CHAPTER VII

Thermophysical Properties of Binary Mixtures of N, N- Dimethylformamide with Isomeric Butanols at 298.15, 308.15, and 318.15 K

7.1. Introduction

The volumetric and viscometric properties of mixed solvent systems and their dependence on composition find applications in many important chemical, industrial and biological processes. The study of functions such as excess molar volume and deviation in viscosity, etc. of binary mixtures are useful in understanding the nature and strength of molecular interactions between the component molecules.[1-2] N, N- dimethylformamide and alcohols are versatile solvents used in the separation of saturated and unsaturated hydrocarbons and in pharmaceutical synthesis and serves as solvents for many polymers. N, N- dimethylformamide is a polar aprotic solvent, whereas alcohols are polar and self-associated through hydrogen bonding in the pure state.[3] Thermodynamic and transport properties of binary mixtures of N, N-dimethylformamide with different organic liquids have been studied by many authors.[4-7] In the present paper we report density (ρ) and viscosity (η) for the binary mixtures of N, N- dimethylformamide with isomeric butanols at different temperatures and at atmospheric pressure. The calculated excess quantities from such data have been interpreted in terms of molecular interactions and structural effects.

7.2. Experimental Section

7.2.1. Chemicals

N, N- dimethylformamide (S. D. fine chemicals, India, analytical grade) was purified by the method described by Y. Zhao et al.[8] 1-butanol, 2-methyl-1-propanol, 2-butanol and 2-methyl-2-propanol (all S. D. fine chemicals, India, analytical grade) were purified by using the methods described in the literature.[9]

7.2.2. Measurements

Densities (ρ) were measured with an Ostwald –Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The measurements were done in a thermostated bath controlled to ± 0.01K. The viscosity (η) was measured by means of a suspended Ubbelohde type viscometer, which was calibrated at 298.15, 308.15 and 318.15 K with triply distilled water and purified methanol using density and viscosity values from the literature.[10-12] The flow times were accurate to ± 0.1s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was ± 2 x 10^{-4} mPa.s. The details of the methods and techniques had been described earlier.[13, 14]

The mixtures were prepared by mixing known volume of pure liquids in airtight-stopper glass bottles to avoid evaporation. The reproducibility in mole fraction was within ± 0.0002 units. The weighings were done on a Mettler AG-285 electronic balance with a precision of ± 0.01mg. The precision of density measurements was ± 3 x 10^{-4} g cm^{-3}.

7.3. Results and Discussion

The physical properties of various pure liquids along with their literature values at 298.15 K are recorded in Table 1. The experimental values of density and viscosity for all the binary mixtures at different temperatures were fitted to a polynomial equation[15] of the following type:

$$a = \sum_{i=0}^{3} a_i x_1^i \qquad (1)$$

where a is ρ or η, a_i is an adjustable coefficient and x_1 is the mole fraction of N, N- dimethylformamide in the mixtures. The values of the coefficients (a_i) are recorded in Table 2. The experimental densities, viscosities, excess molar volumes (V^E) and deviations in viscosity (ΔV^E) for the binary mixtures studied at different temperatures are recorded in Table 3.

The excess molar volumes (V^E) were calculated using the equation,

$$V^E = \sum_{i=1}^{j} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \qquad (2)$$

where ρ is the density of the mixture and M_i, x_i and ρ_i are the molecular weight, mole fraction and density of i^{th} component in the mixture, respectively. The estimated uncertainty for excess molar volumes (V^E) is ± 0.005 $cm^3.mol^{-1}$.

The values of excess molar volume for all the four mixtures are positive at 298.15 and 308.15 K but negative at 318.15 K over the entire composition range. As stated earlier, alcohols are self-associated through hydrogen bonding in pure state.[3] Hydrogen bonded structure of isomeric butanols is perturbed when N, N-dimethylformamide is introduced in the systems. This effect leads to an expansion in volume and thus a positive contribution to V^E values. The negative values of V^E for all the systems at 318.15 K over the entire composition range suggest weak dipole- dipole interactions between the mixing components. Another important contribution leading to positive V^E values arises from the molecular sizes[16] of N, N-dimethylformamide and isomeric butanols that are not too different and thus the component molecules do not fit well into each other's structure resulting in volume expansion. Figure 1 depicts excess molar volumes (V^E) of the binary mixtures as a function of mole fraction (x_1) of N, N-dimethylformamide at 298.15 K. It is evident from the figure 1 that V^E values become increasingly positive in the order: 1-butanol<2-methyl-1-propanol<2-butanol<2-methyl-2-propanol, i.e., V^E values become more positive as the branching in the alcohol molecule increases. Also V^E values decrease as the temperature of the mixtures increases, thereby indicating increase in intermolecular interactions between the component molecules.

