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# Theoretical evaluation of various thermodynamic properties of acrylates with a higher straight chain alkanol at 298.15 K

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## ABSTRACT

New experimental thermodynamic data involving density and viscosity of binary liquid mixtures of methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate with dodecane-1-ol at temperature 298.15 K and at atmospheric pressure have been measured. These experimental values were correlated by Jouyban-Acree model. These basic parameters further used to evaluate excess molar volume and deviation in viscosity and were fitted to Redlich-Kister polynomial equation. Mixture viscosities were correlated by Hind, Choudhary-Katti, Grunberg-Nissan, Tamura and Kurata, Heric-Brewer two body model, McAllister's three and four body model equations. The calculated values of excess molar volumes were found to be positive and deviations in viscosity were found to be negative for all binary liquid mixtures.

**Keywords** Binary Mixtures; Dodecane-1-ol; Excess Molar Volume; Viscosity Deviation; Heric-Brewer; Choudhary-Katti.

## INTRODUCTION

Equilibrium properties of a liquid mixture are strongly dependent on its local structure, often expressed as packing density, free volume or more exactly in terms of radial distribution functions. This local structure depends on forces between molecules and volumes of molecules; in general, it will change with composition. This change in turn will be reflected in thermodynamic properties of mixtures. Contributions of this nature have either been ignored altogether, or correction to a state of null volume change on mixing has been adopted as a means of compensating for the effects referred. It will be apparent, however that, adjustment of one thermodynamic quantity (e. g. volume in this manner) will not in general, affect a simultaneous correction of others (e. g. free energy of that part of it relating to local structure) to their linearly interpolated values. The choice of volume as property to be considered is arbitrary and there is assurance that nullity of volume change obviates consideration of other characteristic properties of liquid. [1]

Knowledge of thermodynamic and physical properties of liquid-liquid systems is of considerable importance due to their wide range of applicability as solvent media in various physicochemical studies, in processing and product formation in many industrial applications. Measurements of some of bulk properties like density, viscosity, etc. of liquids provide an insight into investigation of intermolecular arrangement of liquids and help to understand thermodynamic and acoustic properties of liquid mixtures.

To best of our knowledge, no literature data are available for excess molar volumes and viscosity deviation of binary liquid mixtures of dodecane-1-ol with methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate at 298.15 K. In view of these considerations, it was planned to study liquid-liquid binary systems containing polar and or hydrogen bonded or nonpolar liquids in association with industrially as well as biologically important solvent at various temperatures over entire range of compositions.

### MATERIALS AND METHODS

Chemicals used in present study were of analytical grade and supplied by S. D. Fine Chemicals Pvt., Mumbai (India) with quoted mass fraction purities: methyl acrylate, MA, (> 0.997), ethyl acrylate, EA, (> 0.998), butyl acrylate, BA, (> 0.995), methyl methacrylate, MMA, (> 0.997) and dodecane-1-ol (> 0.998). Prior to use all liquids were stored over 0.4 nm molecular sieves to reduce water content and were degassed. All four acrylic esters were distilled before use. Binary mixtures of varying composition were prepared by mass in special air-tight bottles. The solutions of each composition were prepared fresh and all properties were measured on the same day. The masses were recorded on a Mettler one pan balance, which can read up to fifth place of decimal, with an accuracy of  $\pm 0.01$  mg. Care was taken to avoid evaporation and contamination during mixing. Estimated uncertainty in mole fraction was  $< 1 \times 10^{-4}$ .

#### Experimental Part

Densities of solutions were measured using a single capillary pycnometer made up of borosil glass with a bulb of 8 cm<sup>3</sup> and capillary with internal diameter of 0.1 cm. An average of triplicate measurement was taken in to account. The reproducibility of density measurement was  $\pm 5 \times 10^{-5}$  g/cm<sup>3</sup>.

Dynamic viscosities were measured using an Ubbelohde suspended level viscometer, calibrated with conductivity water. An electronic digital stop watch with readability of  $\pm 0.01$  s was used for flow time measurements. At least three repetitions of each data reproducible to  $\pm 0.05$  s were obtained and results were averaged. The uncertainties in dynamic viscosities were of order of  $\pm 0.003$  mPa.s.

A comparison of measured values of pure components with literature values as presented in Table 1 shows a good agreement.

Table 1. Densities ( $\rho$ ) and Viscosities ( $\eta$ ) for Pure Components at T= 298.15 K.

