	0.5474	66.453	−20.429	854.29
0.1039	0.3042	0.5919	1.8315	1.3870	0.5203	62.813	−19.599	891.68
0.1324	0.3856	0.4820	1.7169	1.4231	0.5458	60.956	−17.431	1067.83
0.1576	0.4593	0.3831	1.6596	1.4776	0.5914	57.397	−17.333	1181.87
0.1806	0.5268	0.2926	1.5521	1.5883	0.6940	55.831	−15.548	1451.05
0.2015	0.5881	0.2104	1.4652	1.5894	0.6877	53.807	−14.529	1502.08
0.2208	0.6448	0.1343	1.3966	1.6721	0.7638	51.268	−14.243	1640.95
0.2385	0.6967	0.0648	1.2914	1.6519	0.7373	50.332	−12.612	1683.30
0.2666	0.7011	0.0323	1.2632	1.7193	0.7728	50.661	−12.628	1738.33
0.3091	0.6569	0.0340	1.2756	1.9190	0.0257	53.830	−12.871	1908.88
0.3756	0.5479	0.0765	1.3984	2.2610	1.1429	57.805	−16.499	1966.53
0.4329	0.4858	0.0814	1.4091	2.4226	1.2194	62.063	−16.994	1960.74
0.4979	0.4152	0.0869	1.4507	2.6277	1.3281	65.453	−18.983	1894.34
0.6124	0.2384	0.1492	1.4905	2.8980	1.4137	76.871	−20.040	1660.08
0.6588	0.2405	0.1007	1.5173	3.2297	1.6913	74.833	−22.939	1746.05
0.7601	0.1306	0.1093	1.5357	3.4261	1.7374	81.549	−24.615	1478.53
0.8133	0.1320	0.0547	1.5378	3.9029	2.1519	80.750	−26.459	1641.88
0.8133	0.1320	0.0547	1.5378	3.9029	2.1519	80.750	−26.459	1641.88
			o-Nitrotoluene + methyl alcohol + 1,4-dioxane					
0.0669	0.1959	0.7373	1.1860	1.1791	0.1632	67.803	−11.820	210.00
0.0966	0.2828	0.6207	1.2140	1.1619	0.1612	63.426	−13.178	240.00
0.1247	0.3631	0.5122	1.2380	1.2515	0.2642	59.665	−14.161	490.00
0.1502	0.4377	0.4121	1.2650	1.2890	0.3148	56.073	−15.160	610.00
0.1740	0.5076	0.3184	1.2800	1.3099	0.3479	53.266	−15.536	710.49
0.1963	0.5729	0.2309	1.3030	1.4134	0.4627	50.361	−16.179	936.54
0.2171	0.6340	0.1488	1.3200	1.5805	0.6407	47.877	−16.520	1258.53
0.2366	0.6910	0.0724	1.3220	1.6911	0.7612	46.117	−16.309	1487.73
0.2654	0.6980	0.0366	1.3300	1.8102	0.8562	46.606	−16.428	1640.55
0.3076	0.6538	0.0385	1.3700	2.0609	1.0444	48.558	−17.851	1812.91
0.3721	0.5426	0.0853	1.4000	2.2637	1.1295	54.236	−19.350	1776.61
0.4285	0.4808	0.0907	1.4140	2.4310	1.2117	58.105	−20.128	1774.07
0.4925	0.4107	0.0968	1.3998	2.5355	1.2197	63.746	−19.759	1709.86
0.6008	0.2338	0.1654	1.3839	2.6908	1.1825	75.482	−19.612	1396.06
0.6506	0.2375	0.1120	1.3769	2.9308	1.3765	77.495	−19.043	1568.52
0.7497	0.1288	0.1215	1.3601	3.0343	1.3306	86.497	−18.202	1308.33
0.8072	0.1310	0.0618	1.3571	3.4441	1.6865	88.679	−17.774	1558.26

