

Deviations in viscosity and thermodynamics of viscous flow for binary mixtures of methyl acrylate with 1-alkanols at different temperatures

A K Nain*, P Droliya & J Gupta

Department of Chemistry, Dyal Singh College (University of Delhi), New Delhi 110 003, India

Email: ak_nain@yahoo.co.in

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The viscosities (η) of binary mixtures of methyl acrylate with 1-butanol, 1-hexanol, 1-octanol and 1-decanol, including those of pure liquids, over the entire composition range are reported at different temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K. From the experimental data, the deviations in viscosity ($\Delta\eta$) have been calculated. The $\Delta\eta$ values are found to be negative over the entire composition range for these mixtures, indicating the presence of weak interactions between methyl acrylate and 1-alkanol molecules. The magnitude of negative deviations in $\Delta\eta$ values follows the order: 1-butanol < 1-hexanol < 1-octanol < 1-decanol. It is observed that $\Delta\eta$ values depend upon the length of the alkyl chain in 1-alkanols. Also, the interactions between methyl acrylate and 1-alkanols decrease with increase in alkyl chain length. The thermodynamics of viscous flow has been analyzed by using Eyring and Arrhenius approaches and the results have been compared and discussed in terms of intermolecular interactions between the molecules. Further, the viscosities of these binary mixtures computed theoretically by using various empirical and semi-empirical models correlated well with the experimental findings in terms of average standard deviations.

Keywords: Solution chemistry, Binary mixtures, Viscosity, Methyl acrylate, Alkanols, Molecular interactions, Thermodynamics of viscous flow

The knowledge of physicochemical properties of non-aqueous binary liquid mixtures has relevance in theoretical and applied areas of research, and these data are frequently used in process design (flow, mass transfer, or heat transfer calculations) of many chemical and industrial processes¹⁻¹¹. Viscosity and its derived thermodynamic parameters provide important information regarding the nature and strength of intermolecular interactions in liquid mixtures. Experimental viscosity data of liquid mixtures are helpful in developing and testing various theories and models, which can relate experimental data with theoretical models, which further helps in predicting the data without carrying out the experiment. Methyl acrylate is a very important industrial chemical and is widely used commercially for the production of important high polymeric and latex compounds. It is a polar (dipole moment, $\mu = 1.77$ D at 298.15 K)¹², aprotic and unassociated liquid¹². On the other hand, alkanols are protic, highly associated through hydrogen bonding and this association decreases with increase in alkyl chain length in 1-alkanol¹³. Therefore, the study of intermolecular interactions in methyl acrylate+1-alkanol

mixtures would be interesting owing to their industrial applications¹⁴. To the best of our knowledge, viscometric studies on binary mixtures of methyl acrylate with 1-butanol, 1-hexanol, 1-octanol and 1-decanol at different temperatures are not reported in the literature, except for the work by Sastry *et al.*¹⁵ who reported viscosities of methyl acrylate+1-butanol mixtures at 308.15 and 318.15 K.

In the present paper, we report the viscosities (η) of binary mixtures of methyl acrylate with 1-butanol, or 1-hexanol, or 1-octanol, or 1-decanol, including those of pure liquids at temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K, covering the entire composition range expressed by the mole fraction, x_1 of MA. The density (ρ) data for the calculations have been taken from our earlier study¹⁶. From the experimental data, the deviations in viscosity ($\Delta\eta$) have been calculated. The variations of $\Delta\eta$ with composition and temperature of the mixtures have been discussed in terms of molecular interaction in these mixtures. The effect of alkyl chain length of 1-alkanol molecules on interactions in these mixtures has also been discussed. The thermodynamics of viscous flow has been analyzed by using Eyring and

Arrhenius approaches and the results have been compared and discussed in terms of intermolecular interactions between the molecules. Further, the viscosities of these binary mixtures have been correlated theoretically by using various empirical and semi-empirical models and the results were compared with the experimental findings.

Materials and Methods

Methyl acrylate, 1-butanol, 1-hexanol, 1-octanol and 1-decanol used in the study were AR grade products from S D Fine Chemicals, India and were purified by using the methods described in the literature^{17,18}. The mass fraction purities of these chemicals as determined by gas chromatography were: methyl acrylate >0.995, 1-butanol >0.994, 1-hexanol >0.994, 1-octanol >0.993, and, 1-decanol >0.993. Before use, the chemicals were stored over 0.4 nm molecular sieves for 72 h to remove water content, if any, and were degassed at low pressure. The mixtures were prepared by mass and were kept in special airtight stoppered glass bottles to avoid evaporation. The weighings were done by using an electronic balance (model: GR-202, A&D Co., Japan) with a precision of ± 0.01 mg. The uncertainty in the mole fraction was estimated to be less than $\pm 1 \times 10^{-4}$.