The deviation in the viscosity ($\Delta\eta$) is given by the relation[17]

$$\Delta\eta = \eta - \sum_{i=1}^{j} (x_i \eta_i) \qquad (3)$$

where η is the absolute viscosities of the mixture and x_i, η_i are the mole fraction and viscosity of i^{th} component in the mixture, respectively. The

estimated uncertainty for viscosity deviation $\Delta\eta$ is ± 0.004 mPa.s. Table 3 shows that $\Delta\eta$ values are negative for all the mixtures over the entire composition range at all the experimental temperatures. The negative $\Delta\eta$ values indicate the presence of weak interactions or dispersion forces[13] between the unlike molecules in the mixture. As expected, the values of $\Delta\eta$ become more negative as the branching in the alcohol molecule increases from 1-butanol to 2-methyl-2-propanol (Figure 2) and increase in magnitude as the temperature of the mixtures increase from 298.15 K to 318.15 K. This suggests that the strength of interaction in the mixtures is in the order: 1-butanol>2-methyl-1-propanol>2-butanol>2-methyl-2-propanol and the strength of interaction increases with the increase in temperature. Thus the functions V^E and $\Delta\eta$ complement each other in describing the behaviors of the binary mixtures studied.

Several semi-empirical models have been proposed to estimate the dynamic viscosity (η) of the binary liquid mixtures in terms of pure-component data.[18,19] Grunberg and Nissan[20] have suggested the following equation to correlate the absolute viscosity data:

$$\eta = \exp[\sum_{i=1}^{j}(x_i \ln\eta_i) + d_{12}\prod_{i=1}^{j}x_i] \qquad (4)$$

where d_{12} is an interaction parameter that is a function of the nature of the components and temperature. It is regarded as an approximate measure of the strength of molecular interactions between the mixing components. The negative values of d_{12} indicate the presence of dispersion forces[17] between the mixing components in the mixtures. The d_{12} values have been calculated as a function of the composition of the binary mixtures under investigation and were recorded in Table 3. It has been found that the values of d_{12} are negative for all the binary systems at all the experimental temperatures, indicating that the breaking of butanol self-association is the predominating effect.[17]

Tamura-Kurata[21] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{j} x_i \phi_i \eta_i + 2T_{12} \prod_{i=1}^{j} [x_i \phi_i]^{1/2} \qquad (5)$$

where T_{12} is the interaction parameter and ϕ_i is the volume fraction of i^{th} pure component in the mixture.

Molecular interactions may also be interpreted by the following viscosity model of Hind et al[22]:

$$\eta = \sum_{i=0}^{j} x_i^2 \eta_i + 2H_{12} \prod_{i=1}^{j} x_i \qquad (6)$$

where H_{12} is Hind interaction parameter, which may be attributed to unlike pair interaction.[23] In the present study, the values of interaction parameter T_{12} and H_{12} have been calculated from equations 5 and 6, respectively and were recorded in Table 3. It has been observed that for a particular binary mixture T_{12} and H_{12} do not differ appreciably from each other and this is in agreement with the view put forward by Fort and Moore[17] in regard to the nature of parameter T_{12} and H_{12}.

The excess properties (V^E and $\Delta\eta$) were correlated with the Redlich-Kister equation [24]:

$$Y_{ij}^E = x_i x_j \sum_{k=1}^{m} a_k (x_i - x_j)^k \qquad (7)$$

where Y_{ij}^E refers to an excess property for each i-j binary pair, and x_i is the mole fraction of i^{th} component, and a_k represents the coefficients. The values of coefficients (a_k) were determined by a multiple-regression analysis based on the least-squares method and were summarized along with the standard deviations between the experimental and fitted values of the respective functions in Table 4. The standard deviation was calculated using the relation:

$$\sigma = \left[\sum_{i=1}^{n} \frac{(Y_{i,\exp}^E - Y_{i,cal}^E)^2}{n - p} \right]^{\frac{1}{2}} \qquad (8)$$

where n is the number of experimental points and p is the number of adjustable parameters. The σ values lie between 0.001 - 0.008 $m^3.mol^{-1}$ for V^E and between 0.002 – 0.022 mPa.s for $\Delta\eta$, respectively. The small σ

values for V^E and $\Delta\eta$ indicated that the fits are good and in the present study, V^E and $\Delta\eta$ are quite systematic and function of the composition of the binary mixtures and temperatures.

