J. Indian Chem. Soc.,
Vol. 83, March 2006, pp. 233-240

Volumetric and viscometric studies of binary and ternary mixtures of nitrobenzene with 1,4-dioxane, benzene, toluene and carbon tetrachloride at 303.15 K

(Ms.) Surabhi Varshney and Mukhtar Singh*

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

E-mail : mukhtarsingh2003@rediffmail.com

Manuscript received 10 May 2005, revised 14 November 2005, accepted 1 December 2005

Abstract : Densities and viscosities of binary and ternary mixtures of nitrobenzene with 1,4-dioxane, benzene, toluene and carbon tetrachloride have been measured 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 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 : Viscometric studies, mixed solvents, binary and ternary mixtures.

A thorough knowledge of transport and thermodynamic properties of multicomponent liquid mixtures is essential in many industrial applications. Therefore, the viscosities of multicomponent liquid mixtures are required in many chemical engineering calculations involving fluid flow, heat transfer, and mass transfer. Dominguez[1] and coworkers have carried out studies relating to the thermodynamic and transport properties of binary and ternary mixtures involving butanols, *n*-hexane, 1-chlorobutane, 1-butylamine at 298.15 and 313.15 K. Viscosity deviations ($\Delta\eta$) and thermodynamic excess properties viz. the excess molar volume (V^E), the excess molar Gibbs energy of activation of viscous flow ($\Delta G^{\#E}$) for the ternary systems were determined from density and viscosity data and then fitted to Redlich-Kister's and Cibulka's equations respectively[2].

We have carried out viscometric studies on molecular interactions in ternary liquid mixtures of ethane 1,2-diol and pyridine with some polar and non-polar solvents at 298.15 and 303.15 K respectively[3]. From the density and viscosity data, the viscosity deviations, the excess molar volume and the excess molar Gibbs free energy of activation of viscous flow have been calculated. On the basis of the values of excess thermodynamic properties and that of the parameter *d* of Grunberg and Nissan equation molecular interactions between the mixing components have been discussed.

In recent years some workers have reported studies on the measurements of densities and viscosities of ternary liquid mixtures at different temperatures. From the density and viscosity data, viscosity deviations ($\Delta\eta$) and excess molar volumes (V^E) have been obtained and the results have been discussed in the light of molecular interactions between the mixing components of the ternary mixtures[4].

From the above survey of literature it appears that volumetric and viscometric studied in regard to the binary and ternary liquid mixtures involving nitrobenzene, 1,4-dioxane and some non-polar solvents are sparse. Hence, the title study has been undertaken at 303.15 K with a view to determining densities, viscosities, viscosity deviations and excess thermodynamic properties, viz. excess molar volume (V^E), excess Gibbs free energy of activation of viscous flow ($\Delta G^{\#E}$) for the following binary and ternary liquid mixtures of nitrobenzene with 1,4-dioxane and polar, non-polar solvents :

(i) Binaries : nitrobenzene + 1,4-dioxane; nitrobenzene + benzene; 1,4-dioxane + benzene; nitrobenzene

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

+ toluene; 1,4-dioxane + toluene; nitrobenzene + carbon tetrachloride; 1,4-dioxane + carbon tetrachloride.

(ii) Ternaries : nitrobenzene + 1,4-dioxane + benzene; nitrobenzene + 1,4-dioxane + toluene; nitrobenzene + 1,4-dioxane + carbon tetrachloride.

The main thrust of the title study is to correlate the experimentally determined properties, viz. $\Delta\eta$, V^E and $\Delta G^{\#E}$, in respect of binary and ternary liquid mixtures to their theoretical values obtained by applying Redlich-Kister and Cibulka equations[2].

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.

Table 1. Comparison of experimental densities and viscosities of pure liquids with literature values at 303.15 K

Pure liquid	ρ (g cm^{-3})		η (mPa.S)		Ref.
	Expt.	Lit.	Expt.	Lit.	
Nitrobenzene	1.1940	1.1936	1.6182	1.6187	9
1,4-Dioxane	1.0195	1.0233	1.0500	1.0505	10
Benzene	0.8650	0.8659	0.5640	0.5643	11
Toluene	0.8582	0.8583	0.5229	0.5227	12
Carbon tetrachloride	1.5775	1.5852[a]	0.8300	0.9128[a]	12

[a]At 298.15 K.

The experimental densities (ρ), viscosities (η), viscosity deviations ($\Delta\eta$) and excess thermodynamic properties, viz. the excess molar volume (V^E) and the excess molar Gibbs free energies of activation of viscous flow ($\Delta G^{\#E}$) at 303.15 K in respect of binary and ternary mixtures have been presented in Tables 2 and 3 respectively.