The experimentally determined values of $\Delta\eta$, V^E and $\Delta G^{\#E}$ for binary mixtures were fitted to Redlich-Kister's equation[6],

$$Y^E_{ij} = x_i x_j \sum_{p=0}^{p} Ap(x_i - x_j)^p \qquad (5)$$

where Y^E_{ij} is $\Delta\eta$ or V^E or $\Delta G^{\#E}$, x_i denotes the mole fraction of component i of the i, j mixtures with $x_j = 1-x_i$, and Ap are adjustable parameters. Redlich-Kister's[6] equation is fitted to each set of the experimental values of $\Delta\eta$, V^E and $\Delta G^{\#E}$ for the binary mixtures to evaluate the values of parameters Ap by the least-squares method using a computer. The parameters Ap are then used to evaluate Y^E_{ij} values from eq. (5). The standard deviation $\sigma(Y^E_{ij})$ is defined by equation[9],

$$\sigma(Y_{ij}^{E}) = \left[\frac{\Sigma(Y_{ij}^{E}\,\text{exp t.} - Y_{ij}^{E}\text{calc.})^2}{(n-p)}\right]^{1/2} \quad (6)$$

where n is the number of experimental data and p is the number of parameters. The results have been presented in Table 4. It is seen that for all the binary mixtures the fit is good as evident from very small values of the standard deviation (σ).

The viscosity deviations ($\Delta\eta$), the excess molar volumes (V^E) and the excess Gibbs free energies of activation of viscous flow ($\Delta G^{\#E}$) for the ternary mixtures have been fitted to Cibulka's[7] equation,

$$Y^E = Y^E_{bin} + x_1x_2x_3[B_1 + B_2x_1 + B_3x_2] \quad (7)$$

Table 4. Coefficients of Redlich-Kister's equation and the corresponding standard deviation (σ) for the binary mixtures at 298.15 K

Viscosity deviations ($\Delta\eta$) and excess functions (Y^E)	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	σ
				o-Nitrotoluene + methyl alcohol					
$\Delta\eta$ (mPa.s)	5.373	2.750	-0.780	-	-	-	-	-	0.0051
V^E (cm^3 mol^{-1})	65.709	2.569	1.634	-	-	-	-	-	0.0160
$\Delta G^{\#E}$ (J mol^{-1})	9514.3	10364.0	-46178.5	-348475.9	-321902.3	932282.1	1877836.4	928292.9	0.4066
				Methyl alcohol + benzene					
$\Delta\eta$ (mPa.s)	1.205	0.161	-0.035	-	-	-	-	-	0.0122
V^E (cm^3 mol^{-1})	46.913	5.356	15.078	-	-	-	-	-	0.0956
$\Delta G^{\#E}$ (J mol^{-1})	2999.5	593.8	5685.8	-16483.4	-24852.7	52673.1	23887.9	-42066.7	0.4150
				Methyl alcohol + benzene					
$\Delta\eta$ (mPa.s)	2.285	1.044	-0.472	-	-	-	-	-	0.0033
V^E (cm^3 mol^{-1})	72.351	-4.645	-3.118	-	-	-	-	-	0.0113
$\Delta G^{\#E}$ (J mol^{-1})	3864.0	-467.0	5685.8	-3507.3	12461.3	9177.5	-14676.9	-4660.4	0.3120
				o-Nitrotoluene + toluene					
$\Delta\eta$ (mPa.s)	-0.492	-0.041	0.128	-	-	-	-	-	0.0003
V^E (cm^3 mol^{-1})	-208.402	6.647	19.309	-	-	-	-	-	0.0531
$\Delta G^{\#E}$ (J mol^{-1})	4243.0	-4709.1	-340.2	5452.7	14465.0	48525.1	15459.5	-95236.5	0.3880
				Methyl alcohol + toluene					
$\Delta\eta$ (mPa.s)	-0.492	-0.076	-0.066	-	-	-	-	-	0.0042
V^E (cm^3 mol^{-1})	3.433	-0.021	0.174	-	-	-	-	-	0.0123
$\Delta G^{\#E}$ (J mol^{-1})	-1410.1	196.1	-340.2	-2487.1	13563.0	807.3	-34693.6	22176.5	0.6463
				o-Nitrotoluene + carbon tetrachloride					
$\Delta\eta$ (mPa.s)	-2.764	-0.136	1.553	-	-	-	-	-	0.0130
V^E (cm^3 mol^{-1})	156.536	-21.978	12.720	-	-	-	-	-	0.0135
$\Delta G^{\#E}$ (J mol^{-1})	-2604.3	-949.2	-718.5	6952.8	-10237.2	-31661.2	16592.6	39584.6	0.4760
				Methyl alcohol + carbon tetrachloride					
$\Delta\eta$ (mPa.s)	0.452	0.145	0.227	-	-	-	-	-	0.0111
V^E (cm^3 mol^{-1})	-43.086	-7.482	-18.715	-	-	-	-	-	0.0167
$\Delta G^{\#E}$ (J mol^{-1})	965.4	484.3	-718.5	-9807.2	20086.9	13443.7	-54703.0	31980.9	0.9950
				o-Nitrotoluene + 1,4-dioxane					
$\Delta\eta$ (mPa.s)	0.778	0.515	0.689	-	-	-	-	-	0.0050
V^E (cm^3 mol^{-1})	8.584	-5.783	-0.834	-	-	-	-	-	0.0185
$\Delta G^{\#E}$ (J mol^{-1})	2088.0	30.9	700.5	6771.4	-218.8	-36116.8	3466.3	40636.2	0.0579
				Methyl alcohol + 1,4-dioxane					
$\Delta\eta$ (mPa.s)	0.684	0.229	-0.282	-	-	-	-	-	0.0140
V^E (cm^3 mol^{-1})	-40.348	-2.246	-8.854	-	-	-	-	-	0.0235
$\Delta G^{\#E}$ (J mol^{-1})	1459.9	1016.2	700.5	-2300.6	-30282.4	32793.6	69975.7	-79289.9	0.9934