7.4. Conclusion

The study in summary suggests that the strength of interaction in the mixtures is in the order: 1-butanol>2-methyl-1-propanol>2-butanol>2-methyl-2-propanol and the strength of interaction increases with the increase in temperature. The above order may be attributed to the increase in branching in the alcohol molecules.

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Table 1.

Physical properties of various pure solvents at 298.15 K

Pure Liquid	ρ (g.cm^{-3})		η (mPa.s)	
	Expt.	Lit.	Expt.	Lit.
N, N- dimethylformamide	0.9442	0.9445 [a]	0.8030	0.803 [a]
1-butanol	0.8056	0.8057 [b]	2.5650	2.5439[b]
2-butanol	0.8020	0.8024 [b]	2.9995	3.0038 [b]
2-methyl-1-propanol	0.7976	0.7977 [b]	3.4307	3.3932 [b]
2-methyl-2-propanol	0.7799	0.7805 [b]	4.4340	4.438 [c]

[a]Ref = 25 , [b]Ref= 15 , [c]Ref= 26

Table 2.
Density and viscosity correlation coefficients from equation 1 at various temperatures.

System	a_0	a_1	a_2	a_3
T = 298.15 K				
	ρ (g.cm^{-3})			
DMF + 1-butanol	0.8056	0.1015	0.0498	-0.0128
DMF + 2-butanol	0.8021	0.0958	0.0596	-0.0132
DMF + 2-methyl-1-propanol	0.7976	0.1044	0.0548	-0.0126
DMF + 2-methyl-2-propanol	0.7799	0.1069	0.0708	-0.0135
	η (mPa.s)			
DMF + 1-butanol	2.5207	-5.9595	7.9062	-3.7053
DMF + 2-butanol	2.9904	-8.4987	11.069	-4.7738
DMF + 2-methyl-1-propanol	3.4109	-8.4121	11.011	-5.2536
DMF + 2-methyl-2-propanol	4.4273	-14.028	18.854	-8.4762
T = 308.15 K				
	ρ (g.cm^{-3})			
DMF + 1-butanol	0.7982	0.1126	0.0224	0.0018
DMF + 2-butanol	0.794	0.1141	0.0261	0.0007
DMF + 2-methyl-1-propanol	0.7898	0.1178	0.0256	0.0018
DMF + 2-methyl-2-propanol	0.7699	0.1274	0.0373	0.0003
	η (mPa.s)			
DMF + 1-butanol	1.971	-4.4523	5.9927	-3.8312
DMF + 2-butanol	2.0829	-5.3904	7.2406	-3.2438
DMF + 2-methyl-1-propanol	2.4183	-5.5069	7.0387	-3.2717
DMF + 2-methyl-2-propanol	2.5791	-6.1137	7.4097	-3.1971
T = 318.15 K				
	ρ (g.cm^{-3})			
DMF + 1-butanol	0.7903	0.136	-0.0153	0.015
DMF + 2-butanol	0.7851	0.1245	0.0071	0.0092
DMF + 2-methyl-1-propanol	0.7818	0.1309	0.0029	0.0102
DMF + 2-methyl-2-propanol	0.7635	0.1366	0.0153	0.0104
	η (mPa.s)			
DMF + 1-butanol	1.5743	-2.5647	2.6702	-1.0686
DMF + 2-butanol	1.5053	-3.0773	3.994	-1.8193
DMF + 2-methyl-1-propanol	1.8213	-3.146	3.4457	-1.515
DMF + 2-methyl-2-propanol	1.6736	-3.8371	5.2541	-2.4841

Table 3.
Values of density (ρ), viscosity (η), excess molar volume (V^E), deviation in viscosity ($\Delta\eta$) and various interaction parameters for the binary mixtures of N, N-dimethylformamide with isomeric butanols at different temperatures.