Component	$\rho / (\text{g.m}^{-3})$		$\eta / (\text{mPa.s})$	
	Expt.	Lit.	Expt.	Lit.
Dodecane-1-ol	0.82989	0.82810 [2]	16.134	16.135 [2]
Methyl Acrylate	0.94751	0.94750 [2]	0.449	0.449 [2]
Ethyl Acrylate	0.91632	0.91630 [2]	0.518	0.517 [2]
Butyl Acrylate	0.89399	0.89410 [2]	0.787	0.786 [2]
Methyl Methacrylate	0.93765	0.93760 [3]	0.584	0.584 [3]

#### Computational Part

Twenty one density and viscosity measurements were performed for each binary liquid system namely methyl acrylate (1) + dodecane-1-ol (2), ethyl acrylate (1) + dodecane-1-ol (2), butyl acrylate (1) + dodecane-1-ol (2) and methyl methacrylate(1) + dodecane-1-ol (2) over entire mole fraction range ( $0 < x < 1$ ), at temperature 298.15 K and at atmospheric pressure.

Excess molar volumes ( $V^E$ ) of solutions of molar compositions  $x$  were calculated from densities of pure liquids and their mixtures according to following equation,

$$V^E / \text{cm}^3 \cdot \text{mol}^{-1} = [x_1 M_1 + x_2 M_2] / \rho_{12} - [(x_1 M_1 / \rho_1) + (x_2 M_2 / \rho_2)] \quad (1)$$

where  $\rho_{12}$  is density of mixture and  $x_1$ ,  $M_1$ ,  $\rho_1$ , and  $x_2$ ,  $M_2$ ,  $\rho_2$  are mole fraction, molecular weight and density of pure components 1 and 2, respectively. First term on right hand side of above Eq (1) represents actual molar volume ( $V$ ) of solution and second represents molar volume it would occupy if mixture behaved ideally. In general, while these two molar volumes are similar in size (usually larger than 100 cm<sup>3</sup> mol<sup>-1</sup>) their difference is usually smaller by two to three orders of magnitude and thus may carry a significantly larger error.

Table 2. Densities ( $\rho$ ), Excess Molar Volumes ( $V^E$ ), Viscosities ( $\eta$ ) and Viscosity Deviation ( $\Delta\eta$ ) for Acrylates (1) + Dodecane-1-ol (2) at T = 298.15 K

$X_1$	$\rho$ (g.cm <sup>-3</sup> )	$V^E$ (cm <sup>3</sup> .mol <sup>-1</sup> )	$\eta$ (mPa.s)	$\Delta\eta$ (mPa.s)
Methyl Acrylate (1) + Dodecane-1-ol (2)				
0	0.82989	0.000	16.134	0.000
0.05544	0.83183	0.205	13.228	-2.036
0.09995	0.83382	0.285	11.279	-3.288
0.15550	0.83643	0.394	9.244	-4.451
0.19976	0.83869	0.469	7.888	-5.112
0.25541	0.84181	0.547	6.463	-5.665
0.29988	0.84453	0.598	5.511	-5.919
0.35538	0.84824	0.647	4.517	-6.042
0.39990	0.85152	0.674	3.852	-6.010
0.45531	0.85599	0.693	3.158	-5.834
0.49999	0.85998	0.695	2.691	-5.601
0.55567	0.86547	0.685	2.205	-5.214
0.59987	0.87029	0.665	1.882	-4.843
0.65457	0.87694	0.624	1.547	-4.320
0.69986	0.88309	0.579	1.315	-3.841
0.75530	0.89154	0.509	1.078	-3.209
0.79994	0.89922	0.440	0.919	-2.668
0.85545	0.91006	0.339	0.753	-1.963
0.89993	0.91998	0.246	0.642	-1.376
0.95549	0.93423	0.118	0.526	-0.621
1	0.94751	0.000	0.449	0.000
Ethyl Acrylate (1) + Dodecane-1-ol (2)				
0	0.82989	0.000	16.134	0.000
0.05549	0.83182	0.124	13.331	-1.936
0.09977	0.83348	0.214	11.448	-3.128
0.15546	0.83573	0.312	9.453	-4.254
0.19967	0.83767	0.379	8.119	-4.897
0.25538	0.84031	0.451	6.704	-5.442
0.29976	0.84259	0.497	5.755	-5.698
0.35548	0.84568	0.543	4.751	-5.632
0.39984	0.84835	0.568	4.079	-5.811
0.45539	0.85199	0.586	3.370	-5.653
0.49988	0.85513	0.593	2.892	-5.436
0.55537	0.85944	0.583	2.389	-5.072
0.59993	0.86321	0.566	2.050	-4.716
0.65503	0.86830	0.531	1.696	-4.209
0.69993	0.87285	0.493	1.453	-3.751
0.75543	0.87903	0.432	1.201	-3.136
0.79996	0.88450	0.372	1.030	-2.612
0.85548	0.89203	0.285	0.851	-1.924
0.89997	0.89873	0.204	0.730	-1.350
0.95548	0.90816	0.076	0.603	-0.610
1	0.90632	0.000	0.518	0.000
Butyl Acrylate (1) + Dodecane-1-ol (2)				
0	0.82989	0.000	16.134	0.000
0.05543	0.83186	0.090	13.646	-1.637
0.09973	0.83351	0.159	11.937	-2.666
0.15548	0.83572	0.232	10.087	-3.661
0.19984	0.83756	0.284	8.822	-4.245
0.25553	0.84002	0.338	7.456	-4.757
0.29992	0.84208	0.374	6.520	-5.011
0.35545	0.84482	0.408	5.513	-5.166
0.39979	0.84713	0.428	4.822	-5.176
0.45546	0.85020	0.443	4.076	-5.068
0.49987	0.85280	0.445	3.564	-4.899
0.55545	0.85622	0.443	3.013	-4.596
0.59999	0.85914	0.431	2.634	-4.292
0.65544	0.86300	0.407	2.228	-3.847
0.69990	0.86628	0.380	1.948	-3.445
0.75530	0.87062	0.337	1.647	-2.895
0.79998	0.87435	0.293	1.439	-2.417
0.85546	0.87927	0.230	1.217	-1.788
0.89990	0.88348	0.172	1.064	-1.259
0.95551	0.88900	0.105	0.900	-0.570