where,

$$Y^{E}_{bin} = Y^{E}_{12} + Y^{E}_{13} + Y^{E}_{23} \quad (8)$$

The values of coefficients B_1, B_2, B_3 (eq. (7)) and the standard deviations (σ) obtained by the least-squares method, are presented in Table 5. It is seen that the fit is good as revealed by the small values of σ. Thus, the experimental values of $\Delta\eta$, V^E and $\Delta G^{\#E}$ are well correlated to their theoretical values predicted by Cibulka's equation.

Table 5. Coefficients of Cibulka equation and the corresponding standard deviation (σ), for the ternary mixtures at 298.15 K

Viscosity deviations ($\Delta\eta$) and excess functions (Y^E)	B_1	B_2	B_3	σ
o-Nitrotoluene + methyl alcohol + benzene				
$\Delta\eta$ (mPa.s)	32.426	48.635	-82.292	0.501
V^E (cm^3 mol^{-1})	-2518.288	1281.497	3600.073	0.027
$\Delta G^{\#E}$ (J mol^{-1})	-121389.5	-189543.8	311484.5	4.88
o-Nitrotoluene + methyl alcohol + toluene				
$\Delta\eta$ (mPa.s)	184.484	-145.915	-539.756	1.184
V^E (cm^3 mol^{-1})	-2607.914	-817.301	5034.580	0.035
$\Delta G^{\#E}$ (J mol^{-1})	1097555.590	6569892.083	-5295145.826	0.256
o-Nitrotoluene + methyl alcohol + carbon tetrachloride				
$\Delta\eta$ (mPa.s)	15.510	151.956	-28.364	0.012
V^E (cm^3 mol^{-1})	-1921.872	340.379	2731.689	0.047
$\Delta G^{\#E}$ (J mol^{-1})	-29344.808	-43313.286	195727.121	0.311
o-Nitrotoluene + methyl alcohol + 1,4-dioxane				
$\Delta\eta$ (mPa.s)	-1.164	67.094	-38.989	0.015
V^E (cm^3 mol^{-1})	-376.687	-278.160	572.342	0.036
$\Delta G^{\#E}$ (J mol^{-1})	-61758.923	-296063.544	256898.245	0.936

A perusal of the values of $\Delta\eta$ (Table 3) in respect of the ternary mixtures : *o*-nitrotoluene +methyl alcohol + (benzene or + toluene or + carbon tetrachloride or + 1,4-dioxane), shows that these are positive over the entire range of composition. Further on comparing the values of $\Delta\eta$ at $x_1 \approx 0.5$ it is seen that the values are in the following order : toluene > benzene > carbon tetrachloride > 1,4-dioxane.

Thus, with *o*-nitrotoluene and methyl alcohol being the common components in all the four ternary mixtures, the values of $\Delta\eta$ are dependent upon the nature of third component which is different in all the four ternary mixtures under discussion. From the above order in the values of $\Delta\eta$ it follows that maximum viscosity deviations which are characteristic of the nonideal behaviour of the mixtures, are observed in the ternary mixture *o*-nitrotoluene with methyl alcohol and toluene.

The positive values of $\Delta\eta$ in respect of the above mentioned ternary mixtures arise[10] due to higher viscosity contribution of interactions involving polar molecules of *o*-nitrotoluene and methyl alcohol on the one hand and on the other hand, non-polar molecules of benzene/toluene/carbon tetrachloride/1,4-dioxane.