x_1	ρ (g.cm^{-3})	η (mPa.s)	$V^E \times 10^6$ (m^3.mol^{-1})	$\Delta\eta$ (mPa.s)	d_{12}	T_{12}	H_{12}
T = 298.15 K							
DMF + 1-butanol							
0	0.8056	2.5650	0	0	-	-	-
0.1012	0.8165	1.9416	0.122	-0.445	-1.7678	-1.0086	-0.7613
0.2022	0.8281	1.5877	0.196	-0.621	-1.5176	-0.4168	-0.2407
0.3029	0.8405	1.3113	0.225	-0.720	-1.5116	-0.1552	-0.0209
0.4033	0.8538	1.1874	0.203	-0.667	-1.2542	0.2000	0.2982
0.5034	0.8678	1.1079	0.156	-0.570	-1.0193	0.4705	0.5439
0.6033	0.8822	1.0180	0.117	-0.484	-0.9337	0.6173	0.6729
0.7029	0.8972	0.9352	0.059	-0.391	-0.9224	0.7067	0.7471
0.8022	0.9125	0.8692	0.027	-0.282	-0.9488	0.7675	0.7942
0.9012	0.9281	0.8234	0.010	-0.154	-1.0064	0.8079	0.8212
1	0.9442	0.8030	0	0	-	-	-
DMF + 2-methyl-1-propanol							
0	0.7976	3.4307	0	0	-	-	-
0.1012	0.8087	2.6657	0.166	-0.581	-1.1569	-0.9472	-0.6249
0.2022	0.8208	2.0844	0.260	-0.851	-1.2683	-0.6680	-0.4088
0.3029	0.8337	1.6819	0.306	-0.968	-1.2928	-0.3413	-0.1395
0.4033	0.8477	1.4911	0.280	-0.88	-1.0288	0.1377	0.2888
0.5034	0.8626	1.3390	0.216	-0.743	-0.8391	0.4625	0.5791
0.6033	0.8778	1.2246	0.167	-0.621	-0.6437	0.7277	0.8199
0.7029	0.8936	1.1209	0.116	-0.463	-0.4690	0.9339	1.0087
0.8022	0.9099	0.9919	0.068	-0.331	-0.4788	1.0163	1.0742
0.9012	0.9268	0.8746	0.030	-0.188	-0.6516	1.0230	1.0613
1	0.9442	0.8030	0	0	-	-	-
DMF + 2-butanol							
0	0.8020	2.9995	0	0	-	-	-
0.1012	0.8125	2.2321	0.198	-0.545	-1.7812	-1.4067	-1.0935
0.2022	0.8238	1.6893	0.336	-0.866	-1.9669	-1.0249	-0.7828
0.3029	0.8362	1.2542	0.399	-1.080	-2.2391	-0.8454	-0.6562
0.4033	0.8495	1.0737	0.400	-1.040	-2.0606	-0.3949	-0.2596
0.5034	0.8638	0.9407	0.345	-0.953	-1.9846	-0.1009	-0.0048
0.6033	0.8786	0.8434	0.291	-0.831	-1.9795	0.1003	0.1652
0.7029	0.8942	0.8236	0.209	-0.632	-1.7534	0.3468	0.3881
0.8022	0.9106	0.8195	0.111	-0.418	-1.5146	0.5597	0.5842
0.9012	0.9273	0.8099	0.037	-0.210	-1.3654	0.7111	0.7217
1	0.9442	0.8030	0	0	-	-	-
DMF + 2-methyl-2-propanol							
0	0.7799	4.4340	0	0	-	-	-
0.1012	0.7914	3.1894	0.270	-0.877	-1.7197	-2.7929	-2.2007
0.2022	0.8043	2.2998	0.420	-1.400	-1.9277	-2.1815	-1.7206
0.3029	0.8182	1.6312	0.505	-1.703	-2.2848	-1.7712	-1.4142
0.4033	0.8337	1.2866	0.482	-1.683	-2.2778	-1.1387	-0.8783
0.5034	0.8499	1.0761	0.432	-1.530	-0.2233	-0.6281	-0.4416

Contd...