The viscosities of pure liquids and their binary mixtures were measured by using Ubbelohde type suspended level viscometer. The viscometer was calibrated with triply distilled water. The viscometer containing the test liquid was allowed to stand for about 30 min in a thermostatic water bath so that the thermal fluctuations in viscometer were minimized. The time of flow was recorded with a digital stopwatch with an accuracy of ± 0.01 second. The viscosity data were reproducible within $\pm 1 \times 10^{-6}$ N s m⁻².

The temperature of the test liquids during the measurements was maintained within an uncertainty of ± 0.01 K in an electronically controlled thermostatic water bath (model: ME-31A, Julabo, Germany). The reliability of experimental measurements of η was ascertained by comparing the experimental data of pure liquids with the corresponding values available in the literature^{2,18} at 298.15 K. The agreement between the experimental and the literature values is found good in general (Supplementary Data, Table S1).

Results and Discussion

The experimental values of η for the binary mixtures of methyl acrylate with 1-butanol,

1-hexanol, 1-octanol and 1-decanol, with methyl acrylate as a common component, over the entire composition range expressed in mole fraction, x_1 of methyl acrylate at different temperatures are listed in Table 1.

Deviations in viscosity

The values of $\Delta\eta$ were calculated by using the following relationship,

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad \dots(1)$$

where the subscripts 1 and 2 represent the pure components, i.e., methyl acrylate and 1-alkanol, respectively. The $\Delta\eta$ values were fitted to a Redlich-Kister type¹⁹ polynomial equation (Eq. 2).

$$\Delta\eta = x_1(1-x_1) \sum_{i=0}^n A_i(1-2x_1)^i \quad \dots(2)$$

The values of coefficients (A_i) evaluated by using least-squares method with all points weighted equally, and the corresponding standard deviations (σ) are listed in Table S2 (Supplementary Data). The variation of $\Delta\eta$ with composition and temperature, along with smoothed values using Eq. (2) are presented graphically in Fig. 1. Figure 1 indicates that $\Delta\eta$ values are negative for all the four mixtures over the entire mole fraction range and at all investigated temperatures. As stated earlier, the molecules of 1-alkanols are associated through hydrogen bonding in pure state¹³. Mixing of methyl acrylate with 1-alkanols would induce mutual dissociation of the hydrogen-bonded structures present in pure alkanols with subsequent formation of (new) H-bonds (C=O.....HO and O.....HO) between oxygen atoms of methyl acrylate and hydrogen atom of hydroxyl group of 1-alkanol molecules. The observed negative values of $\Delta\eta$ for these methyl acrylate+1-alkanol binary mixtures indicate weak interactions between the component molecules of the mixture^{20,21}. The magnitudes of negative $\Delta\eta$ values (Fig. 1) at equimolar composition of these mixtures follow the order: 1-butanol < 1-hexanol < 1-octanol < 1-decanol, which indicates that the order of the interactions between methyl acrylate and 1-alkanol molecules in these mixtures follows the sequence: 1-butanol > 1-hexanol > 1-octanol > 1-decanol. This is due to the reason that the hydrogen bonding ability of 1-alkanols

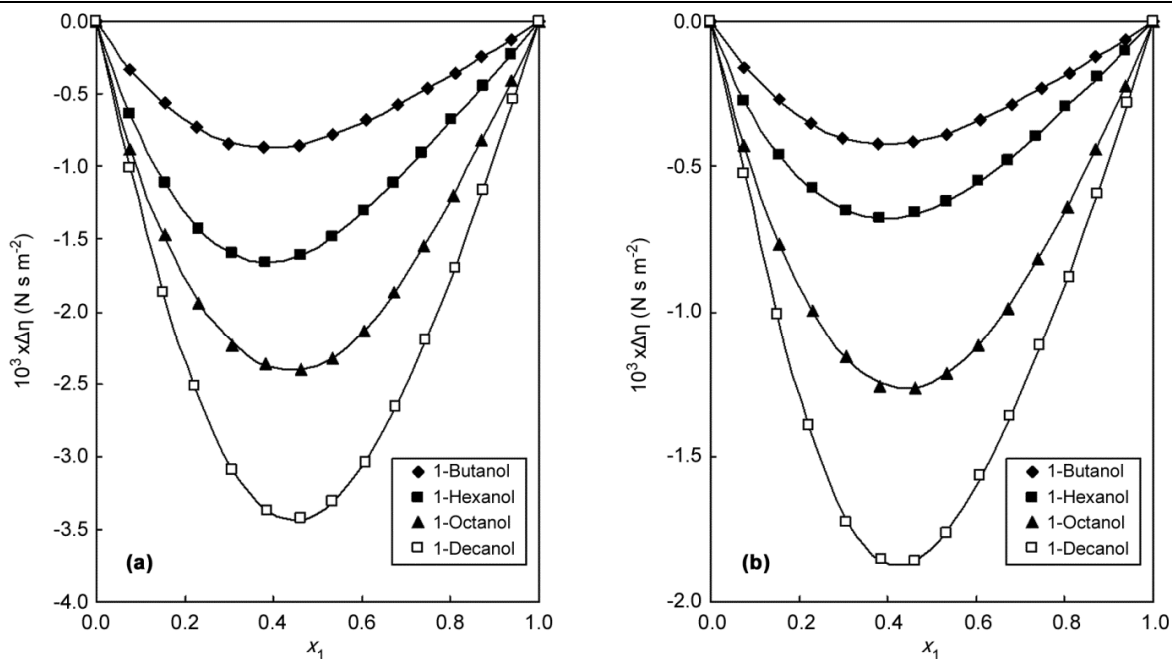
Table 1 — Viscosities (η) as function of mole fraction (x_1) of methyl acrylate for methyl acrylate+1-alkanol mixtures at varying temperatures (288.15–318.15) K