1	0.89399	0.000	0.787	0.000
Methyl Methacrylate (1) + Dodecane-1-ol (2)				
0	0.82989	0.000	16.134	0.000
0.05549	0.83239	0.111	13.420	-1.851
0.09977	0.83442	0.221	11.586	-2.997
0.15546	0.83723	0.328	9.631	-4.086
0.19967	0.83964	0.402	8.316	-4.713
0.25538	0.84292	0.481	6.912	-5.251
0.29976	0.84574	0.532	5.966	-5.507
0.35548	0.84957	0.582	4.958	-5.648
0.39984	0.85288	0.611	4.279	-5.637
0.45539	0.85738	0.632	3.559	-5.494
0.49988	0.86128	0.640	3.070	-5.291
0.55537	0.86662	0.630	2.554	-4.944
0.59993	0.87128	0.613	2.203	-4.602
0.65503	0.87759	0.577	1.835	-4.114
0.69993	0.88322	0.537	1.581	-3.670
0.75543	0.89089	0.474	1.315	-3.072
0.79996	0.89769	0.410	1.134	-2.561
0.85548	0.90707	0.318	0.943	-1.888
0.89997	0.91544	0.232	0.814	-1.326
0.95548	0.92711	0.112	0.677	-0.600
1	0.93765	0.000	0.584	0.000

Viscosity deviations ( $\Delta\eta$ ) were calculated using equation,

$$\Delta\eta / \text{mPa.s} = \eta_{12} - x_1\eta_1 - x_2\eta_2 \quad (2)$$

where  $\eta_{12}$  is viscosity of mixture and  $x_1$ ,  $x_2$  and  $\eta_1$ ,  $\eta_2$  are mole fraction and viscosity of pure components 1 and 2 respectively [4]. Other required values were taken from literature [5, 6].

Experimental values of densities ( $\rho$ ), excess molar volume ( $V^E$ ), viscosities ( $\eta$ ) and deviation in viscosity ( $\Delta\eta$ ) of these mixtures at 298.15 K are listed in Table 2.

Excess molar volumes ( $V^E$ ) and deviations in viscosity ( $\Delta\eta$ ) were fitted to Redlich- Kister equation of type,

$$Y = x_1x_2 \sum_i^n a_i (x_1 - x_2)^i \quad (3)$$

Where Y is either  $V^E$  or  $\Delta\eta$  and n is degree of polynomial. Coefficient  $a_i$  was obtained by fitting Eq 3 to experimental results using a least-squares regression method. In each case, optimum number of coefficients is ascertained from an examination of variation in standard deviation ( $\sigma$ ).