In the case of binary mixtures : *o*-nitrotoluene + methyl alcohol; *o*-nitrotoluene + benzene; *o*-nitrotoluene + toluene; *o*-nitrotoluene+ 1,4-dioxane; methyl alcohol + carbon tetrachloride and methyl alcohol + 1,4-dioxane the values of $\Delta\eta$ are positive. However, in the case of binary mixtures : *o*-nitrotoluene + carbon tetrachloride and methyl alcohol + toluene the values of $\Delta\eta$ are negative. The negative values of $\Delta\eta$ suggest that dispersive type of force are predominant in these mixtures[11].

The value of V^E for all the ternary mixtures under discussion are negative over the entire range of composition. These negative values may be ascribed[12] to intermolecular dipolar interactions and geometrical fitting between mixing components in the ternary mixtures.

So far as the values of V^E in regard to constituent binary mixtures are concerned it is seen that the values of V^E are negative in all the binary mixtures except for the mixtures : *o*-nitrotoluene + carbon tetrachloride and methyl alcohol + toluene; where the values are positive. The positive values of V^E in these binaries may be attributed to dispersive interactions between unlike molecules of mixing components.

The values of excess molar Gibbs free energies of activation of viscous flow ($\Delta G^{\#E}$) for all ternary mixtures are positive over the entire composition range which suggest that the flow of ternary mixtures is difficult as compared to the behaviour of pure components. The positive values of $\Delta\eta$ for these mixtures support this conclusion.

The values of $\Delta G^{\#E}$ in the case of constituent binary mixtures are positive except for the mixtures of *o*-nitrotoluene + carbon tetrachloride and methyl alcohol + toluene for which the values of $\Delta G^{\#E}$ are negative. The negative values of $\Delta G^{\#E}$ in these mixtures point out the easier flow of the mixtures compared with the behaviour of pure liquids[13]. The negative values of $\Delta\eta$ for these mixtures support this conclusion.

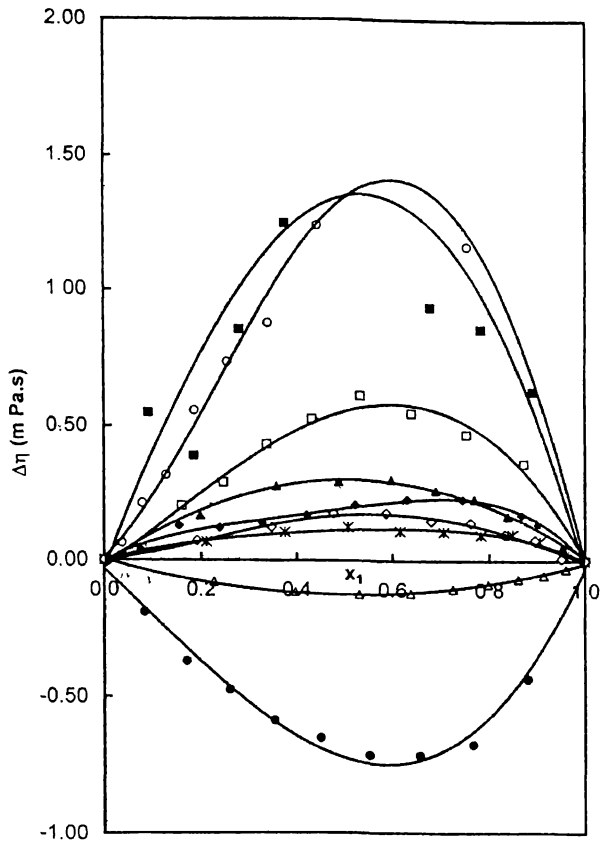

Fig. 1. Variation of viscosity deviations ($\Delta\eta$) with mole fraction x_1 of the first component in binary liquid mixture of (○) *o*-nitrotoluene + methyl alcohol, (□) *o*-nitrotoluene + benzene, (▲) methyl alcohol + benzene, (■) *o*-nitrotoluene + toluene, (Δ) methyl alcohol + toluene, (•) *o*-nitrotoluene + carbon tetrachloride, (*) methyl alcohol + carbon tetrachloride, (♦) *o*-nitrotoluene + 1,4-dioxane and (◇) methyl alcohol + 1,4-dioxane at 298.15 K.

