

Volumetric and Viscometric Studies of Molecular Interactions in Binary N,N-Dimethylacetamide + Benzyl Alcohol Mixtures at Different Temperatures

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ABSTRACT

The densities, ρ , and viscosities, η , of pure N,N-dimethylacetamide (DMA) and benzyl alcohol (BA), and nine of their binary mixtures covering the entire composition range have been measured at 25, 30, 35, 40 and 45°C. The experimental ρ and η values were correlated with composition and temperature by using some empirical relations. The excess volumes, V^E , deviation in viscosities, $\Delta\eta$, excess Gibbs energies of activation of viscous flow, ΔG^{*E} , and partial molar volumes, \bar{V}_1^0 and \bar{V}_2^0 , of DMA in BA and BA in DMA, respectively, at infinite dilution have been evaluated from the experimental data. The variations of these parameters with composition and temperature indicate the presence of specific interactions, namely hydrogen bonding and dipole-dipole forces between unlike molecules, which decrease with rise in temperature. Furthermore, the enthalpies, ΔH^* , and entropies, ΔS^* , of activation of viscous flow have also been obtained by using the Eyring viscosity equation and fitting the results to some empirical relations. The ΔH^* values were found to be dependent on temperature. The dependencies of ΔH^* and ΔS^* on the compositions of the mixtures have been discussed.

KEYWORDS

Density, viscosity, binary mixtures, molecular interactions.

1. Introduction

The important role played by solvents in chemistry and chemical industry has been well recognized. Mixed solvents, rather than single pure liquids, are extensively used in industrial and chemical processes as they provide a wide range of solvents with variable physical properties. In previous work we have presented a systematic study of the thermodynamic, acoustic and transport properties of binary mixtures of amides with alcohols.^{1–6} The objective underlying such studies is to improve our understanding of molecular interactions for characterizing the physico-chemical behaviour of mixtures at the molecular level, which is essential for understanding many chemical and biological processes in these media. The present work is focused on the study of binary mixtures of N,N-dimethylacetamide (DMA) with benzyl alcohol (BA) over the entire composition range at five different temperatures. The molecules of DMA are aprotic and highly polar (dipole moment, $\mu = 3.72\text{D}$)⁷, but are practically unassociated; whereas molecules of BA are moderately polar ($\mu = 1.66\text{D}$)⁷ and are associated through hydrogen bonding.⁸ To the best of our knowledge, no temperature-dependent study on volumetric and viscometric properties has been made on this system. Although studies on amide + aliphatic alcohols have been extensively carried out by many workers,^{1–6,9–13} relatively little attention has been paid to the studies of amides with aromatic alcohols rich in π -electrons. Furthermore, the amides are convenient model systems for investigating peptide and protein interactions and BA forms esters, which are used in perfumery and cosmetics.¹⁴ Therefore, the study of molecular interactions in binary mixtures of DMA with BA will also be useful owing to their applied nature.

In this paper we report densities, ρ , and viscosities, η , of nine

binary mixtures of DMA with BA, as well as pure DMA and BA, covering the entire composition range at 25, 30, 35, 40 and 45°C. The dependence of ρ and η on composition and temperature of the mixtures has been checked by using various empirical relations. From the experimental values of ρ and η , the excess molar volume, V^E , deviation in viscosity, $\Delta\eta$, excess Gibbs energy of activation of viscous flow, ΔG^{*E} , apparent molar volumes, $V_{\phi,1}$ and $V_{\phi,2}$, and partial molar volumes, \bar{V}_1^0 and \bar{V}_2^0 of DMA in BA and BA in DMA, respectively, at infinite dilution have been calculated. The variations of these functions with composition and temperature have been used to explain the nature of the interactions between the component molecules of the mixtures. From the temperature dependence of the viscosity, η , the Gibbs energy, ΔG^* , enthalpy, ΔH^* , and entropy, ΔS^* , of activation of viscous flow have also been calculated using the theory of Eyring and coworkers.¹⁵ The dependencies of these properties on the composition and temperature of the mixtures have been discussed.

2. Experimental

DMA and BA (both s.d. fine chemicals, AR grade) were purified by using the standard methods described in the literature.^{16,17} Before use, the liquids were stored over 0.4 nm molecular sieves to reduce water content, if any, and were degassed. The purities of DMA and BA determined by GLC were found to be >99.5%. The mixtures were prepared by mass in a dry box and were kept in special airtight bottles. The weighing was done on an Afcoset ER-120A electronic balance with a precision of $\pm 0.1\text{mg}$.