$\sigma$  was calculated using relation,

$$\sigma(Y) = \left[ \frac{\sum (Y_{\text{exp}t} - Y_{\text{calc}})^2}{N - n} \right]^{1/2} \quad (4)$$

Where N is number of data points and n is number of coefficients [5]. Calculated values of coefficients  $a_i$  along with standard deviations ( $\sigma$ ) are given in Table 3.

Several relations have been proposed to evaluate dynamic viscosity ( $\eta$ ) of liquid mixtures and these are classified according to number of adjustable parameters used to account for deviation from some average. An attempt has been made to check suitability of equation for experimental data fits by taking into account number of empirical adjustable coefficients. The equations of Hind, Choudhary-Katti, Grunberg-Nissan, Tamura and Kurata have one adjustable parameter.

Hind [7] proposed following equation,

$$\eta_{12} = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1x_2H_{12} \quad (5)$$

where  $H_{12}$  is interaction parameter.

**Table 3. Adjustable parameters of Eq 3 and 4 for Excess Functions for Acrylates (1) +Dodecane-1-ol (2) at T= 298.15 K**

Property	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$\sigma$
Methyl Acrylate (1) + Dodecane-1-ol (2)						
$V^E / (\text{cm}^3 \text{mol}^{-1})$	2.8143	0.1305	-0.4514	-0.8543	1.3059	0.01092
$\Delta\eta / (\text{mPa.s})$	-22.4022	12.0655	-5.1136	1.9108	-0.5814	0.00108
Ethyl Acrylate (1) + Dodecane-1-ol (2)						
$V^E / (\text{cm}^3 \text{mol}^{-1})$	2.3420	0.0938	0.3559	-0.3923	-0.7685	0.00679
$\Delta\eta / (\text{mPa.s})$	-21.7425	11.3331	-4.6383	1.6517	-0.4782	0.00058
Butyl Acrylate (1) + Dodecane-1-ol (2)						
$V^E / (\text{cm}^3 \text{mol}^{-1})$	1.8111	-0.1189	-0.3761	0.5041	0.8356	0.00821
$\Delta\eta / (\text{mPa.s})$	-19.5912	9.1591	-3.3313	1.0412	-0.2663	0.00060
Methyl Methacrylate (1) + Dodecane-1-ol (2)						
$V^E / (\text{cm}^3 \text{mol}^{-1})$	2.5398	-0.0813	0.1820	0.3693	-0.4346	0.00492
$\Delta\eta / (\text{mPa.s})$	-21.1597	10.7107	-4.2485	1.4638	-0.3933	0.00069

Choudhary-Katti [8] proposed following equation,

$$\ln(\eta_n V_m) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1 x_2 [W_{vis}/(RT)] \quad (6)$$

where  $W_{vis}$  is interaction energy for activation of viscous flow.

Grunberg-Nissan provided following empirical equation containing one adjustable parameter. The expression is,

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad (7)$$

where  $G_{12}$  is a parameter proportional to interchange energy.

Tamura and Kurata developed expression for viscosity of binary mixtures as,

$$\eta = x_1 \phi_1 \eta_1 + x_2 \phi_2 \eta_2 + 2(x_1 x_2 \phi_1 \phi_2)^{1/2} T_{12} \quad (8)$$

where  $T_{12}$  is interaction parameter,  $\phi_1$  and  $\phi_2$  are volume fractions.

These are presented with their standard percentage deviation ( $\sigma$  %) in Table 4.

**Table 4. Adjustable parameters of Eq 5, 6 7, 8 and 12 for Acrylates (1) + Dodecane-1-ol (2) at T = 298.15 K**

$H_{12}$	$\sigma$	$W_{vis}$	$\sigma$	$G_{12}$	$\sigma$	$T_{12}$	$\sigma$
Methyl Acrylate (1) + Dodecane-1-ol (2)							
-3.440	62.333	0.421	0.882	-0.001	0.039	-6.987	27.904
Ethyl Acrylate (1) + Dodecane-1-ol (2)							
-3.024	52.254	0.270	0.448	-0.001	0.037	5.802	96.178
Butyl Acrylate (1) + Dodecane-1-ol (2)							
-1.676	30.401	0.109	0.117	-0.001	0.024	-3.352	47.190
Methyl Methacrylate (1) + Dodecane-1-ol (2)							
-2.658	44.915	0.289	0.517	-0.001	0.013	-5.497	84.818