x_1	$10^3 \times \eta$ (N s m ⁻²) at T (K)						
	288.15	293.15	298.15	303.15	308.15	313.15	318.15
<i>Methyl acrylate+1-butanol</i>							
0.0000	3.327	2.938	2.585	2.265	1.989	1.744	1.570
0.0777	2.632	2.350	2.086	1.836	1.628	1.445	1.317
0.1555	2.081	1.883	1.688	1.493	1.335	1.205	1.107
0.2273	1.673	1.525	1.373	1.223	1.106	1.007	0.938
0.2990	1.357	1.233	1.113	1.007	0.925	0.848	0.797
0.3791	1.092	0.983	0.906	0.825	0.774	0.712	0.678
0.4593	0.901	0.822	0.761	0.700	0.663	0.613	0.587
0.5344	0.782	0.721	0.667	0.622	0.588	0.545	0.521
0.6095	0.703	0.657	0.610	0.566	0.532	0.497	0.477
0.6789	0.651	0.612	0.570	0.530	0.498	0.462	0.443
0.7483	0.614	0.578	0.537	0.501	0.465	0.437	0.415
0.8099	0.594	0.553	0.514	0.479	0.445	0.416	0.393
0.8715	0.570	0.530	0.492	0.457	0.420	0.392	0.371
0.9358	0.561	0.509	0.473	0.437	0.406	0.373	0.352
1.0000	0.554	0.501	0.465	0.427	0.392	0.360	0.334
<i>Methyl acrylate+1-hexanol</i>							
0.0000	6.293	5.344	4.588	3.815	3.321	2.856	2.470
0.0770	4.821	4.155	3.632	3.029	2.665	2.322	2.033
0.1542	3.621	3.213	2.834	2.402	2.153	1.906	1.680
0.2299	2.735	2.462	2.214	1.909	1.735	1.565	1.401
0.3057	2.102	1.898	1.731	1.502	1.401	1.281	1.166
0.3834	1.615	1.473	1.351	1.196	1.130	1.048	0.973
0.4612	1.266	1.165	1.082	0.982	0.930	0.876	0.825
0.5340	1.032	0.969	0.900	0.842	0.799	0.751	0.710
0.6068	0.886	0.832	0.782	0.738	0.694	0.658	0.622
0.6720	0.785	0.740	0.701	0.664	0.625	0.588	0.554
0.7370	0.719	0.671	0.639	0.598	0.567	0.532	0.499
0.8046	0.668	0.620	0.588	0.550	0.520	0.485	0.456
0.8722	0.622	0.575	0.541	0.504	0.474	0.440	0.413
0.9361	0.582	0.533	0.496	0.460	0.430	0.398	0.370
1.0000	0.554	0.501	0.465	0.427	0.392	0.360	0.334
<i>Methyl acrylate+1-octanol</i>							
0.0000	10.660	8.782	7.362	6.126	5.256	4.606	4.086
0.0770	8.486	7.023	5.945	4.996	4.321	3.800	3.367
0.1554	6.698	5.635	4.819	4.042	3.506	3.076	2.738
0.2304	5.325	4.512	3.836	3.242	2.823	2.486	2.223
0.3053	4.192	3.570	3.024	2.554	2.242	1.983	1.781
0.3830	3.201	2.731	2.350	1.983	1.735	1.551	1.392
0.4603	2.401	2.051	1.782	1.526	1.356	1.216	1.096
0.5321	1.786	1.551	1.366	1.203	1.066	0.964	0.878
0.6038	1.323	1.184	1.065	0.948	0.843	0.771	0.705

(Contd.)