The densities of the pure liquids and their binary mixtures were measured using a single-capillary pycnometer^{2,6} made of Borosil glass, having a bulb capacity of $8 \times 10^{-6}\text{m}^3$. The capillary, with graduated marks, had a uniform bore, and could be closed

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Table 1 Density, ρ , and viscosity, η , of binary mixtures of DMA with BA as a function of mole fraction, x_1 , of DMA at different temperatures.

x_1	T / °C				
	25	30	35	40	45
	ρ / g cm ⁻³				
0.0000	1.0401	1.0365	1.0329	1.0293	1.0257
0.1102	1.0340	1.0300	1.0260	1.0219	1.0180
0.2179	1.0261	1.0218	1.0176	1.0134	1.0091
0.3233	1.0169	1.0124	1.0080	1.0036	0.9992
0.4263	1.0069	1.0023	0.9977	0.9931	0.9886
0.5271	0.9962	0.9914	0.9867	0.9820	0.9774
0.6258	0.9849	0.9801	0.9753	0.9706	0.9660
0.7223	0.9731	0.9683	0.9636	0.9590	0.9545
0.8168	0.9610	0.9564	0.9518	0.9473	0.9429
0.9094	0.9487	0.9443	0.9399	0.9356	0.9313
1.0000	0.9366	0.9324	0.9282	0.9240	0.9198
	η / cP				
0.0000	4.9565	4.1352	3.6781	3.2061	2.8907
0.1102	4.4238	3.6935	3.2957	2.8879	2.6133
0.2179	3.9172	3.2766	2.9308	2.5771	2.3414
0.3233	3.4277	2.8733	2.5827	2.2767	2.0753
0.4263	2.9630	2.4861	2.2431	1.9855	1.8182
0.5271	2.5276	2.1202	1.9245	1.7140	1.5759
0.6258	2.1271	1.7920	1.6287	1.4600	1.3541
0.7223	1.7708	1.4989	1.3692	1.2433	1.1522
0.8168	1.4659	1.2494	1.1495	1.0482	0.9774
0.9094	1.2124	1.0375	0.9574	0.8823	0.8296
1.0000	0.9940	0.8595	0.8027	0.7474	0.7078

by a well-fitted glass cap. The marks on the capillary were calibrated by using triply-distilled water. The accuracy in density measurements was found to be ± 0.0001 g cm⁻³.

The viscosities of the pure liquids and their binary mixtures were measured by using Ubbelohde-type suspended-level viscometers.^{2,6} The viscometer containing the test liquid was allowed to stand for about 30 minutes in a thermostatic water bath so that the thermal fluctuations in the viscometers were minimized. The accuracy in viscosity measurement was found to be ± 0.003 cP.

The accuracy of experimental measurements was checked by comparing the values of ρ and η of the pure components with the corresponding literature values. For example, the experimental values of ρ for pure DMA and BA at 25°C are 0.9366 and 1.0401 g cm⁻³, respectively (literature values 0.9367¹⁸ and 1.04011¹⁹ g cm⁻³); the experimental η values of pure DMA at 35°C and BA at 25°C are 0.8027 and 4.9565 cP, respectively (literature values 0.8027⁴ and 4.9289¹⁹ cP).

The temperature of the test liquids during the measurements was maintained to an accuracy of ± 0.02 °C in an electronically controlled thermostatic water bath.

3. Results and Discussion

The results of the experimental measurements of the densities, ρ , and viscosities, η , of pure DMA, BA and nine binary mixtures over the whole composition range, expressed as the mole fraction, x_1 , of DMA at 25, 30, 35, 40 and 45°C are listed in Table 1. The dependence of ρ and η of the mixtures on temperature were checked by using a polynomial equation

$$a = \sum_{i=0}^4 a_i T^i \quad (1)$$

where a is ρ or $\ln \eta$ and T is the temperature in °C. The coefficients, a_i (ρ_i or $\ln \eta_i$), of Eq. (1) evaluated by using the method of least squares, along with the standard deviations σ (a) for each

composition are listed in Table 2. It is found that Eq. (1) reproduces the experimental density and viscosity values with an average uncertainty of ± 0.000069 g cm⁻³ and ± 0.0022 cP, respectively, for the binary mixtures under study. The dependencies of ρ and η of the mixtures on the mole fraction, x_1 , of DMA have been established using a polynomial equation of the type