Heric –Brewer [9] proposed two parameter model of following form,

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln(x_1 M_1 + x_2 M_2) + x_1 x_2 [\alpha_{12} + \alpha_{21}(x_1 - x_2)] \quad (9)$$

where  $M_1$  and  $M_2$  are molecular weights of components of 1 and 2,  $\alpha_{12}$  and  $\alpha_{21}$  are interaction parameters which can be calculated from least square method and other terms involved have their usual meaning.

McAllister's multibody interaction model was widely used to correlate kinematic viscosity ( $\nu$ ) data. The two parameter McAllister equation based on Eyring's theory of absolute reaction rates, taken into account interactions of both like and unlike molecules by a two dimensional three body model. The three body model was defined by relation,

$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3 x_1^2 x_2 \ln Z_{12} + 3 x_1 x_2^2 \ln Z_{21} - \ln [x_1 + (x_2 M_2 / M_1)] + 3 x_1^2 x_2 \ln [(2/3) + (M_2 / 3M_1)] + 3 x_1 x_2^2 \ln [(1/3) + (2M_2 / 3M_1)] + x_2^3 \ln (M_2 / M_1) \quad (10)$$

Similarly, four body model was defined by relation,

$$\ln \nu = x_1^4 \ln \nu_1 + 4 x_1^3 x_2 \ln Z_{1112} + 6 x_1^2 x_2^2 \ln Z_{1122} + 4 x_1 x_2^3 \ln Z_{2221} + x_2^4 \ln \nu_2 - \ln [x_1 + x_2 (M_2 / M_1)] + 4 x_1^3 x_2 \ln [(3 + M_2 / M_1) / 4] + 6 x_1^2 x_2^2 \ln [1 + M_2 / M_1] / 2 + 4 x_1 x_2^3 \ln [(1 + 3M_2 / M_1) / 4] + x_2^4 \ln (M_2 / M_1) \quad (11)$$

Where  $Z_{12}$ ,  $Z_{21}$ ,  $Z_{1112}$ ,  $Z_{1122}$  and  $Z_{2221}$  are model parameters and  $M_i$  and  $\nu_i$  are molecular mass and kinematic viscosity of pure component  $i$ .

To perform a numerical comparison of correlating capability of above Eq (5 to 11) we have calculated standard percentage deviation ( $\sigma$  %) using relation,

$$\sigma \% = [1 / (\eta_{\text{expt}} - k) \times \sum (100 (\eta_{\text{expt}} - \eta_{\text{cal}}) / \eta_{\text{expt}})^2]^{1/2} \quad (12)$$

where  $k$  represents number of numerical coefficients in respective equations.

The terms  $H_{12}$ ,  $W_{vis}$ ,  $G_{12}$ ,  $T_{12}$ ,  $\alpha_{12}$ ,  $\alpha_{21}$ ,  $Z_{12}$ ,  $Z_{21}$ ,  $Z_{1112}$ ,  $Z_{1122}$  and  $Z_{2221}$  in above Eq 5 to 11 have been considered as adjustable parameters and were estimated by a non-linear regression analysis based on a least-squares method. The Eq 12 is particularly selected because characteristic constant parameter  $G_{12}$  allows for positive and negative deviations from additivity rule [10]. These are presented with their standard percentage deviation ( $\sigma$  %) in Table 5.

Table 5. Adjustable parameters of Eq 9, 10, 11 and 12 for Acrylates (1) + Dodecane-1-ol (2) at  $T = 298.15$  K

$\alpha_{12}$	$\alpha_{21}$	$\sigma$	$Z_{12}$	$Z_{21}$	$\sigma$	$Z_{1112}$	$Z_{1122}$	$Z_{2221}$	$\sigma$
Methyl Acrylate (1) + Dodecane-1-ol (2)									
0.425	0.122	0.161	1.828	5.873	0.161	1.299	2.025	7.940	17.830
Ethyl Acrylate (1) + Dodecane-1-ol (2)									
0.270	0.060	-0.052	1.961	6.165	0.052	1.430	2.414	8.198	19.853
Butyl Acrylate (1) + Dodecane-1-ol (2)									
0.109	0.016	0.019	2.534	7.042	0.019	1.942	3.435	9.069	28.552
Methyl Methacrylate (1) + Dodecane-1-ol (2)									
0.291	0.074	0.088	2.117	6.380	0.088	1.556	2.533	8.438	21.372