0.6033	0.8673	0.9995	0.343	-1.244	-1.9179	-0.1115	0.0196
0.7029	0.8853	0.9519	0.255	-0.930	-1.6167	0.3004	0.3919
0.8022	0.9042	0.8960	0.160	-0.625	-1.4396	0.5876	0.0483
0.9012	0.9237	0.8666	0.089	-0.295	-1.0393	0.9166	0.9614
1	0.9442	0.8030	0	0	-	-	-
T = 308.15 K							
DMF + 1-butanol							
0	0.7982	1.9911	0	0	-	-	-
0.1012	0.8098	1.5633	0.028	-0.298	-1.5098	-0.4558	-0.2873
0.2022	0.8219	1.2719	0.044	-0.460	-1.4844	-0.2040	-0.0755
0.3029	0.8344	1.0729	0.050	-0.530	-1.4479	-0.0022	0.0952
0.4033	0.8474	0.9852	0.046	-0.489	-1.1942	0.2634	0.3342
0.5034	0.8608	0.9153	0.039	-0.431	-1.0306	0.4362	0.4881
0.6033	0.8747	0.8608	0.029	-0.357	-0.9021	0.5647	0.6044
0.7029	0.8890	0.8182	0.022	-0.272	-0.7848	0.6692	0.6990
0.8022	0.9039	0.7709	0.013	-0.192	-0.7622	0.7244	0.7453
0.9012	0.9192	0.7199	0.006	-0.116	-0.9786	0.6911	0.6986
1	0.9350	0.7093	0	0	-	-	-
DMF + 2-methyl-1-propanol							
0	0.7898	2.4449	0	0	-	-	-
0.1012	0.8019	1.8982	0.042	-0.371	-1.4048	-0.6913	-0.4616
0.2022	0.8146	1.5559	0.060	-0.538	-1.2503	-0.2608	-0.0904
0.3029	0.8278	1.2842	0.063	-0.635	-1.2742	-0.0597	0.0734
0.4033	0.8416	1.1429	0.057	-0.602	-1.0859	0.2263	0.3263
0.5034	0.8558	1.0462	0.048	-0.525	-0.9037	0.4506	0.5271
0.6033	0.8706	0.9579	0.038	-0.440	-0.7961	0.5987	0.6579
0.7029	0.8858	0.8880	0.029	-0.337	-0.6847	0.7241	0.7703
0.8022	0.9016	0.8127	0.021	-0.240	-0.6856	0.7868	0.8209
0.9012	0.9180	0.7438	0.009	-0.137	-0.8407	0.7881	0.8076
1	0.9350	0.7093	0	0	-	-	-
DMF + 2-butanol							
0	0.7940	2.1106	0	0	-	-	-
0.1012	0.8057	1.5708	0.053	-0.398	-2.0335	-0.9968	-0.777
0.2022	0.8181	1.2513	0.070	-0.576	-1.8741	-0.5332	-0.3753
0.3029	0.8309	1.0162	0.078	-0.670	-1.8975	-0.2949	-0.1766
0.4033	0.8443	0.8955	0.071	-0.650	-1.7353	-0.0256	0.0595
0.5034	0.8582	0.8142	0.062	-0.591	-1.6146	0.1674	0.2279
0.6033	0.8725	0.7632	0.049	-0.502	-1.5014	0.3197	0.3612
0.7029	0.8873	0.7377	0.035	-0.388	-1.3636	0.4542	0.4811
0.8022	0.9027	0.7215	0.024	-0.265	-1.2518	0.5599	0.5750
0.9012	0.9185	0.7147	0.012	-0.133	-1.1247	0.6565	0.6629
1	0.9350	0.7093	0	0	-	-	-
DMF + 2-methyl-2-propanol							
0	0.7700	2.6097	0	0	-	-	-
0.1012	0.7831	2.0028	0.086	-0.414	-1.4594	-0.9094	-0.6181
0.2022	0.7972	1.5829	0.117	-0.642	-1.4662	-0.5559	-0.3317
0.3029	0.8119	1.3222	0.128	-0.712	-1.3515	-0.1945	-0.0262
0.4033	0.8274	1.1297	0.118	-0.714	-1.2961	0.0491	0.1769
0.5034	0.8436	1.0013	0.094	-0.652	-1.2088	0.2599	0.3559
0.6033	0.8605	0.8938	0.073	-0.569	-1.1934	0.3991	0.4699
0.7029	0.8780	0.8383	0.054	-0.436	-1.0536	0.5649	0.6164
0.8022	0.8962	0.7609	0.035	-0.324	-1.1820	0.6062	0.6374

Contd...