$$b = \sum_{i=0}^4 b_i x^i \quad (2)$$

where b is $1/\rho$ or η . The coefficients, b_i ($1/\rho_i$ or η_i), of Eq. (2), along with the standard deviations, σ (b), at each investigated temperature are listed in Table 3. Eq. (2) reproduces the experimental ρ and η values with an average uncertainty of ± 0.000038 g cm⁻³ and ± 0.00216 cP for the present binary system. The standard deviations, σ , for fitting Eqs.(1) and (2) of the mixtures have been evaluated by using the relation

$$\sigma = \left[\sum (Z_{\text{expt}} - Z_{\text{cal}})^2 / n \right]^{1/2} \quad (3)$$

where Z is ρ or η and n is the number of data points. The magnitude of the average uncertainty in reproducing the experimental ρ and η values clearly illustrates the usefulness of the polynomial Eqs.(1) and (2) for the binary system under study. The significance of data fitting using similar polynomial equations in reproducing the experimental data has also been reported by others for N,N-dimethylformamide + 1,2-ethanediol⁹ and propylamine + 1-alkanol²⁰ binary mixtures.

The excess functions V^E , $\Delta\eta$ and ΔG^{*E} were calculated by using the following equations

$$V^E = x_1 M_1 (1/\rho - 1/\rho_1) + x_2 M_2 (1/\rho - 1/\rho_2) \quad (4)$$

$$\Delta\eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (5)$$

$$\Delta G^{*E} = RT [\ln(\bar{v}) - x_1 \ln(\eta_1 V_1) - x_2 \ln(\eta_2 V_2)] \quad (6)$$

where M is the molar mass, R is the universal gas constant, T is the absolute temperature, subscripts 1 and 2 refer to the pure

Table 2 Coefficients, a_i , of Eq. (1) and standard deviations, σ (a), for the binary mixtures at different compositions.

x_1	a_0	a_1	a_2	a_3	a_4	σ (a)
ρ /g cm ⁻³						
	ρ_0	$\rho_1 \times 10^2$	$\rho_2 \times 10^4$	$\rho_3 \times 10^5$	$\rho_4 \times 10^8$	$\times 10^{-4}$
0.0000	1.1965	-1.7074	7.1249	-1.3580	9.5638	0.928
0.1102	1.1582	-1.3246	5.4888	-1.0599	7.5651	0.497
0.2179	1.1706	-1.5287	6.2295	-1.1754	8.1946	0.746
0.3233	0.8847	1.7641	-8.2041	1.5882	-11.3475	1.117
0.4263	0.9292	1.1104	-5.2896	1.0172	-7.2185	0.917
0.5271	0.9644	5.8344	-3.0489	0.5975	-4.3067	1.897
0.6258	1.1245	-1.4538	5.8842	-1.1173	7.8593	0.876
0.7223	0.9178	8.5329	-4.1882	0.8067	-5.7135	0.632
0.8168	1.1416	-1.9625	8.1934	-1.5719	11.1612	1.013
0.9094	0.8754	1.7380	-5.2179	1.0236	-7.3997	0.775
1.0000	0.9577	-0.0778	-0.0639	0.0194	-0.1868	0.427
η /cP						
	$\ln \eta_0$	$\ln \eta_1$	$\ln \eta_2 \times 10^2$	$\ln \eta_3 \times 10^4$	$\ln \eta_4 \times 10^6$	$\times 10^{-2}$
0.0000	4.9962	-0.3062	1.0507	-1.7574	1.1166	0.653
0.1102	4.8288	-0.2966	0.9927	-1.6143	0.9959	0.655
0.2179	4.8078	-0.3084	1.0424	-1.7033	1.0568	0.632
0.3233	4.9079	-0.3365	1.1635	-1.9264	1.2085	0.664
0.4263	4.6783	-0.3249	1.1003	-1.7829	1.0942	1.537
0.5271	4.7263	-0.3131	1.1524	-1.8234	1.0847	0.714
0.6258	4.4815	-0.3376	1.1417	-1.8289	1.1120	0.646
0.7223	4.0344	-0.2978	0.9221	-1.3076	0.6716	0.536
0.8168	3.8623	-0.3045	0.9662	-1.4079	0.7519	0.575
0.9094	3.5014	-0.2826	0.8601	-1.1845	0.5857	0.480
1.0000	3.3059	-0.2848	0.8669	-1.1698	0.5528	0.506

components, DMA and BA, respectively, and V is the molar volume evaluated by using the equation

$$V = (x_1 M_1 + x_2 M_2) / \rho \quad (7)$$

The values of V^E , $\Delta\eta$ and ΔG^{*E} of the mixtures at each investigated temperature were fitted to a Redlich-Kister-type²¹ polynomial equation