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 equations[5].

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

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

Table 2. Densities, viscosities and thermodynamic excess properties of binary liquid mixtures at 303.15 K

x_1	ρ (g cm^{-3})	η (mPa.S)	$\Delta\eta$ (mPa.S)	V^E (cm^3 mol^{-1})	$\Delta G^{\#E}$ (J mol^{-1})
		Nitrobenzene + 1,4-dioxane			
0.0000	1.0195	1.0500	0.0000	0.0000	0.00
0.0852	1.0423	1.0585	−0.0407	−0.4281	−83.00
0.1732	1.0614	1.0580	−0.0921	−0.5436	−181.98
0.2650	1.0797	1.0872	−0.1161	−0.5784	−213.82
0.3592	1.0974	1.1073	−0.1504	−0.5753	−270.00
0.4563	1.1148	1.1480	−0.1658	−0.5526	−285.00
0.5574	1.1318	1.2116	−0.1607	−0.4881	−259.00
0.6625	1.1484	1.2744	−0.1587	−0.3847	−246.00
0.7711	1.1650	1.3688	−0.1270	−0.2857	−185.00
0.8829	1.1815	1.4695	−0.0910	−0.1887	−130.00
1.0000	1.1940	1.6182	0.0000	0.0000	0.00
		Nitrobenzene + benzene			
0.0000	0.8650	0.5640	0.0000	0.0000	0.00
0.0887	0.9010	0.6013	−0.0571	−0.2902	−82.00
0.1796	0.9362	0.6540	−0.1012	−0.4869	−117.00
0.2737	0.9712	0.7103	−0.1450	−0.6247	−162.59
0.3694	1.0051	0.7841	−0.1730	−0.6804	−169.75
0.4673	1.0381	0.8650	−0.1963	−0.6603	−182.70
0.5682	1.0704	0.9589	−0.2097	−0.5655	−190.00
0.6723	1.1027	1.0749	−0.2045	−0.4605	−178.00
0.7788	1.1343	1.2179	−0.1749	−0.3104	−145.00
0.8874	1.1658	1.3900	−0.1184	−0.1733	−100.00
1.0000	1.1940	1.6182	0.0000	0.0000	0.00
		1,4-Dioxane + benzene			
0.0000	0.8650	0.5640	0.0000	0.0000	0.00
0.1042	0.8724	0.5856	−0.0290	0.8323	−45.00
0.2068	0.8771	0.6089	−0.0556	1.9135	−77.00
0.3093	0.8841	0.6367	−0.0777	2.7464	−102.00
0.4108	0.8945	0.6733	−0.0904	3.2066	−107.00
0.5110	0.9083	0.7157	−0.0967	3.3017	−107.00
0.6104	0.9237	0.7617	−0.0990	3.2392	−107.00
0.7093	0.9452	0.8235	−0.0852	2.5914	−83.00
0.8073	0.9675	0.8907	−0.0657	1.9064	−58.00
0.9036	0.9987	0.9689	−0.0342	0.4600	−38.00
1.0000	1.0195	1.0500	0.0000	0.0000	0.00
		Nitrobenzene + toluene			
0.0000	0.8582	0.5229	0.0000	0.0000	0.00
0.1037	0.8954	0.6185	−0.0190	−0.4073	117.12
0.2066	0.9330	0.7113	−0.0399	−0.8200	165.00
0.3093	0.9689	0.8188	−0.0459	−0.9800	222.00

Table-2 (contd.)