Table 1 — Viscosities (η) as function of mole fraction (x_1) of methyl acrylate for methyl acrylate+1-alkanol mixtures at varying temperatures (288.15–318.15) K (Contd.)

x_1	$10^3 \times \eta$ (N s m ⁻²) at T (K)						
<i>Methyl acrylate+1-octanol (contd.)</i>							
	288.15	293.15	298.15	303.15	308.15	313.15	318.15
0.6724	1.019	0.943	0.856	0.766	0.688	0.630	0.573
0.7410	0.836	0.777	0.702	0.636	0.578	0.531	0.486
0.8052	0.723	0.661	0.606	0.556	0.507	0.461	0.426
0.8698	0.655	0.605	0.555	0.507	0.461	0.426	0.392
0.9350	0.585	0.540	0.500	0.451	0.417	0.383	0.354
1.0000	0.554	0.501	0.465	0.427	0.392	0.360	0.334
<i>Methyl acrylate+1-decanol</i>							
0.0000	16.371	13.653	11.254	9.240	7.642	6.396	5.370
0.0762	13.556	11.405	9.423	7.726	6.373	5.331	4.465
0.1523	11.106	9.326	7.741	6.344	5.203	4.328	3.596
0.2225	9.168	7.668	6.332	5.182	4.222	3.465	2.856
0.3073	7.202	5.905	4.843	3.953	3.172	2.586	2.096
0.3848	5.636	4.575	3.725	3.002	2.405	1.932	1.576
0.4622	4.353	3.521	2.836	2.276	1.841	1.472	1.182
0.5356	3.276	2.683	2.166	1.752	1.403	1.125	0.906
0.6092	2.522	2.023	1.645	1.334	1.081	0.893	0.729
0.6768	1.908	1.585	1.292	1.055	0.875	0.716	0.598
0.7443	1.484	1.233	1.022	0.852	0.708	0.594	0.502
0.8089	1.135	0.972	0.823	0.694	0.588	0.502	0.427
0.8736	0.886	0.774	0.671	0.583	0.502	0.432	0.375
0.9412	0.694	0.620	0.557	0.495	0.442	0.393	0.352
1.0000	0.554	0.501	0.465	0.427	0.392	0.360	0.334

Fig. 1 — Variation of deviations in viscosity ($\Delta\eta$) against mole fraction (x_1) of methyl acrylate for methyl acrylate+1-alkanol binary mixtures at (a) $T = 298.15$ K, and, (b) $T = 318.15$ K. The points show experimental values and curves show smoothed values using Eq. (2).

decrease with increases in alkyl chain length, hence MA-alkanol interactions decrease with increase in alkyl chain length of alkanol molecules. This is in agreement with the results obtained from the variations of excess molar volumes in our earlier study¹⁶.

Thermodynamic parameters of viscous flow

Further, the thermodynamic parameters of viscous flow have been investigated by using the Eyring viscosity relation^{8,22,23},

$$\eta = \left(\frac{hN}{V} \right) \exp \left(\frac{\Delta G^*}{RT} \right) \quad \dots(3)$$

where h is Planck's constant, N is Avogadro number and ΔG^* is the free energy of activation of viscous flow. Eq. (3) on combining with $\Delta G^* = \Delta H^* - T\Delta S^*$ gives Eq. (4),

$$R \ln \left(\frac{\eta V}{hN} \right) = \left(\frac{\Delta H^*}{T} \right) - \Delta S^* \quad \dots(4)$$

where ΔH^* and ΔS^* are the enthalpy and entropy of activation of viscous flow, respectively. The plots of the left-hand side of Eq. (4), i.e., $R \ln(\eta V/hN)$ versus $1/T$ for all the four binary systems were found to be almost linear for each composition. This indicates that ΔH^* is independent of temperature in the investigated temperature range. The values of ΔH^* and ΔS^* were obtained by using linear regression of $R \ln(\eta V/hN)$ versus $1/T$ at each composition. The values of ΔG^* , ΔH^* , and ΔS^* along with the linear regression coefficient (r^2) are shown in Figs 2-4 (see also Supplementary Data, Table S3).

From Table S3 and Fig. 2, it is observed that the values of Gibbs free energy of activation, ΔG^* are positive and decrease with increase in the concentration of MA for all the systems investigated at 298.15 K. The present activation energy values are consistent with values provided by Anderton *et al.*²⁴ within the permissible limits of error. According to Reed²⁵, Meyer²⁶ and Oswal²⁷, positive values of ΔG^* are observed in binary mixtures where specific interactions such as H-bonding, dipole-dipole, etc., are prevalent among the participating molecules while negative values of ΔG^* are indication of dispersion forces. ΔG^* is the minimum energy required by 1-alkanol molecules to penetrate into the layers of