$$Y^E = x_1 x_2 \sum_{i=1}^5 A_i (1 - 2x_1)^{i-1} \quad (8)$$

where Y^E is V^E , $\Delta\eta$ or ΔG^{*E} . The coefficients, A_i , of the fitting Eq. (8), along with the standard deviation, σ (Y^E), calculated as

$$\sigma(Y^E) = \left[\sum (Y^E_{\text{expt}} - Y^E_{\text{cal}})^2 / (h - k) \right]^{1/2}, \quad (9)$$

where h is the number of data points and k is the number of coefficients considered ($k = 5$ in the present calculation) are given in Table 4. Y^E_{cal} has been calculated from Eq. (8) using the best-fit values of A_i .

The variation of excess volume, V^E , with mole fraction, x_1 , of DMA for the binary mixtures at different temperatures is presented in Fig. 1. The V^E values for the system under study are found to be negative over the whole composition range and at each temperature investigated. Negative V^E values indicate the presence of significant interactions between the component molecules of the mixtures. A qualitative explanation for the variation of V^E with composition and temperature can be suggested. Mixing of DMA with BA will induce dissociation of hydrogen-bonded BA-BA associates, and subsequent formation of (new) hydrogen bonds ($C=O \cdots H-O$) between the hydrogen

Table 3 Coefficients, b_i , of Eq. (2) and standard deviations, σ (b), for the binary mixtures at different temperatures.

T /°C	b_0	b_1	b_2	b_3	b_4	σ (b)
ρ /g cm ⁻³						
	$1/\rho_0$	$1/\rho_1$	$1/\rho_2$	$1/\rho_3$	$1/\rho_4$	$\times 10^{-5}$
25	0.9613	0.0459	0.0714	-0.0105	-0.0003	7.387
30	0.9648	0.0487	0.0739	-0.0165	0.0017	5.937
35	0.9681	0.0521	0.0734	-0.0179	0.0016	3.359
40	0.9715	0.0552	0.0737	-0.0206	0.0025	3.965
45	0.9749	0.0599	0.0680	-0.0159	0.0003	4.630
η /cP						
	η_0	η_1	η_2	η_3	η_4	$\times 10^{-3}$
25	4.9543	-4.7562	-0.2195	0.8936	0.1253	3.955
30	4.1324	-3.8977	-0.3520	0.9738	0.0057	6.503
35	3.6760	-3.4008	-0.1653	0.4799	0.2150	11.86
40	3.2050	-2.8124	-0.4982	0.9164	-0.0627	6.552
45	2.8900	-2.4592	-0.4142	0.6435	0.0484	5.950

Table 4 Coefficients, A_i , of Eq. (8) and the standard deviations, $\text{sss} (Y^E)$, for the binary mixtures at different temperatures