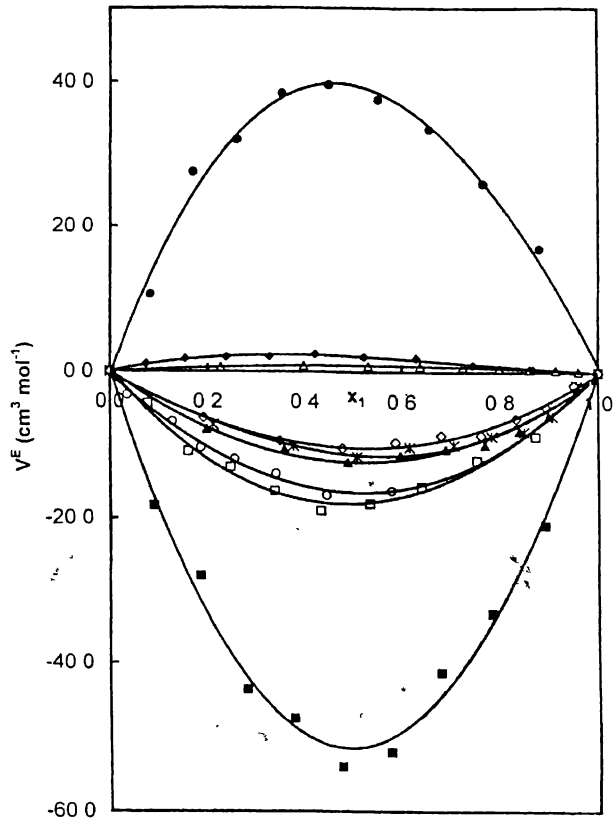

Fig. 2. Variation of excess molar volume (V^E) with mole fraction x_1 of first component of binary liquid mixture of (○) *o*-nitrotoluene +methyl alcohol, (□) *o*-nitrotoluene + benzene, (▲) methyl alcohol + benzene, (■) *o*-nitrotoluene + toluene, (Δ) methyl alcohol + toluene, (•) *o*-nitrotoluene + carbon tetrachloride, (*) methyl alcohol + carbon tetrachloride, (♦) *o*-nitrotoluene + 1,4-dioxane and (◇) methyl alcohol + 1,4-dioxane at 298.15 K.

The plots of $\Delta\eta$, V^E and $\Delta G^{\#E}$ versus x_1 in respect of the binary mixtures have been presented in Figs. 1-3. It is seen that in each case the plots are of parabolic shape and are characterized by the presence of well-defined maxima/minima which indicate the presence of complex formation[14,15] between the mixing components of binary mixtures.

Experimental

All the organic liquids used in the present study were of analytical reagent grade and were obtained from B.D.H., Merck. They were further purified according to the procedure described in literature[16-18]

Binary and ternary liquid mixtures of various compositions were prepared by mass in a 25 cm^3 flask using a Mettler analytical balance. The uncertainty in the mole fraction of the mixtures is estimated to be less than $\pm 1.0 \times 10^{-4}$. Density and viscosity measurements were carried out using a thermostatically controlled, well-stirred water bath, where temperatures were measured with a digital thermometer with an accuracy of ± 0.01 K.

Densities of pure liquids and their binary and ternary mixtures were measured at 298.15 K with a digital vibrating tube densimeter (Anton Parr, Austria). The uncertainty of the density measurements was estimated to be less than $\pm 1 \times 10^{-4}$ g cm^{-3}. The viscosities (η) of pure organic liquids and their binary and ternary liquid mixtures were determined using a Ostwald viscometer which was suspended in a thermostat maintained at 298.15 $\pm$ 0.01 K. The details of the procedure have been re-