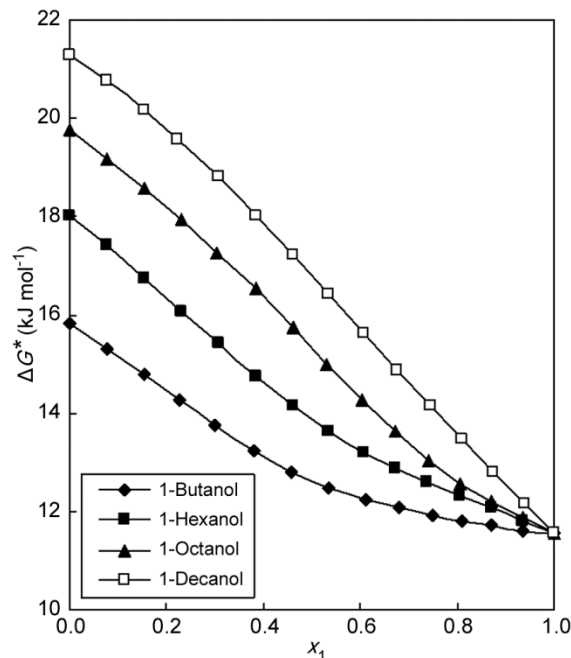


Fig. 2 — Variation of free energy of activation of viscous flow (ΔG^*) against mole fraction (x_1) of methyl acrylate for the binary mixtures at $T = 298.15$ K.

MA. 1-alkanols are bound together by stronger H-bonding as opposed to dipole-dipole interactions that hold the acrylate molecules together. Therefore, formation of activated species, necessary for viscous flow, is easier in MA-rich region in comparison to 1-alkanol-rich region. The variation in ΔG^* values is found to be: 1-butanol < 1-hexanol < 1-octanol < 1-decanol over the entire composition range. This variation is attributed to increased steric hindrance caused by the increase in chain length of 1-alkanols. The sterically hindered 1-alkanol molecules may not be able to approach MA molecules easily. More energy shall be required for 1-decanol molecules to approach MA molecules as compared to 1-butanol. Furthermore, H-bonding formed between 1-alkanol molecules and MA molecules weakens as the chain length increases. This suggests that higher value of ΔG^* is required to activate 1-decanol molecules as compared to 1-butanol molecules.

From Figs 3 and 4 and Table S3, it is observed that for MA+1-alkanol mixtures, the values of ΔH^* and ΔS^* depends sharply on mole fraction, x_1 , of MA molecules. In the case of MA+1-decanol/1-octanol, there appears a maximum at around $x_1 = 0.5$, which indicates that total intermolecular interactions, including interactions between like and unlike molecules, becomes largest in terms of enthalpy and

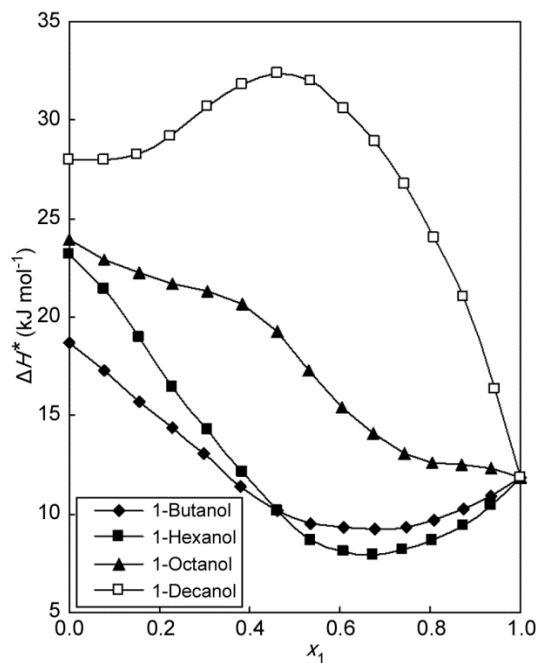


Fig. 3 — Variation of enthalpy of activation of viscous flow (ΔH^*) against mole fraction (x_1) of methyl acrylate for the binary mixtures at $T = 298.15$ K.

entropy of activation around this mole fraction, while in the case of MA+1-hexanol/1-butanol, weaker interactions are present between the molecules. This suggests that the formation of an activated species that is necessary for viscous flow is easier in near equimolar compositions as compared to MA/alkanol-rich region in the case of MA+1-decanol/1-octanol.

In MA+1-decanol mixture, ΔH^* and ΔS^* have large positive values in 1-decanol-rich region as compared to other 1-alkanols. This is clearly attributed to hydrophobic hydration, i.e., the structural enhancement of the hydrogen bond network. When MA molecules are added to 1-decanol molecules, the hydrogen bond network of 1-decanol molecules is highly stabilized around MA molecules. In other words, arrangement of 1-decanol molecules becomes much more ordered in the presence of MA molecules than that in pure 1-decanol.