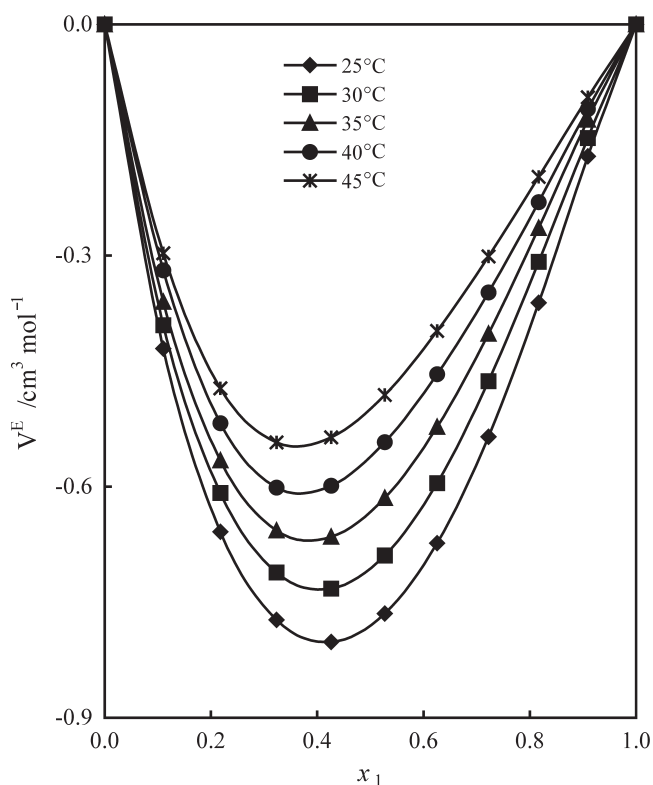
$T/^\circ\text{C}$	A_1	A_2	A_3	A_4	A_5	$\sigma (Y^E)$
$V^E / \text{cm}^3 \text{mol}^{-1}$						
25	-3.1212	-1.0058	-0.2674	-0.5935	0.1586	0.0052
30	-2.8268	-1.1226	-0.0605	-0.4061	-0.1445	0.0041
35	-2.5332	-1.2343	-0.2049	-0.1983	0.1073	0.0033
40	-2.2455	-1.3269	-0.3986	0.2032	0.4612	0.0028
45	-1.9978	-1.2745	-0.3405	0.1506	0.2579	0.0025
$\Delta\eta / \text{cP}$						
25	-1.3316	0.6440	-0.1266	-0.2862	0.1750	0.0006
30	-1.1198	0.5675	0.0340	-0.2869	-0.086	0.0012
35	-0.9289	0.5221	-0.0700	-0.2177	-0.0031	0.0010
40	-0.7734	0.4283	0.1385	-0.099	-0.2031	0.0019
45	-0.6355	0.3888	-0.0103	-0.0732	-0.0061	0.0005
$\Delta G^E / \text{kJ mol}^{-1}$						
25	1.6659	0.0773	-0.4393	-0.1599	0.3560	0.0006
30	1.5792	0.1574	-0.3074	-0.1689	0.0773	0.0013
35	1.5441	0.1831	-0.3779	-0.0399	0.0077	0.0017
40	1.4286	0.1770	-0.0808	0.0579	-0.3253	0.0032
45	1.4117	0.1925	-0.3327	0.0808	0.0024	0.0011

atom of the hydroxyl group of BA and a lone pair of electrons of the proton-acceptor oxygen atom of the carbonyl group of the DMA. The former effect contributes to positive values while the latter has a negative contribution to the V^E values. The observed negative V^E values (Fig. 1) over the whole composition range suggest that the formation of hydrogen bonds between DMA and BA molecules dominates over the dissociative effects of hydrogen-bonded BA-BA associates present in the mixture, i.e., the DMA-BA interaction is stronger than the DMA-DMA or BA-BA interactions in the mixtures. Negative V^E values have also been reported by others for binary mixtures of benzyl alcohol +

iso-amy/iso-propyl alcohol²² and DMA + ethanol.²³ It is clearly evident from Fig. 1 that V^E values become less negative with rise in temperature of the mixture, indicating that the system tends towards ideal behaviour. This may be due to the fact that the increase in temperature causes the rupture of hydrogen bonds formed between unlike molecules (DMA and BA) in the mixture, leading to an expansion in volume of the mixture, hence decreasing the magnitude of the negative V^E values.

The variation of the deviation in viscosity, $\Delta\eta$, with mole fraction, x_1 , of DMA for the binary mixtures at different temperatures is shown in Fig. 2. The values of $\Delta\eta$ for the system under study are negative over the whole range of composition and temperature investigated. Negative $\Delta\eta$ values are observed in systems in which dipole-dipole forces are primarily responsible for interactions between the component molecules.^{24,25} As mentioned above, addition of DMA to BA causes disruption of associates present in the latter releasing more free alcohol molecules. These free BA molecules may interact through dipole-dipole interactions, in addition to hydrogen bonding, with DMA molecules in the mixture. It is observed (Fig. 2) that the magnitude of the negative $\Delta\eta$ values decreases and tends towards zero as the temperature of the mixtures increases, i.e., the system tends towards ideal behaviour with rise in temperature.

The variation of the excess Gibbs energy of activation of viscous flow, ΔG^E , with mole fraction, x_1 , of DMA for the binary mixtures at different temperatures is presented in Fig. 3. The values of ΔG^E are found to be positive over the whole range of composition and temperature investigated. In general, the positive contributions to the ΔG^E values may be attributed to the presence of specific interactions (hydrogen bonding and dipole-dipole interactions), whereas negative contributions may be ascribed to the dispersion forces.^{26,27} The observed positive ΔG^E values suggest the formation of hydrogen bonds and dipolar interactions between the unlike molecules in the system under study. Positive ΔG^E values have also been reported by others for formamide + 1-pentanol,²⁸ acetonitrile + 1-alkanols (C_7, C_8, C_9)²⁹ and propylamine + 1-alkanol²⁰ binary mixtures. As expected, like V^E and $\Delta\eta$, the ΔG^E values tend towards zero with increase in the temperature of the mixture, indicating that

**Figure 1** Variation of excess volume, V^E , with mole fraction x_1 of DMA for binary mixture at different temperatures.