0.9012	0.9151	0.7148	0.023	-0.182	-1.3589	0.6260	0.6360
1	0.9350	0.7093	0	0	-	-	-
			T = 318.15 K				
			DMF + 1-butanol				
0	0.7902	1.5781	0	0	-	-	-
0.1012	0.8039	1.3388	-0.229*	-0.142	-0.7624	0.2235	0.3173
0.2022	0.8174	1.1488	-0.372	-0.235	-0.7912	0.2918	0.3692
0.3029	0.8306	1.0150	-0.439	-0.272	-0.7430	0.3918	0.4535
0.4033	0.8435	0.9027	-0.438	-0.288	-0.7471	0.4502	0.4997
0.5034	0.8566	0.8301	-0.407	-0.264	-0.6784	0.5303	0.5693
0.6033	0.8699	0.7668	-0.355	-0.231	-0.6484	0.5834	0.6140
0.7029	0.8835	0.7235	-0.289	-0.179	-0.5738	0.6448	0.6688
0.8022	0.8974	0.6755	-0.211	-0.132	-0.6003	0.6654	0.6827
0.9012	0.9115	0.6436	-0.123	-0.068	-0.5970	0.7018	0.7140
1	0.9258	0.6170	0	0	-	-	-
			DMF + 2-methyl-1-propanol				
0	0.7818	1.8338	0	0	-	-	-
0.1012	0.7951	1.5236	-0.122	-0.187	-0.8245	0.0680	0.1978
0.2022	0.8086	1.3018	-0.193	-0.286	-0.7588	0.2363	0.3389
0.3029	0.8221	1.1383	-0.223	-0.327	-0.6960	0.3693	0.4511
0.4033	0.8357	1.0241	-0.217	-0.319	-0.5955	0.4975	0.5626
0.5034	0.8497	0.9312	-0.202	-0.290	-0.5171	0.5928	0.6454
0.6033	0.8641	0.8497	-0.184	-0.250	-0.4683	0.6602	0.7031
0.7029	0.8788	0.7826	-0.149	-0.196	-0.4116	0.7211	0.7562
0.8022	0.8941	0.7207	-0.114	-0.137	-0.3788	0.7653	0.7937
0.9012	0.9097	0.6642	-0.062	-0.073	-0.3807	0.7932	0.8154
1	0.9258	0.6170	0	0	-	-	-
			DMF + 2-butanol				
0	0.7851	1.5210	0	0	-	-	-
0.1012	0.7978	1.2155	-0.070	-0.214	-1.4604	-0.2315	-0.1069
0.2022	0.8107	1.0198	-0.105	-0.318	-1.3475	-0.0107	0.0819
0.3029	0.8238	0.8803	-0.124	-0.367	-1.2959	0.1298	0.2000
0.4033	0.8370	0.8104	-0.113	-0.346	-1.1039	0.2987	0.3501
0.5034	0.8507	0.7529	-0.105	-0.313	-0.9958	0.4047	0.4430
0.6033	0.8648	0.7108	-0.088	-0.265	-0.9040	0.4877	0.5158
0.7029	0.8793	0.6775	-0.073	-0.208	-0.8360	0.5506	0.5707
0.8022	0.8943	0.6544	-0.053	-0.141	-0.7543	0.6094	0.6232
0.9012	0.9098	0.6308	-0.031	-0.075	-0.7527	0.6376	0.6450
1	0.9258	0.6170	0	0	-	-	-
			DMF + 2-methyl-2-propanol				
0	0.7635	1.6847	0	0	-	-	-
0.1012	0.7774	1.3246	-0.035	-0.252	-1.5252	-0.4045	-0.2339
0.2022	0.7918	1.0838	-0.064	-0.385	-0.1475	-0.1714	-0.0424
0.3029	0.8066	0.9163	-0.083	-0.445	-1.4433	-0.0006	0.0971
0.4033	0.8218	0.8311	-0.077	-0.423	-1.2528	0.2006	0.2720
0.5034	0.8374	0.7682	-0.065	-0.379	-1.1185	0.3402	0.3928
0.6033	0.8537	0.7306	-0.052	-0.310	-0.9590	0.4045	0.5032
0.7029	0.8707	0.7052	-0.044	-0.229	-0.7889	0.5736	0.6026
0.8022	0.8883	0.6854	-0.030	-0.143	-0.5899	0.6774	0.7008
0.9012	0.9067	0.6542	-0.018	-0.068	-0.4570	0.7481	0.7674
1	0.9258	0.6170	0	0	-	-	-

* = data not fitted to equation 7.

Table 4.
Values of coefficients of equation 7 and standard deviations for excess properties of the binary mixtures of N, N- dimethylformamide studied at different temperatures.