For MA+1-decanol/1-octanol mixtures, the values of ΔS^* are found positive (Fig. 4 and Table S3). ΔS^* values increase to a maximum and then decrease as x_1 of MA increases, in the mixture. The increase in ΔS^* values for MA+1-decanol/1-octanol mixtures with increase in MA concentration indicates that, during the viscous flow, there is more orderedness in MA/alkanol-rich regions as compared to that in near equimolar region where ΔS^* values are large. In the

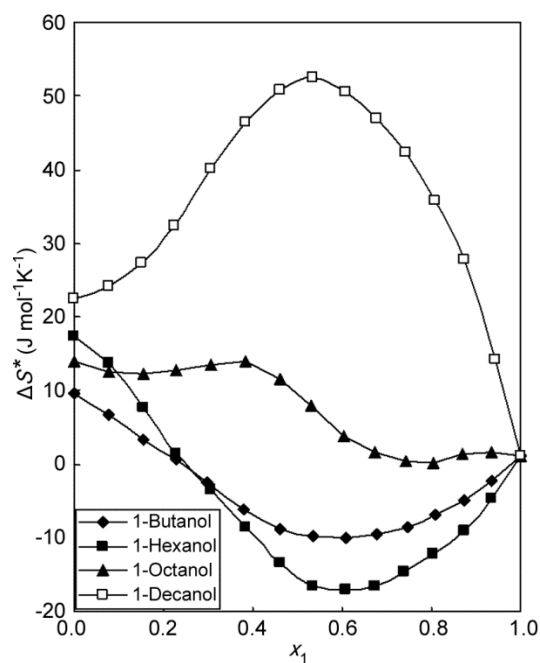


Fig. 4 — Variation of entropy of activation of viscous flow (ΔS^*) against mole fraction (x_1) of methyl acrylate for the binary mixtures at $T = 298.15$ K.

case of MA+1-hexanol/1-butanol mixtures, the ΔS^* values change sign from positive to negative and then exhibit a minima as the concentration of MA in the mixture increases. The decrease in ΔS^* values for MA+1-hexanol/1-butanol mixtures with increase in MA concentration indicates that, during the viscous flow, there is more structuredness in near equimolar region where ΔS^* values are large as compared to those in MA/alkanol-rich regions. Similar trends for ΔH^* and ΔS^* values have also been observed for ethanol-water binary systems²⁸ by Takaki.

Arrhenius activation energy approach

The Arrhenius activation energy (E_a) has been calculated from viscosity data by using the Andrade relationship²⁹ (Eq. 5),

$$\eta = A_s \exp\left(\frac{E_a}{RT}\right) \quad \dots(5)$$

where A_s is the Arrhenius entropic factor corresponding theoretically to the viscosity at infinite temperature. Taking logarithm of both sides, Eq. (5) can be rewritten as Eq. (6).

$$\ln \eta = \ln A_s + \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \quad \dots(6)$$

The plots of $\ln \eta$ versus $1/T$ for all the binary systems were found to be almost linear for each composition. This indicates that E_a is independent of temperature in the investigated temperature range. The values of E_a/R and A_s were obtained as slopes and intercepts, by using linear regression of $\ln \eta$ versus $1/T$ at each composition. The values of E_a and A_s along with linear regression coefficient, r^2 are included in Table S4 (Supplementary Data) and the values of E_a as function of x_1 are shown graphically in Fig. 5.

Figure 5 shows that for MA+1-alkanol mixtures, the values of Arrhenius activation energy are affected by the change in mole fraction, x_1 of MA molecules (see also Table S4). In the case of MA+1-decanol/1-octanol, there appears a maximum at around $x_1 = 0.5$ which indicates that it is easier to form an activated species near equimolar region than in MA/alkanols-rich region, while in case of MA+1-hexanol/1-butanol, there appears a minimum near equimolar concentration region, which signifies the difficulty in formation of activated species in that region.

Partial molar activation energy

The Arrhenius activation energy (E_a) and the enthalpy of activation of viscous flow (ΔH^*) indicate quasi-equality^{29,30} (as mentioned in the earlier section and Tables S3 and S4), therefore, we can consider E_a as a thermodynamic property and the partial molar activation energies, $E_{a,1}$ and $E_{a,2}$ for methyl acrylate