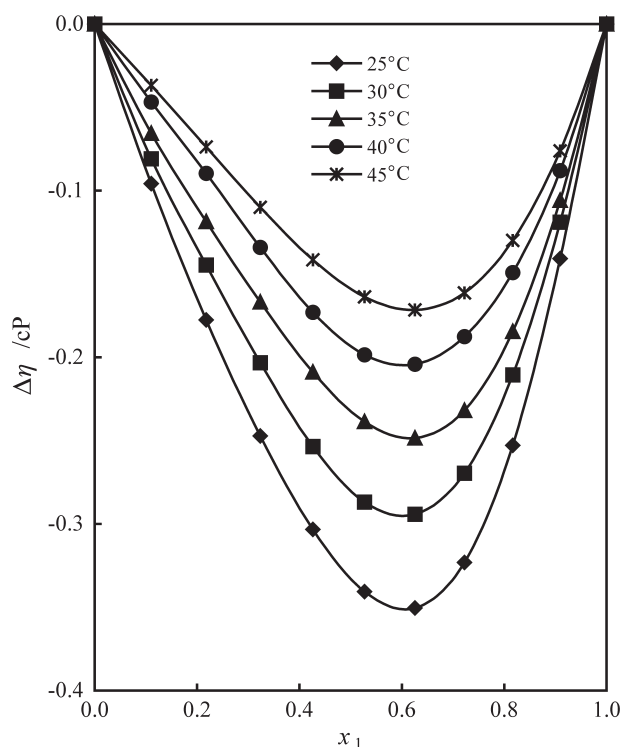


Figure 2 Variation of deviation in viscosity, $\Delta\eta$, with mole fraction x_1 of DMA for binary mixture at different temperatures.

the system approaches ideal behaviour with rise in temperature. Thus for the system DMA + BA, the functions V^E , $\Delta\eta$ and ΔG^{*E} truly support each other over the entire composition range and at all five temperatures investigated.

The apparent molar volumes, $V_{\phi,1}$ and $V_{\phi,2}$, of DMA in BA and BA in DMA, respectively, at each investigated temperature were evaluated by using the relations³⁰

$$V_{\phi,1} = V_1^* + (V^E/x_1) \quad (10)$$

$$V_{\phi,2} = V_2^* + (V^E/x_2) \quad (11)$$

where V_1^* and V_2^* are the molar volumes of pure DMA and BA, respectively. The partial molar volumes, \bar{V}_1^o and \bar{V}_2^o , of DMA in BA and BA in DMA, respectively, at infinite dilution were calculated by using a method described in the literature.³¹ The deviations in \bar{V}^o at infinite dilution, ΔV_1 and ΔV_2 , for DMA and BA have been calculated by using the relations³⁰

$$\Delta V_1 = \bar{V}_1^o - V_1^* \quad (12)$$

$$\Delta V_2 = \bar{V}_2^o - V_2^* \quad (13)$$

The values of \bar{V}_1^o , V_1^* , \bar{V}_2^o , V_2^* and ΔV_2 are given in Table 5. It is observed that the partial molar volumes, \bar{V}_1^o and \bar{V}_2^o , of both the components, DMA and BA, at infinite dilution are lower than

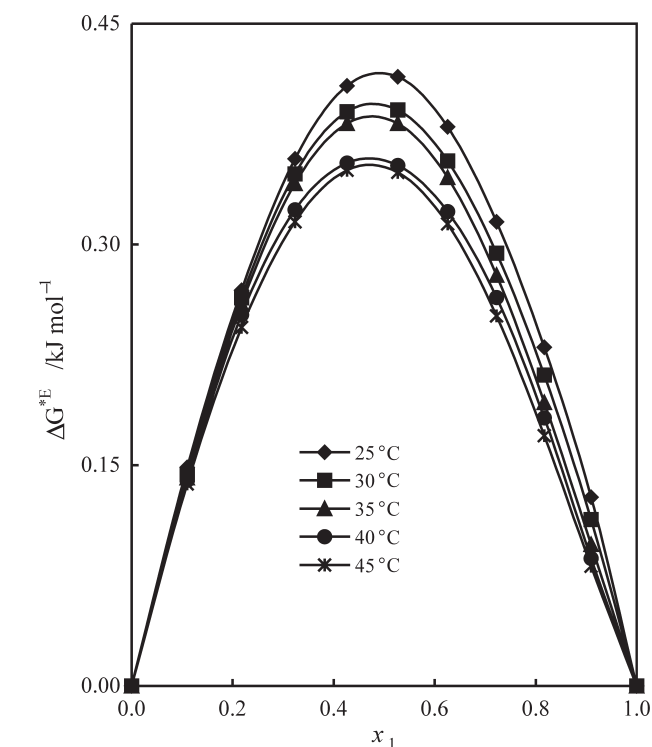


Figure 3 Variation of excess Gibbs energy of activation of viscous flow, ΔG^{*E} , with mole fraction x_1 of DMA for binary mixture at different temperatures.