Excess property	Temperature (K)	a_0	a_1	a_2	a_3	s
		DMF + 1-butanol				
$V^E \times 10^6$ ($m^3.mol^{-1}$)	298.15	0.655	-0.996	0.121	0.341	0.005
	308.15	0.156	-0.173	0.097	0.036	0.001
	318.15	-1.638	0.894	-0.535	-0.212	0.003
$\Delta\eta$ (mPa.s)	298.15	-2.346	1.867	1.489	-	0.015
	308.15	-1.746	1.529	-0.859	-0.429	0.007
	318.15	-1.066	0.564	-0.171	-0.109	0.004
		DMF + 2-methyl-1-propanol				
$V^E \times 10^6$ ($m^3.mol^{-1}$)	298.15	0.901	-1.172	0.652	0.419	0.007
	308.15	0.193	-0.201	0.167	-	0.002
	318.15	-0.823	0.405	-0.351	-	0.003
$\Delta\eta$ (mPa.s)	298.15	-3.058	2.901	-1.881	-0.405	0.016
	308.15	-2.135	1.718	-0.971	-0.290	0.011
	318.15	-1.173	0.761	-0.424	-	0.002
		DMF + 2-butanol				
$V^E \times 10^6$ ($m^3.mol^{-1}$)	298.15	1.441	-1.124	-0.136	-	0.008
	308.15	0.249	-0.229	0.088	-0.063	0.002
	318.15	-0.419	0.275	-0.223	-	0.003
$\Delta\eta$ (mPa.s)	298.15	-3.902	2.365	-0.476	-	0.022
	308.15	-2.378	1.523	-0.806	0.352	0.008
	318.15	-1.265	0.916	-0.520	-	0.005
		DMF + 2-methyl-2-propanol				
$V^E \times 10^6$ ($m^3.mol^{-1}$)	298.15	1.729	-1.501	0.340	0.427	0.007
	308.15	0.384	-0.434	0.302	-	0.003
	318.15	-0.264	0.266	-0.222	-0.245	0.002
$\Delta\eta$ (mPa.s)	298.15	-6.138	4.558	-0.571	-1.155	0.018
	308.15	-2.618	1.597	-1.049	-	0.008
	318.15	-1.528	1.245	-0.378	-	0.004