0.4103	1.0047	0.9254	−0.0510	−1.1500	237.17
0.5105	1.0386	1.0367	−0.0504	−1.1200	237.22
0.6098	1.0723	1.1512	−0.0457	−1.0703	218.02
0.7094	1.1060	1.2679	−0.0391	−0.9808	178.22
0.8071	1.1368	1.3820	−0.0330	−0.6700	123.09
0.9039	1.1683	1.4960	−0.0260	−0.4508	50.87
1.0000	1.1940	1.6182	0.0000	0.0000	0.00
		1,4-Dioxane + toluene			
0.0000	0.8582	0.5229	0.0000	0.0000	0.00
0.1216	0.8611	0.5749	−0.0121	1.6156	70.00
0.2367	0.8675	0.6251	−0.0226	2.7058	110.00
0.3473	0.8724	0.6780	−0.0280	3.9200	154.36
0.4530	0.8837	0.7299	−0.0318	4.3200	167.89
0.5541	0.8994	0.7810	−0.0340	4.2000	160.34
0.6504	0.9174	0.8368	−0.0289	3.8337	157.00
0.7438	0.9373	0.8912	−0.0238	3.3162	138.00
0.8327	0.9621	0.9416	−0.0203	2.3538	93.00
0.9180	0.9896	0.9965	−0.0102	1.2281	52.00
1.0000	1.0195	1.0500	0.0000	0.0000	0.00
		Nitrobenzene + carbon tetrachloride			
0.0000	1.5775	0.8300	0.0000	0.0000	0.00
0.0951	1.5427	0.8421	−0.0638	−0.2006	−130.00
0.1913	1.5081	0.8672	−0.1155	−0.4300	−224.89
0.2891	1.4710	0.8934	−0.1674	−0.5172	−318.00
0.3875	1.4351	0.9219	−0.2174	−0.6827	−410.00
0.4865	1.3968	0.9908	−0.2275	−0.6755	−396.00
0.5871	1.3585	1.0587	−0.2400	−0.6799	−399.98
0.6886	1.3188	1.1595	−0.2201	−0.5800	−340.47
0.7915	1.2782	1.2505	−0.2113	−0.4009	−320.49
0.8947	1.2384	1.4362	−0.1079	−0.2607	−143.51
1.0000	1.1940	1.6182	0.0000	0.0000	0.00
		1,4-Dioxane + carbon tetrachloride			
0.0000	1.5775	0.8300	0.0000	0.0000	0.00
0.1116	1.5267	0.9070	0.0524	−0.3200	150.84
0.2198	1.4748	0.9914	0.1130	−0.5700	305.45
0.3258	1.4214	1.1147	0.2131	−0.7400	534.32
0.4295	1.3677	1.1374	0.2129	−0.9200	518.94
0.5302	1.3118	1.1627	0.2160	−0.9318	514.16
0.6286	1.2549	1.1640	0.1957	−0.8810	459.55
0.7245	1.1962	1.1610	0.1716	−0.6863	400.86
0.8187	1.1370	1.1182	0.1081	−0.4630	255.60
0.9100	1.0790	1.0781	0.0479	−0.2808	113.46
1.0000	1.0195	1.0500	0.0000	0.0000	0.00

$$V^E = V - \sum_{i=1}^{n} x_i V_i \qquad (2)$$

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 weights M_i as below :

$$V = \sum_{i=1}^{n} x_i M_i/\rho \qquad (3)$$

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

where the letters have their usual significance.

The experimentally determined values of $\Delta\eta$, V^E and $\Delta G^{\#E}$ for binary mixtures were fitted to Redlich-Kister's equation[2],

$$Y_{ij}^E = x_i x_j \sum_{p=0}^{P} A_p (x_i - x_j)^p \qquad (5)$$

where Y_{ij}^E 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 A_p are adjustable parameters. Redlich-Kister's 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 A_p by the least-squares method using a computer. The parameters A_p are then used to evaluate Y_{ij}^E values from eq. (5). The standard deviation $\sigma(Y_{ij}^E)$ is defined by the equation[6],

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

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 viscous flow ($\Delta G^{\#E}$) for the ternary mixtures have been fitted to Cibulka's equation[2],

Table 3. Densities, viscosities and thermodynamic excess properties of ternary liquid mixtures at 303.15 K