their corresponding molar volumes at each investigated temperature. The values of V_1 and V_2 are negative for the system under study, suggesting that on mixing there is a contraction in the volume of the mixture, which may be due to the presence of significant interaction between the DMA and BA molecules. However, as the temperature increases, V_1 and V_2 become less negative, thereby indicating the weakening of the interaction between the component molecules in the mixture. This further supports our earlier conclusion that DMA-BA interactions (hydrogen bonding and dipole-dipole) are stronger than DMA-DMA or BA-BA interactions in the system under study.

Further, by using the temperature dependence of viscosity data the activation parameters of viscous flow have also been investigated. The Eyring viscosity equation^{15,32} is given as

$$\eta = (hN/V) \exp(\Delta G^*/RT) \quad (14)$$

where h is Planck's constant, N is Avogadro's constant and ΔG^* is the Gibbs energy of activation of viscous flow. Combining Eq. (14) with $\Delta G^* = \Delta H^* - \Delta TS^*$ gives the equation

$$R \ln(\eta V/hN) = (\Delta H^*/T) - \Delta S^* \quad (15)$$

where ΔH^* and ΔS^* are the enthalpy and entropy of activation of viscous flow, respectively. The plots of the left hand side of

Table 5 The values of \bar{V}_1^o , V_1^* , ΔV_1 , \bar{V}_2^o , V_2^* and ΔV_2 for the binary mixtures at different temperatures.

T/°C	\bar{V}_1^o	V_1^*	ΔV_1	\bar{V}_2^o	V_2^*	ΔV_2
	$\text{cm}^3 \text{mol}^{-1}$					
25	89.68	93.02	-3.34	101.74	103.97	-2.23
30	90.36	93.44	-3.08	102.38	104.33	-1.95
35	91.03	93.86	-2.83	103.02	104.70	-1.68
40	91.73	94.29	-2.56	103.60	105.06	-1.46
45	92.39	94.72	-2.33	104.16	105.43	-1.27

Table 6 Coefficients, c_i , of Eq. (16) and the standard deviations, $\sigma(c)$, for the binary mixtures at different compositions.

x_1	$c_0 \times 10^2$	$c_1 \times 10^4$	$c_2 \times 10^7$	$c_3 \times 10^9$	$\sigma(c) \times 10^2$
0.0000	1.0843	-1.4141	-1.2184	3.5935	2.307
0.1102	1.1731	-1.5838	-1.3773	3.9541	2.431
0.2179	1.2489	-1.8500	-1.4442	4.1595	2.518
0.3233	1.2469	-1.7976	-1.4868	4.2126	2.338
0.4263	1.3367	-2.0254	-1.6196	4.5388	2.487
0.5271	1.4176	-2.0631	-1.8432	4.9867	2.687
0.6258	1.6198	-2.8781	-1.9335	5.4043	2.865
0.7223	1.5491	-2.2687	-2.1206	5.5652	2.897
0.8168	1.5304	-2.2712	-2.0808	5.4547	2.968
0.9094	1.7478	-2.9506	-2.2945	6.0757	2.623
1.0000	1.6874	-2.5994	-2.3339	5.9954	3.013

Eq. (15), i.e., $\text{Rln}(\eta V/hN)$ against $1/T$ for DMA + BA binary mixtures at different compositions are shown in Fig. 4 and were found to be non-linear for each composition of the system under study. This indicates that ΔH^* is dependent on temperature. Hence, the left hand side of Eq. (15) was fitted to the following polynomial equation

$$\text{Rln}(\eta V/hN) = c_0 + c_1/T + c_2/T^2 + c_3/T^3 = \sum_{i=0}^3 c_i/T^i \quad (16)$$