Recently Jouyban and Acree proposed a model for correlating density and viscosity of liquid mixtures at various temperatures. The proposed equation is,

$$\ln y_{mT} = f_1 \ln y_{1T} + f_2 \ln y_{2T} + f_1 f_2 \sum [A_j (f_1 - f_2)^j / T] \quad (13)$$

where  $y_{mT}$ ,  $y_{1T}$  and  $y_{2T}$  is density or viscosity of mixture and solvents 1 and 2 at temperature  $T$ , respectively,  $f_1$  and  $f_2$  are volume fractions of solvents in case of density and mole fraction in case of viscosity, and  $A_j$  are model constants. The correlating ability of Jouyban - Acree model was tested by calculating average percentage deviation (APD) between experimental and calculated density and viscosity as,

$$\text{APD} = (100/N) \sum [(|y_{\text{expt}} - y_{\text{cal}}|) / y_{\text{expt}}] \quad (14)$$

Where  $N$  is number of data points in each set. The optimum numbers of constants  $A_j$ , in each case, were determined from examination of average percentage deviation value. The constants  $A_j$  calculated from least square analysis along with average percentage deviation (APD) are presented in Table 6.

Table 6. Adjustable parameters of Eq 13 and 14 for Acrylates (1) + Dodecane-1-ol (2)

Property	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$\sigma$	APD
Methyl Acrylate (1) + Dodecane-1-ol (2)							
$\rho / (\text{g.m}^{-3})$	-35.8822	-14.4987	-4.7883	-1.6088	-3.1256	8.0418	0.0355
$\eta / (\text{mPa.s})$	-0.3910	1.2563	4.4627	-4.1517	-8.5936	4.7799	0.0249
Ethyl Acrylate (1) + Dodecane-1-ol (2)							
$\rho / (\text{g.m}^{-3})$	-22.1031	-7.5597	-3.6048	0.4497	2.3879	5.2287	0.0453
$\eta / (\text{mPa.s})$	-0.1873	0.0605	-0.5018	-1.7158	-0.9880	4.9217	0.0158
Butyl Acrylate (1) + Dodecane-1-ol (2)							
$\rho / (\text{g.m}^{-3})$	-11.4653	-2.1140	0.4519	-1.0777	-2.1107	3.0751	0.0216
$\eta / (\text{mPa.s})$	-0.1818	0.2020	-0.0970	-1.2300	-0.9196	5.3158	0.0145
Methyl Methacrylate (1) + Dodecane-1-ol (2)							
$\rho / (\text{g.m}^{-3})$	-27.6933	-9.0012	-2.8447	-1.8270	-0.8159	6.3393	0.0335
$\eta / (\text{mPa.s})$	-0.2253	0.1431	0.4657	-1.4437	-1.9474	5.0259	0.0138

The proposed model provides reasonably accurate calculations for density and viscosity of binary liquid mixtures and could be used in data modeling [11, 12].

## RESULTS AND DISCUSSION

A graphical comparison of dependence of excess molar volume ( $V^E$ ) at 298.15 K for binary mixtures of each acrylic ester with dodecane-1-ol is given in Fig. 1.