x_1	x_2	x_3	ρ (g cm^{-3})	η (mPa.S)	Δη (mPa.S)	V^E (cm^3 mol^{-1})	$\Delta G^{\#E}$ (J mol^{-1})
			Nitrobenzene + 1,4-dioxane + benzene				
0.0444	0.0525	0.9031	0.8960	0.6000	−0.0368	−0.6600	−62.25
0.0883	0.1056	0.8062	0.9210	1.2700	0.5607	−0.7300	1625.60
0.0855	0.8166	0.0979	0.9500	0.9419	−0.1100	6.6591	−28.50
0.1781	0.2121	0.6097	0.9749	1.4000	0.5434	−1.1900	1455.33
0.1764	0.4209	0.4027	1.0053	1.2700	0.3137	−1.0997	889.39
0.1749	0.6258	0.1993	1.0364	1.6000	0.5457	−1.0700	1155.68
0.2699	0.3207	0.4094	1.0251	2.0000	0.9929	−1.2699	1938.11
0.2686	0.4259	0.3054	1.0439	1.8800	0.8232	−1.5299	1614.67
0.3659	0.2173	0.4167	1.0475	2.0600	1.0011	−1.6800	1908.72
0.3642	0.3249	0.3109	1.0634	1.8000	0.6905	−1.6900	1404.11
0.3625	0.4315	0.2060	1.0783	1.9500	0.7905	−1.6100	1446.02
0.4651	0.1110	0.4239	1.0679	2.5100	1.3971	−1.9200	2301.46
0.4585	0.4368	0.1047	1.1150	2.3400	1.0758	−1.8800	1634.86
0.5633	0.2232	0.2135	1.1168	2.3400	1.0681	−1.8603	1689.68
0.5600	0.3333	0.1066	1.1335	2.3800	1.0581	−1.9491	1567.89
0.6657	0.2258	0.1085	1.1471	2.3400	0.9578	−1.6000	1419.25
0.7741	0.1154	0.1104	1.1605	2.4600	1.0162	−1.2400	1437.26
0.8303	0.0582	0.1114	1.1658	2.4000	0.9242	−0.9300	1321.21
0.8287	0.1162	0.0551	1.1722	2.1200	0.6176	−0.8000	925.24
0.8856	0.0587	0.0557	1.1797	2.1600	0.6250	−0.6900	911.75
			Nitrobenzene + 1,4-dioxane + toluene				
0.0519	0.0614	0.8868	0.8780	0.6284	0.0157	0.6479	224.45
0.1013	0.1211	0.7777	0.8985	0.6461	−0.0526	1.1265	62.79
0.0869	0.8297	0.0833	1.0025	1.1286	0.0724	1.6635	286.66
0.1972	0.2348	0.5681	0.9445	0.7017	−0.1630	1.4621	−190.94
0.1883	0.4495	0.3621	0.9820	0.8328	−0.1351	0.8241	−120.88
0.1806	0.6462	0.1732	1.0059	0.9221	−0.1410	1.5549	−169.50
0.2885	0.3429	0.3686	0.9974	0.8023	−0.2202	1.0739	−310.82
0.2824	0.4478	0.2698	1.0127	0.8409	−0.2302	1.1288	−356.49
0.3917	0.2326	0.3756	1.0162	0.8285	−0.2499	0.9663	−336.56
0.3833	0.3419	0.2749	1.0246	0.8535	−0.2733	1.6961	−410.26
0.3748	0.4461	0.1792	1.0434	0.9087	−0.2637	1.3798	−417.67
0.4985	0.1190	0.3826	1.0298	0.8819	−0.2548	1.3808	−280.69
0.4664	0.4443	0.0893	1.0792	0.9941	−0.2785	1.1525	−456.36
0.5830	0.2310	0.1860	1.0809	1.0797	−0.2094	1.1970	−209.83
0.5699	0.3392	0.0909	1.0929	1.0943	−0.2373	1.5232	−318.04
0.6776	0.2299	0.0925	1.1116	1.2534	−0.1397	1.4497	−96.84
0.7882	0.1175	0.0942	1.1304	1.4750	0.0190	1.3512	189.09
0.8456	0.0593	0.0951	1.1356	1.7188	0.2300	1.6914	517.97
0.8354	0.1172	0.0475	1.1423	1.6384	0.1303	1.7642	327.80
0.8929	0.0592	0.0480	1.1526	2.0246	0.4835	1.6382	793.31

Table-3 (contd.)

			Nitrobenzene + 1,4-dioxane + carbon tetrachloride				
0.0476	0.0563	0.8961	1.5155	0.8885	0.0081	0.9537	83.23
0.0939	0.1123	0.7938	1.4270	0.8800	–0.0497	3.8360	21.65
0.0861	0.8224	0.0915	1.4450	0.9030	–0.1767	–21.6302	–1119.98
0.1865	0.2221	0.5913	1.3300	0.8970	–0.1306	4.3317	–136.33
0.1818	0.4339	0.3843	1.3160	0.9310	–0.1396	–2.6919	–343.63
0.1775	0.6349	0.1876	1.3270	0.9390	–0.1724	–11.0488	–684.63
0.2784	0.3308	0.3908	1.2600	0.9471	–0.1779	2.7160	–259.14
0.2747	0.4356	0.2897	1.2570	0.9874	–0.1577	–1.2567	–313.80
0.3777	0.2243	0.3981	1.2200	0.9719	–0.2090	7.4601	–185.40
0.3726	0.3324	0.2950	1.2220	1.0014	–0.1992	2.8269	–276.59
0.3680	0.4380	0.1939	1.2130	1.0158	–0.2042	–0.8532	–389.43
0.4802	0.1146	0.4051	1.1900	1.0730	–0.1654	11.7383	51.18
0.4620	0.4401	0.0979	1.1840	1.0850	–0.2106	–1.5862	–403.90
0.5721	0.2267	0.2012	1.1780	1.1264	–0.2101	4.9712	–205.57
0.5644	0.3359	0.0997	1.1626	1.1339	–0.2205	1.6186	–321.56
0.6709	0.2276	0.1015	1.1580	1.2503	–0.1653	3.5624	–145.88
0.7803	0.1163	0.1033	1.1780	1.3986	–0.0797	3.3646	8.94
0.8370	0.0587	0.1043	1.2086	1.4930	–0.0180	1.4915	62.57
0.8320	0.1167	0.0513	1.1813	1.4809	–0.0389	1.4407	16.78
0.8892	0.0589	0.0518	1.2154	1.5949	0.0423	–0.6926	86.99