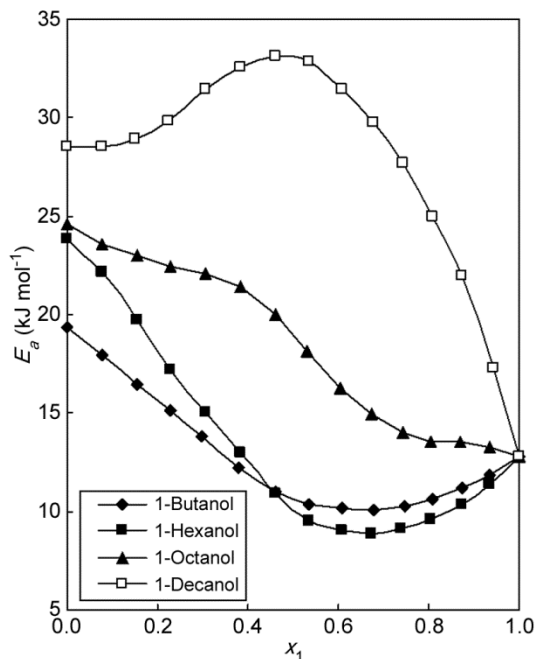


Fig. 5 — Variation of activation energy (E_a) against mole fraction (x_1) of methyl acrylate for the binary mixtures at $T = 298.15$ K.

and alkanol in the mixtures, can be expressed by the following relationships²⁴

$$E_{a,1} = E_a + x_2 \left(\frac{\partial E_a}{\partial x_1} \right) \quad \dots (7)$$

$$E_{a,2} = E_a - x_1 \left(\frac{\partial E_a}{\partial x_1} \right) \quad \dots (8)$$

where $E_{a,1}$ and $E_{a,2}$ are the partial molar activation energies for methyl acrylate and alkanols, respectively.

The values of $E_{a,1}$ and $E_{a,2}$ follows the order 1-decanol > 1-octanol > 1-butanol > 1-hexanol (Figs S1 and S2, Supplementary Data). The low value in MA+1-hexanol mixture suggests that the transition state is highly organized and solvation of the transition state by polar alkanol molecules may also be involved. The increase in partial molar activation energies ($E_{a,1}$) as 1-decanol/1-octanol concentration increases and ($E_{a,2}$) as 1-decanol concentration increases is probably an indication that more and more hydrogen bonds are to be ruptured before the activated complex can be formed. It may also be inferred that a decreasing amount of solvent rearrangement takes place as the activated complex is formed. In other words, reactants are already well solvated with alkanols molecules and formation of activated species necessary for viscous flow, requires mainly rearrangement of the solvent, and not the addition of new molecules. Similar trends for partial molar activation energies have been obtained by Lovering and Laidler³¹ while studying alcohol-isocyanate reactions.

Correlating models for viscosity

Several empirical and semi-empirical models, viz., one-parameter models by Grunberg and Nissan³², Hind, McLaughlin and Ubbelohde³³, and Katti and Chaudhri³⁴; two-parameter models by Heric and Brewer^{35,36} and McAllister³⁷ (3-body interactions); and three-parameter models by Heric and Brewer^{35,36}, McAllister³⁸ (4-body interactions) and Auslander³⁹, have been used to calculate the viscosities of the mixtures theoretically from data of the pure components. The values of the parameters of these models, evaluated by the least-squares method, and those of their standard percentage deviations σ (%) obtained from the experimental viscosity data, as described by Heric and Brewer³⁵, are given in Table 2.

The analysis of the results for one-parameter models reveals that σ (%) values (Table 2) are in the range 0.0334 to 0.1232% for MA+1-butanol, 0.0673

to 0.2341% for MA+1-hexanol, 0.113 to 0.3311% for MA+1-octanol and 0.1063 to 0.5557% for MA+1-decanol binary mixtures. These results indicate that all the one-parameter models predict the viscosity data satisfactorily, with Hind, McLaughlin and Ubbelohde model showing maximum σ (%) values, followed by nearly equal σ (%) values for other models for each of the binary system.

For two-parameter relations, the σ (%) values (Table 2) are in the range of 0.0296–0.0297% for MA+1-butanol, 0.0292–0.0292% for MA+1-hexanol, 0.037–0.037% for MA+1-octanol and 0.0963–0.0964% for MA+1-decanol binary mixtures, indicating that all

the two-parameter models predict the viscosity data well, with Lobe relation showing minimum values of σ (%), whereas Heric-Brewer and McAllister models, exhibit equal values of σ (%) for each system.