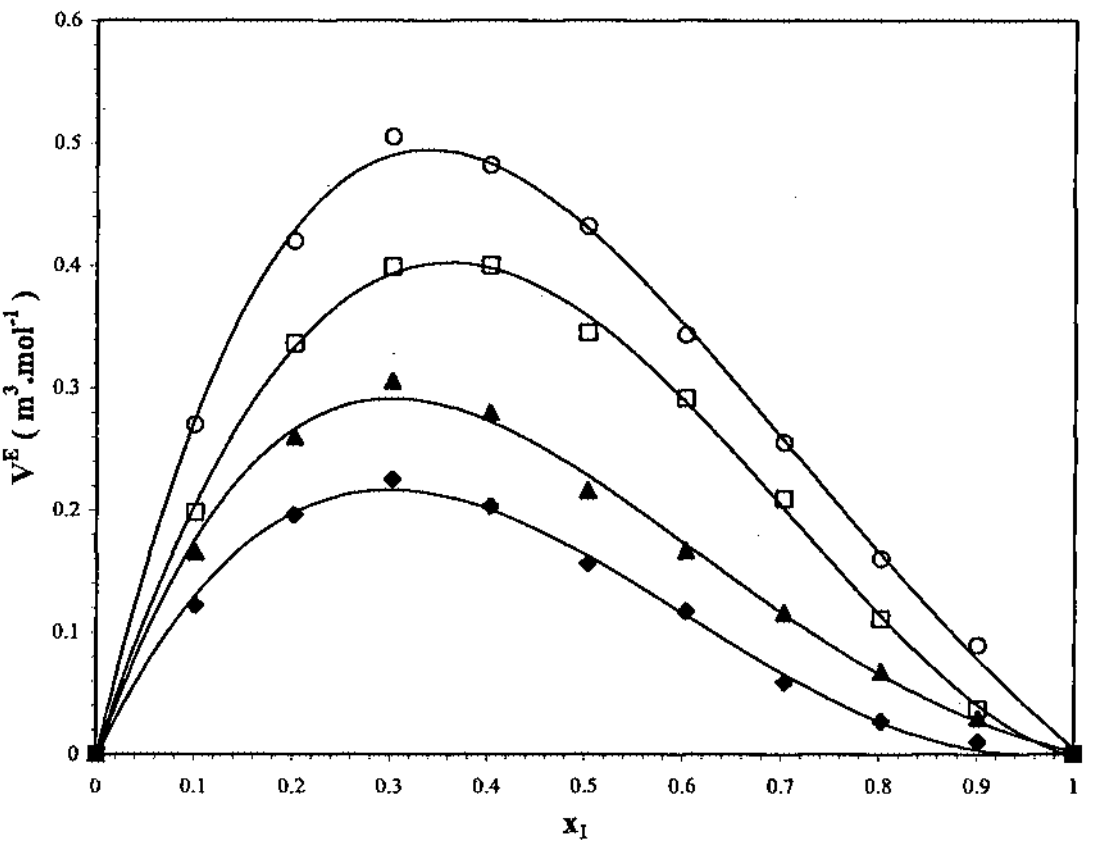

Figure 1. Variation of excess molar volumes (V^E) against mole fraction (x_i) of N, N-dimethylformamide at 298.15K: (□) 1-butanol; (▲) 2-methyl-1-propanol; (□) 2-butanol; (O) 2-methyl-2-propanol.

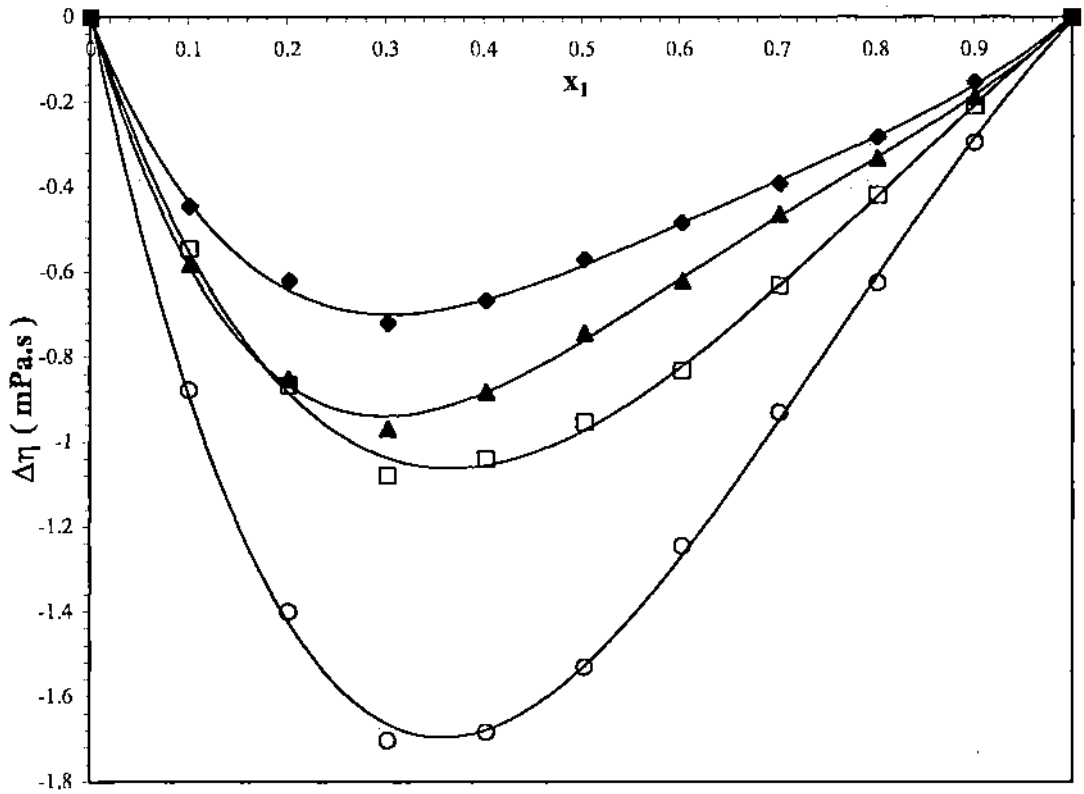

Figure 2. Variation of deviations in viscosity ($\Delta\eta$) against mole fraction (x_i) of N, N-dimethylformamide at 298.15 K: (□) 1-butanol; (▲) 2-methyl-1-propanol; (▫) 2-butanol; (O) 2-methyl-2-propanol.