Table 4. Coefficients of Redlich-Kister's eq. and the corresponding standard deviation (σ), for the binary mixtures at 303.15 K

Viscosity deviations (Δη) and excess functions (Y^E)	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	σ
				Nitrobenzene + 1,4-dioxane					
Δη (mPa.S)	–0.657	0.127	–0.359	–3.419	2.116	12.700	–	–	0.00002
V^E (cm^3 mol^{-1})	2.120	–1.172	–0.130	–2.053	4.384	5.283	–	–	0.0011
$\Delta G^{\#E}$ (J mol^{-1})	–1098.8	598.3	–618.9	–7556.6	4003.6	27999.8	–6004.7	–28490.1	0.0480
				1,4-Dioxane + benzene					
Δη (mPa.S)	–0.388	–0.133	–0.070	0.781	0.391	–2.564	–	–	0.0010
V^E (cm^3 mol^{-1})	–13.401	–2.073	4.160	30.007	–9.112	–118.426	–	–	0.0057
$\Delta G^{\#E}$ (J mol^{-1})	–432.5	–73.8	–327.5	1763.2	1795.5	–5335.8	–2127.8	4460.1	1.4887
				Nitrobenzene + benzene					
Δη (mPa.S)	–0.807	–0.345	–0.253	0.902	0.419	–2.954	–	–	0.0006
V^E (cm^3 mol^{-1})	2.525	–1.657	0.667	3.333	–3.830	–9.426	–	–	0.0043
$\Delta G^{\#E}$ (J mol^{-1})	–740.1	–293.2	–327.5	3165.7	1200.5	–10308.4	–1447.1	9347.0	2.4738
				1,4-Dioxane + toluene					
Δη (mPa.S)	–0.134	–0.041	0.128	0.484	–0.480	–1.616	–	–	0.0003
V^E (cm^3 mol^{-1})	17.207	–3.198	1.410	34.170	–29.836	–57.682	–	–	0.0077
$\Delta G^{\#E}$ (J mol^{-1})	659.6	–149.4	473.6	2245.4	–2341.3	–5905.3	2563.3	4183.3	0.6328

Table-4 (contd.)

				Nitrobenzene + toluene					
$\Delta\eta$ (mPa.S)	−0.204	0.054	0.101	−0.254	−0.717	1.042	–	–	0.0003
V^E (cm^3 mol^{-1})	−4.542	1.426	−1.258	−21.457	2.710	84.147	–	–	0.0077
$\Delta G^{\#E}$ (J mol^{-1})	947.2	−121.9	473.6	−1308.8	−2256.7	5752.2	2726.5	−6972.8	1.1127
				1,4-Dioxane + carbon tetrachloride					
$\Delta\eta$ (mPa.S)	0.842	−0.136	1.553	−0.861	−9.235	8.683	–	–	0.0007
V^E (cm^3 mol^{-1})	−3.802	−0.216	3.008	−2.875	−5.484	18.663	–	–	0.0016
$\Delta G^{\#E}$ (J mol^{-1})	2017.2	−535.4	3928.8	−2329.7	−21779.3	21868.7	23041.3	−27388.5	1.6364
				Nitrobenzene + carbon tetrachloride					
$\Delta\eta$ (mPa.S)	−0.943	−0.177	0.334	−0.051	−2.919	−4.558	–	–	0.0006
V^E (cm^3 mol^{-1})	−2.789	0.541	0.524	−10.266	1.963	42.869	–	–	0.0024
$\Delta G^{\#E}$ (J mol^{-1})	−1648.9	261.3	3928.8	−1337.4	−4748.6	−5541.1	6308.2	11083.8	1.7310

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

where, $Y^E_{bin} = Y^E_{12} + Y^E_{13} + Y^E_{23}$ (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.