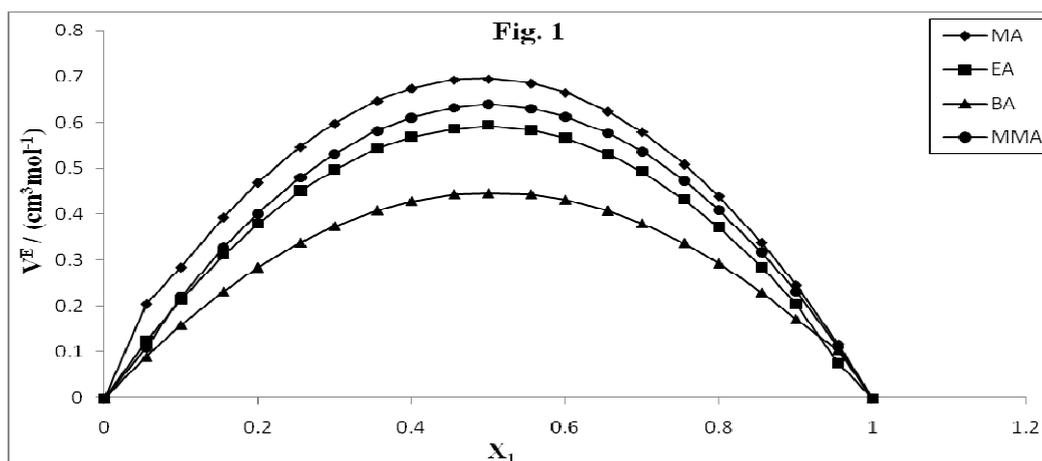


Figure 1. Variation of excess molar volumes for Acrylates (1) + Dodecane-1-ol (2) at 298.15 K

A systematic decrease in  $V^E$  is noted with increase in carbon chain length of acrylic esters from methyl acrylate to butyl acrylate at 298.15 K in all binary mixtures. Strength of interaction between component molecules of binary mixtures is well reflected in deviation of excess functions from ideality. Thermodynamic excess functions are found to be very sensitive towards mutual interactions between component molecules of liquid mixture. Sign and extent of deviations of these functions from ideality depends upon strength of interaction between unlike molecules. Excess molar volumes found to be positive and increases with increase in chain length of solute molecules. Disruption of hydrogen bonds in alkane-1-ol associates and dipole-dipole repulsive interactions between multimer and unimer alkane-1-ol species are mainly responsible for observed positive values of  $V^E$ .

A graphical comparison of dependence of deviation in viscosity ( $\Delta\eta$ ) at 298.15 K for binary mixtures of each acrylic ester with dodecane-1-ol is given in Fig. 2.

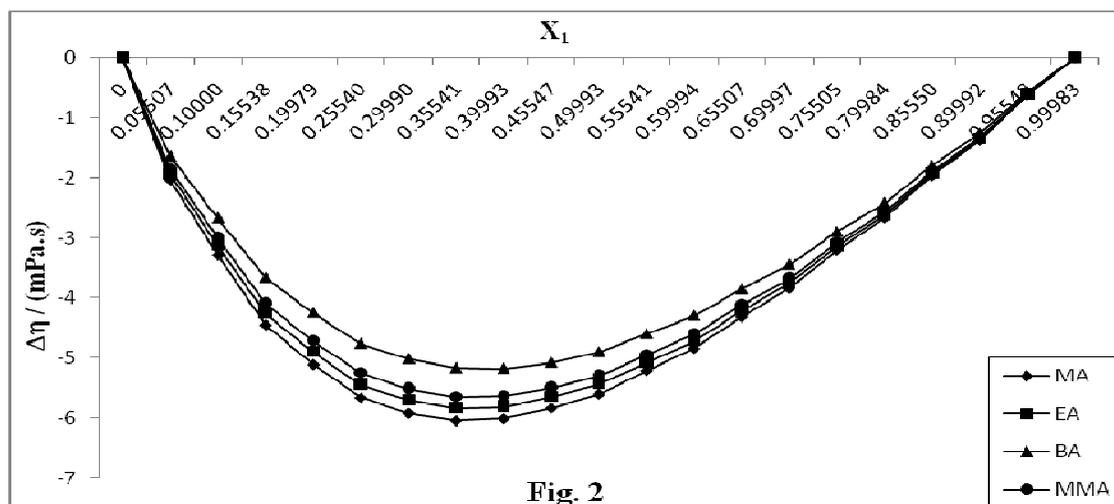


Figure 2. Variation of deviation in viscosity for Acrylates (1) + Dodecane-1-ol (2) at 298.15 K

Negative values of  $\Delta\eta$  over whole composition range suggests that, viscosities of associates formed between unlike molecules are relatively less than those of pure components, which is exhibited by decreased values of viscosity with mole fraction. This decrease in viscosity attributed to breaking of dipolar association of alcohol into small dipoles. Weak types of dipole- induced dipole type of interactions are not sufficient to produce bulky or less mobile entities in system and hence decreased trend of viscosity.

### CONCLUSION

Observed positive values of excess molar volume ( $V^E$ ) over entire composition range are due to rupture of hydrogen bonded associates of alkanols dominates over that of hydrogen bonding between unlike molecules. Weak types of dipole- induced dipole type of interactions are not sufficient to produce bulky or less mobile entities in system and hence decreased trend of viscosity is observed in present binary liquid mixture of acrylics esters with branched alcohol.

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