The values of the adjustment coefficients, c_i , evaluated using the method of least squares, and the corresponding standard deviations, $\sigma(C)$, are listed in Table 6. The values of ΔH^* and ΔS^* have been calculated by using the relations

$$\Delta H^* = c_1 + 2c_2/T + 3c_3/T^2 \quad (17)$$

$$\Delta S^* = -c_0 + c_2/T^2 + 2c_3/T^3 \quad (18)$$

The values of ΔH^* and ΔS^* are given in Table 7. A perusal of Table 7 indicates that the H^* values, for the system under study,

are positive over the investigated temperature range. Also, the ΔH^* values decrease with increase in mole fraction of DMA and rise in the temperature of the mixtures. This implies that in the DMA-rich region, the formation of the activated species necessary for viscous flow appears easier in comparison with that in the BA-rich region. The ΔS^* values are positive (Table 7) at lower temperature and decrease with increase in mole fraction of DMA, except at 25°C, where the ΔS^* values do not follow any specific trend. The decrease in ΔS^* with increasing amount of DMA in the mixture again supports the above view.

Further, ΔS^* values change sign and become increasingly negative (Table 7) with rise in temperature of the system at all the mole fractions of DMA. The decrease in ΔS^* values with rise in temperature may be due to the breaking up of the associates formed in the mixture, facilitating the process of viscous flow. Similar results for ΔH^* and ΔS^* values have also been observed for the ethanol + 1,4-dioxane³³ and ethan-1,2-diol + water³⁴ binary systems.

Table 7 Enthalpy, ΔH^* , and entropy, ΔS^* , of activation of viscous flow for binary mixtures of DMA with BA as a function of mole fraction, x_1 of DMA at different temperatures.

x_1	T /°C				
	25	30	35	40	45
	$\Delta H^* / \text{kJ mol}^{-1}$				
0.0000	25.403	22.784	20.312	17.978	15.773
0.1102	25.217	22.376	19.695	17.165	14.775
0.2179	24.999	22.004	19.180	16.513	13.995
0.3233	24.458	21.452	18.617	15.941	13.415
0.4263	24.278	21.059	18.023	15.159	12.455
0.5271	24.020	20.554	17.287	14.206	11.299
0.6258	23.904	20.076	16.468	13.063	9.847
0.7223	22.879	19.081	15.503	12.131	8.950
0.8168	21.795	18.074	14.570	11.267	8.152
0.9094	21.623	17.454	13.526	9.823	6.329
1.0000	19.783	15.745	11.944	8.362	4.985
	$\Delta S^* / \text{J K}^{-1} \text{mol}^{-1}$				
0.0000	25.68	16.97	8.88	1.36	-5.62
0.1102	26.13	16.68	7.91	-0.24	-7.81
0.2179	26.53	16.57	7.32	-1.26	-9.24
0.3233	25.94	15.94	6.66	-1.95	-9.95
0.4263	26.64	15.93	6.00	-3.22	-11.79
0.5271	27.20	15.67	4.98	-4.94	-14.15
0.6258	28.32	15.59	3.78	-7.18	-17.37
0.7223	26.49	13.86	2.15	-8.70	-18.78
0.8168	24.50	12.13	0.66	-9.97	-19.84
0.9094	25.58	11.71	-1.14	-13.06	-24.13
1.0000	21.13	7.70	-4.74	-16.27	-26.97

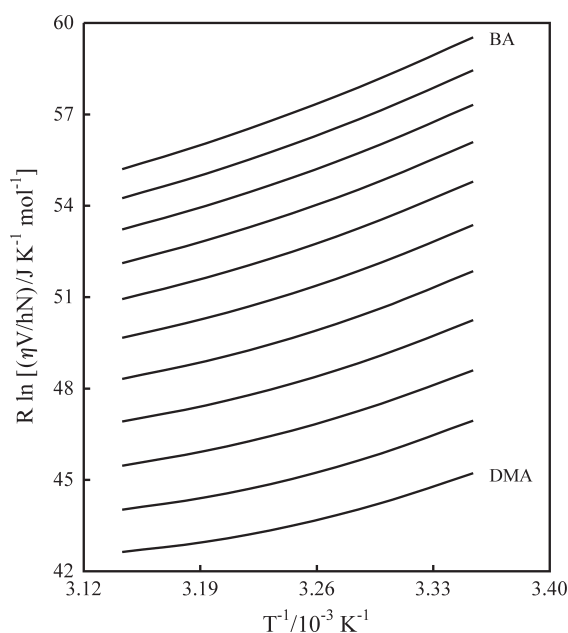


Figure 4 Plots of $R \ln[(\eta V/hN)/J K^{-1} mol^{-1}]$ against $1/T$ for binary mixture at different compositions.

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