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

Table 5. Coefficients of Cibulka eq. and the corresponding standard deviation (σ), for the ternary mixtures at 303.15 K

Viscosity deviations ($\Delta\eta$) and excess functions (Y^E)	B_1	B_2	B_3	σ
		Nitrobenzene + 1,4-dioxane + benzene		
$\Delta\eta$ (mPa.S)	13.995	96.521	−28.969	0.030
V^E (cm^3 mol^{-1})	−125.093	5.896	132.482	0152
$\Delta G^{\#E}$ (J mol^{-1})	63744.0	80628.2	−781488.8	0.51
		Nitrobenzene + 1,4-dioxane + toluene		
$\Delta\eta$ (mPa.S)	−2.064	−5.333	−6.164	0.146
V^E (cm^3 mol^{-1})	−96.32	280.15	12.21	0.052
$\Delta G^{\#E}$ (J mol^{-1})	−19355.9	144.197	8438.5	1.667
		Nitrobenzene + 1,4-dioxane + carbon tetrachloride		
$\Delta\eta$ (mPa.S)	−1.108	1.094	−16.524	0.070
V^E (cm^3 mol^{-1})	738.82	−16.42	−1937.34	0.405
$\Delta G^{\#E}$ (J mol^{-1})	7292.5	25996.2	−68489.9	0.259

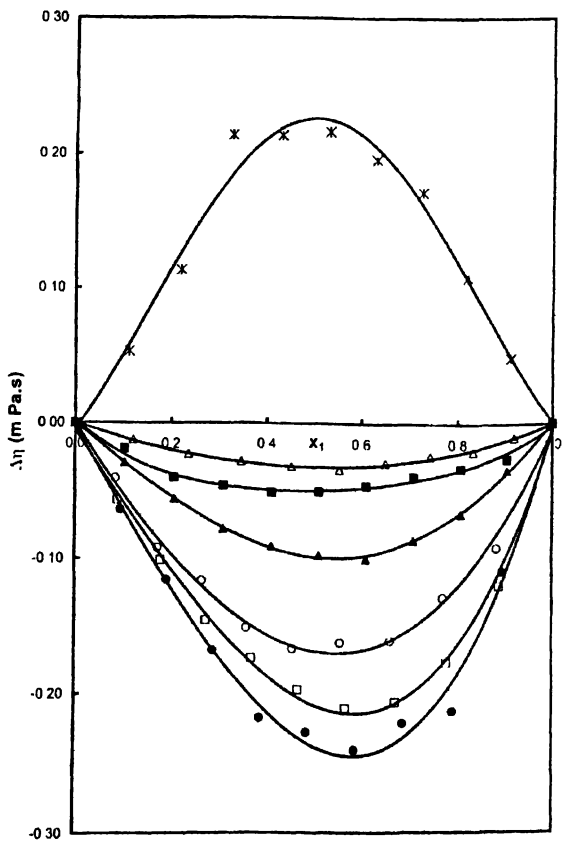

Fig. 1. Variation of viscosity deviations ($\Delta\eta$) with mole fraction (x_1) of the first component in binary liquid mixtures of (○) nitrobenzene + 1,4-dioxane, (□) nitrobenzene + benzene, (■) nitrobenzene + toluene, (●) nitrobenzene + carbon tetrachloride, (▲) 1,4-dioxane + benzene, (△) 1,4-dioxane + toluene and (*) 1,4-dioxane + carbon tetrachloride at 303.15 K.

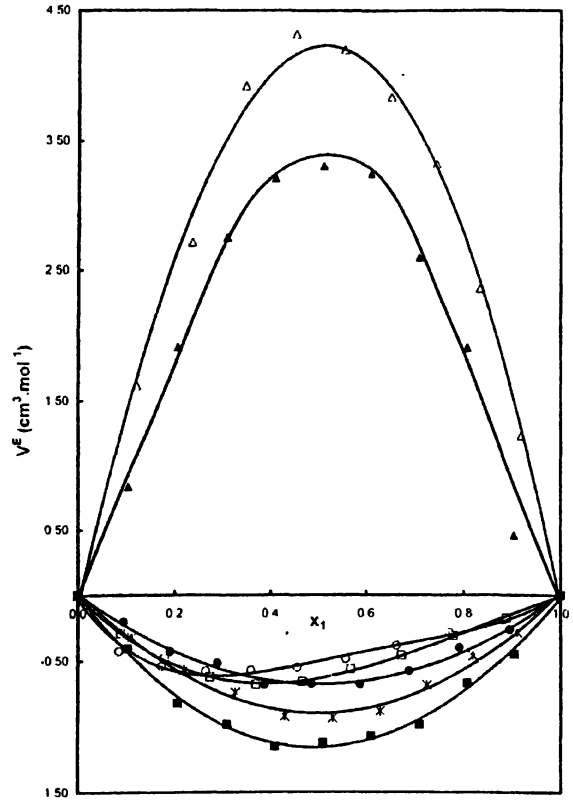

Fig. 2. Variation of excess molar volume (V^E) with mole fraction (x_1) of the first component in binary liquid mixtures of (○) nitrobenzene + 1,4-dioxane, (□) nitrobenzene + benzene, (■) nitrobenzene + toluene, (●) nitrobenzene + carbon tetrachloride, (▲) 1,4-dioxane + benzene, (△) 1,4-dioxane + toluene and (*) 1,4-dioxane + carbon tetrachloride at 303.15 K.