For three-parameter relations, the σ (%) values (Table 2) are in the range 0.0101–0.042% for MA+1-butanol, 0.0122–0.0157% for MA+1-hexanol, 0.0108–0.011% for MA+1-octanol and 0.0236–0.0467% for MA+1-decanol mixtures. The analysis of the results indicates that McAllister (four-body interaction) and Heric-Brewer (three-parameter) models predict the viscosity data better than Auslander model for both the binary mixtures

Table 2 — Values of parameters calculated from various one-, two-, and three-parameter models of viscosity, along with the standard deviations (σ) of fit and average percentage deviations (APD) between theoretical and experimental η values for the binary mixture at $T = 298.15$ K

Model	Parameters			σ	APD
<i>Methyl acrylate+1-butanol</i>					
Grunberg-Nissan	$G_{12} = -1.5262$			0.0348	2.540
Hind <i>et al.</i>	$H_{12} = -0.0995$			0.1232	14.81
Katti-Chaudhri	$W_{vis}/RT = -1.5296$			0.0334	2.543
Heric-Brewer (2-parameter)	$\alpha_{12} = -1.6350$	$\alpha_{21} = -0.4027$		0.0297	3.015
McAllister (3-body int.)	$Z_{12} = 0.4216$	$Z_{21} = 1.1354$		0.0296	3.028
Heric-Brewer (3-parameter)	$a = -1.7350$	$b = -0.1121$	$c = 0.8253$	0.0101	0.840
Auslander	$A_{21} = 0.8536$	$B_{12} = 5.9989$	$B_{21} = -0.1908$	0.0420	1.881
<i>Methyl acrylate+1-hexanol</i>					
Grunberg-Nissan	$G_{12} = -1.3104$			0.0703	5.021
Hind <i>et al.</i>	$H_{12} = -0.5798$			0.2341	76.03
Katti-Chaudhri	$W_{vis}/RT = -1.2111$			0.0673	5.294
Heric-Brewer (2-parameter)	$\alpha_{12} = -1.4842$	$\alpha_{21} = -0.7437$		0.0292	2.597
McAllister (3-body int.)	$Z_{12} = 0.5916$	$Z_{21} = 1.9384$		0.0292	5.597
Heric-Brewer (3-parameter)	$a = -1.5273$	$b = -0.4654$	$c = 0.5822$	0.0122	0.546
Auslander	$A_{21} = 0.1332$	$B_{12} = 0.4239$	$B_{21} = 0.5337$	0.0157	1.063
<i>Methyl acrylate+1-octanol</i>					
Grunberg-Nissan	$G_{12} = -0.7631$			0.1202	10.12
Hind <i>et al.</i>	$H_{12} = -1.1424$			0.3311	98.24
Katti-Chaudhri	$W_{vis}/RT = -0.5425$			0.1130	10.26
Heric-Brewer (2-parameter)	$\alpha_{12} = -0.9027$	$\alpha_{21} = -0.8552$		0.0370	2.325
McAllister (3-body int.)	$Z_{12} = 0.9662$	$Z_{21} = 3.2879$		0.0370	2.325
Heric-Brewer (3-parameter)	$a = -0.8859$	$b = -1.1784$	$c = -0.5713$	0.0109	0.698
Auslander	$A_{21} = 0.3067$	$B_{12} = 1.0388$	$B_{21} = 0.0543$	0.0110	0.769
<i>Methyl acrylate+1-decanol</i>					
Grunberg-Nissan	$G_{12} = -0.3226$			0.1191	8.230
Hind <i>et al.</i>	$H_{12} = -1.9646$			0.5557	112.58
Katti-Chaudhri	$W_{vis}/RT = -0.0131$			0.1063	7.756
Heric-Brewer (2-parameter)	$\alpha_{12} = -0.1985$	$\alpha_{21} = -0.4019$		0.0964	4.424
McAllister (3-body int.)	$Z_{12} = 1.9078$	$Z_{21} = 4.6315$		0.0963	2.971
Heric-Brewer (3-parameter)	$a = -0.1821$	$b = -1.0784$	$c = -1.1097$	0.0236	1.635
Auslander	$A_{21} = 0.4159$	$B_{12} = 1.5141$	$B_{21} = 0.0155$	0.0467	2.635

investigated. Also, all the viscosity models predict the viscosity data better for these mixtures.

The values of σ (%) for these binary systems under study (Table 2) indicate that for each system three-parameter models predict the data best, followed by two-parameter models and then by one-parameter models. Therefore, it may be concluded that the predicting ability of these correlating relations increases as the number of adjustable parameters in the relation increases.

Conclusions

The viscosities of methyl acrylate+1-butanol, or +1-hexanol, or +1-octanol, or 1-decanol binary mixtures have been measured over the entire composition range at different temperatures and the values of $\Delta\eta$ were calculated. The results indicate the presence of weak interactions in these mixtures and the order of the interactions between methyl acrylate and 1-alkanol molecules follows the sequence: 1-butanol > 1-hexanol > 1-octanol > 1-decanol, i.e., interactions decrease with increase in alkyl chain length in 1-alkanol molecules. The thermodynamics of viscous flow has also been discussed. The viscosity data of these binary mixtures were correlated theoretically by using various empirical and semi-empirical models and it has been observed that all the models correlate the data well for all the four systems, and the predicting ability of these correlating relations increases as the number of adjustable parameters in the relation increases.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_57A\(06\)761-769_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_57A(06)761-769_SupplData.pdf).

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