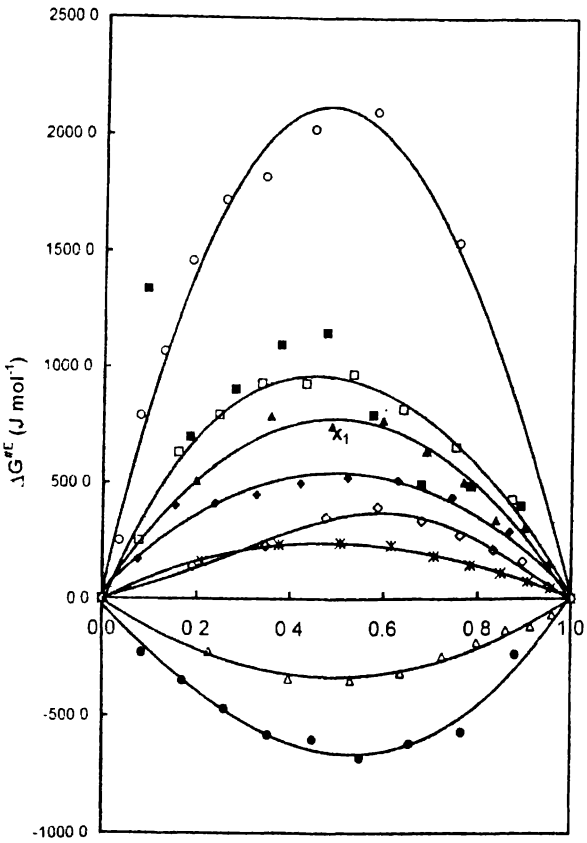

Fig. 3. Variation of excess Gibbs free energy of activation of flow ($\Delta G^{\#E}$) with fraction (x_1) of the first component in binary liquid mixture of (○) *o*-nitrotoluene + methyl alcohol, (□) *o*-nitrotoluene + benzene, (▲) methyl alcohol + benzene, (■) *o*-nitrotoluene + toluene, (Δ) methyl alcohol + toluene, (•) *o*-nitrotoluene + carbon tetrachloride, (*) methyl alcohol + carbon tetrachloride, (♦) *o*-nitrotoluene + 1,4-dioxane and (◇) methyl alcohol + 1,4-dioxane at 298.15 K.

ported in an earlier publication[19]. The uncertainty of calculated absolute viscosities was $\pm 1 \times 10^{-4}$ mPa.s.

References

1. R. R. Yadava and V. N. Singh, *Indian J. Chem., Sect. A*, 1982, **21**, 17.
2. R. R. Yadava, S. S. Yadava and V. N. Singh, *J. Chem. Eng. Data*, 1988, **33**, 402.
3. R. R. Yadava, V. N. Singh and S. S. Yadava, *J. Chem. Eng. Data*, 1994, **39**, 705.
4. D. Agarwal and M. Singh, *J. Indian Chem. Soc.*, 2004, **81**, 850.
5. S. Varshney and M. Singh, *J. Indian Chem. Soc.*, 2006, **83**, 233.
6. O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, 1948, **40**, 345.
7. I. Cibulka, *Coll. Czech. Chem. Commun.*, 1982, **47**, 1414.
8. M. Dominguez, J. Santafe, M. C. Lopez, F. M. Royo and J. S. Urieta, *Fluid Phase Equilib.*, 1998, **152**, 133.
9. R. Francesconi and F. Comelli, *J. Chem. Eng. Data*, 1992, **37**, 230.
10. N. Swain and V. Chakravortty, *Indian J. Chem., Sect. A*, 1996, **35**, 395.
11. T. M. Aminabhavi and S. S. Joshi, *Indian J. Tech.*, 1992, **30**, 197.
12. H. C. Ku and C. H. Tu, *J. Chem. Eng. Data*, 2005, **50**, 608.
13. M. Dominguez, J. I. Prado, I. Gascon, F. M. Royo and J. S. Urieta, *Fluid Phase Equilib.*, 2000, **169**, 277.
14. G. Maheshwari and M. Singh, *J. Indian Chem. Soc.*, 2002, **79**, 659.
15. R. J. Fort and W. R. Moore, *Trans. Faraday Soc.*, 1966, **62**, 1112.
16. A. I. Vogel, "A Text Book of Practical Organic Chemistry", 5th ed., John Willey, New York, 1989.
17. J. A. Riddich, W. B. Bunger and T. K. Sokano, "Techniques in Chemistry", Vol. 2, Organic Solvents, 4th ed., John Willey, New York, 1986.
18. A. Weissberger, "Techniques of Organic Chemistry", Organic Solvents, Vol. 7, Interscience, New York, 1958.
19. M. Singh, P. C. Gupta and R. N. Kesharwani, *J. Chem. Eng. Data*, 1995, **40**, 358.
20. D. R. Lide (ed.), "CRC Hand Boak of Chemistry and Physics", 75th ed., CRC Press, Boca Raton, FL, 1994.
21. G. Dauheret, A. Khadir and A. Pal, *Thermochim. Acta*, 1989, **142**, 219; M. I. Davis and M. Chacon, *Thermochim. Acta*, 1991, **190**, 259.
22. B. B. Gurung, A. Choudhary and M. N. Roy, *J. Chem. Soc.*, 2004, **81**, 230; M. Singh, P. C. Gupta and R. N. Kesharwani, *J. Chem. Eng. Data*, 1995, **40**, 358.
23. P. S. Nikam and S. J. Kharat, *J. Chem. Eng. Data*, 2005, **50**, 455.
24. M. Contreras, *J. Chem. Eng. Data*, 2001, **46**, 1149.