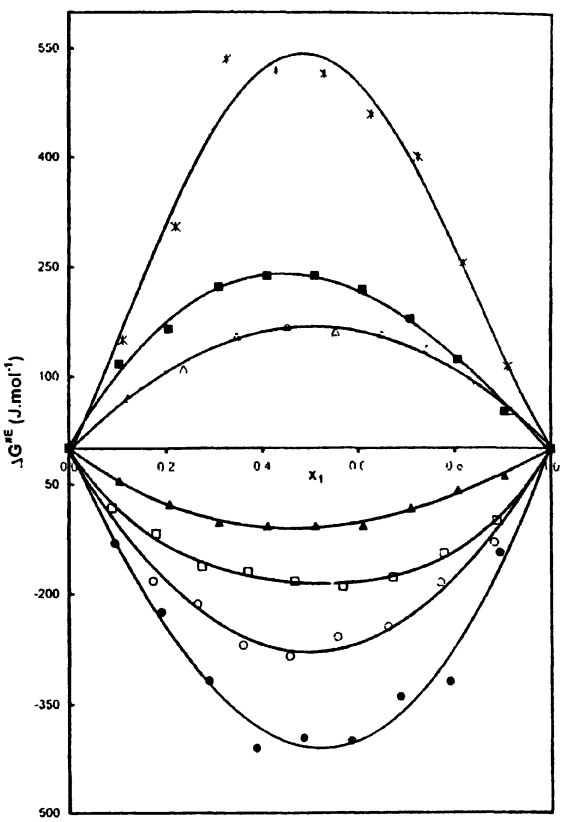

Fig. 3. Variation of excess Gibbs free energy of activation of flow (ΔG^{*E}) with mole fraction (x_1) of the first component in binary liquid mixtures of (○) nitrobenzene + 1,4-dioxane, (□) nitrobenzene + benzene, (■) nitrobenzene + toluene, (●) nitrobenzene + carbon tetrachloride, (▲) 1,4-dioxane + benzene, (△) 1,4-dioxane + toluene and (*) 1,4-dioxane + carbon tetrachloride at 303.15 K.

maxima/minima which indicate the presence of complex formation[7] between the mixing components of the binary mixtures.

Experimental

The chemicals used were of analytical grade. Nitrobenzene (>99.2%), 1,4-dioxane (>99.4%), benzene (>99.7%), toluene (>99.5%) and carbon tetrachloride (>99.3%) were obtained from Merck. The organic liquids were further purified according to the procedure described in the literature and the purity was better than 99%.

Binary and ternary liquid mixtures of various compositions were prepared by mass in 25 cm^3 glass stoppered flasks using Mettler analytical balance. During the preparation of binary and ternary liquid mixtures of varying compositions, the haviour components were charged first to minimize the errors in composition due to evaporation. The average uncertainty of the mole fraction is estimated to be less than 1×10^{-4}. Density and viscosity measurements were carried out using a thermostatically controlled, well-stirred water bath, where a constant temperature was 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 303.15 K with an Anton parr digital vibrating tube densimeter (model 60/602, Anton parr, Austria). The densimeter was calibrated with degassed water and dehumidified air at atmospheric pressure. The uncertainty of the density measurements was estimated to be less than $\pm 1 \times 10^{-4}$ g cm^{-3}.

The viscosities of pure organic liquids and their bi-

nary and ternary mixtures were determined using an Ostwald viscometer, which was suspended in a thermostat maintained at 303.15 ± 0.01 K. The details of the procedure have been reported in an earlier publication[8]. The uncertainty of calculated absolute viscosities was $\pm 1 \times 10^{-4}$ mPa.S. The excess molar volumes were calculated from density data, and the uncertainties were estimated to be within $\pm 5 \times 10^{-3}$ cm^3 mol^{-1}.

References

1. M. Dominguez, H. Artigas, J. Santafe, A. M. Mainar and J. S. Urieta, *Fluid Phase Equilib.*, 1998, **145**, 115; M. Dominguez, P. Cea, M. C. Lopez, F. M. Royo and J. S. Urieta, *Fluid Phase Equilib.*, 1999, **164**, 195; M. Dominguez, C. Lafuente, M. C. Lopez, F. M. Royo and J. S. Urieta, *J. Chem. Thermodyn.*, 2000, **32**, 155; M. Dominguez, I. Gascon, A. Valen, F. M. Royo and J. S. Urieta, *J. Chem. Thermodyn.*, 2000, **32**, 1551; M. Dominguez, H. Artigas, P. Cea, M. C. Lopez and J. S. Urieta, *J. Mol. Liquids*, 2000, **88**, 243; M. Dominguez, J. I. Pardo, I. Gascon, F. M. Royo and J. S. Urieta, *Fluid Phase Equilib.*, 2000, **169**, 277; M. Dominguez, S. Martin, J. Santafe, H. Artigas and F. M. Royo, *Thermochimica Acta*, 2002, **381**, 181.
2. O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, 1948, **40**, 345; I. Cibulka, *Coll. Czech. Chem. Commun.*, 1982, **47**, 1414.
3. S. Singh and M. Singh, *Indian J. Chem., Sect. A*, 2002, **41**, 1588; G. Maheshwari and M. Singh, *J. Indian Chem. Soc.*, 2002, **79**, 659.
4. M. M. Mato, J. Balseiro, J. Salgado, E. Jimenez, J. L. Legido, M. M. Pineiro and M. I. Paz Andrade, *J. Chem. Eng. Data*, 2002, **47**, 4; M. M. Mato, J. Balseiro, E. Jimenez, J. L. Legido, A. V. Galinanes and M. I. Paz Andrade, *J. Chem. Eng. Data*, 2002, **47**, 1436; M. M. Mato, M. Lopez, J. L. Legido, J. Salgado, P. V. Verdes and M. I. Paz Andrade, *J. Chem. Eng. Data*, 2003, **48**, 646; M. Dominguez, E. Langa, A. M. Mainar, J. Santafe and J. S. Urieta, *J. Chem. Eng. Data*, 2003, **48**, 302; M. M. Mato, E. Jimenez, J. L. Legido and M. I. Paz Andrade, *J. Chem. Eng. Data*, 2004, **49**, 928; H. C. Ku and C. H. Tu, *J. Chem. Eng. Data*, 2005, **50**, 608; I. Gascon, A. Villares, M. Haro, S. Martin and H. Artigas, *J. Chem. Eng. Data*, 2005, **50**, 722; J. D. Ye and C. H. Tu, *J. Chem. Eng. Data*, 2005, **50**, 1060; A. E. Baltazar, F. T. Lechuga and G. A. Iglesias-Silva, *J. Chem. Eng. Data*, 2005, **50**, 18; C. Coquelet, A. Valtz and D. Richon, *J. Chem. Eng. Data*, 2005, **50**, 412.
5. M. Dominguez, J. Santafe, M. C. Lopez, F. M. Royo and J. S. Urieta, *Fluid Phase Equilib.*, 1998, **152**, 133; M. M. Palaiologou, *J. Chem. Eng. Data*, 1996, **41**, 1036.
6. R. Francesconi and F. Comelli, *J. Chem. Eng. Data*, 1992, **37**, 230.
7. M. Ibrahim, Ph.D. Thesis, Aligarh Muslim University, Aligarh, 1979; J. M. G. Cowie and P. M. Toporowski, *Can. J. Chem.*, 1961, **39**, 2240.
8. M. Singh, P. C. Gupta and R. N. Kesharwani, *J. Chem. Eng. Data*, 1995, **40**, 358.
9. S. Singh, V. K. Rattan, S. Kapoor, R. Kumar and A. Rampal, *J. Chem. Eng. Data*, 2005, **50**, 288.
10. M. J. Assael, M. Papadaki and W. A. Wakeham, *Int. J. Thermophys.*, 1991, **12**, 449; A. Krishnaiah, K. N. Surendranath and D. S. Viswanath, *J. Chem. Eng. Data*, 1994, **39**, 756.
11. D. R. Lide, ed., "CRC Hand Book of Chemistry and Physics", 75th ed., CRC Press, Boca Raton, FL, 1994; U. Z. Emmerling and G. Figurski, *J. Chem. Eng. Data*, 1998, **43**, 289.
12. C. Yang, P. Ma and Q. Zhou, *J. Chem. Eng. Data*, 2004, **49**, 881; M. J. Lee and M. C. Wel, *J. Chem. Eng. Data*, 1992, **37**, 209.