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# Studies of thermodynamic properties of methyl methacrylate with alkane-1-ols and alkane-2-ols

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## ABSTRACT

*Densities and viscosities binary liquid mixtures of methyl methacrylate with octane-1-ol, decane-1-ol, octane-2-ol and decane-2-ol at 298.15 and 308.15 K and at atmospheric pressure were measured. Excess molar volumes and viscosity deviation were calculated and have been fitted to Redlich-Kister polynomial equation. The mixture viscosities were correlated using Hind, Choudhary-Katti, Grunberg-Nissan, Tamura-Kurata, Heric–Brewer, McAllister three and four body model equations. Recently proposed Jouyban Acree model was also used to correlate density and viscosity. Intermolecular interactions explained in terms of structure breaking dispersion forces. A graphical representation of excess molar volumes shows positive nature whereas deviation in viscosity shows negative nature. Positive values of excess molar volumes show that volume expansion is taking place causing rupture of H-bonds in self associated alcohols. Results are discussed in terms of molecular interactions prevailing in mixture.*

**Keywords:** Excess Molar Volumes, McAllister three and four body model, Tamura and Kurata, Heric–Brewer, Jouyban Acree model.

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## INTRODUCTION

The study of binary mixtures containing acrylic esters and alkane-1-ols is of interest and importance because of wide use of the former as monomers in the production of polymers, emulsion formulations and the latter as industrial solvents and also from theoretical point of view. Thermodynamic studies of such binary systems are also useful in solving many problems associated with heat and fluid flow. The qualitative and quantitative analysis of excess functions provides information about the nature of molecular interactions in the binary mixtures [1]. The production of acrylic esters from lower to higher alkyl homologues is done by either direct esterification with the corresponding alcohol or transesterification reaction in an inert solvent medium. Thus the measurements involving the changes in the various physical properties upon mixing acrylic esters with alcohols provide valuable information for the optimization of various process parameters, for the efficient design of reactors for the transesterification process [2-3]. In particular, for mixtures of acrylic esters with 1-alcohols, data exist only for isothermal vapor-liquid equilibria for methyl methacrylate + methanol or + ethanol [4-5], excess enthalpies, excess volumes and excess molar isobaric heat capacities of methyl methacrylate + methanol or + ethanol [6], densities and viscosities of butyl acrylate + 1-butanol [7].

The availability of free electrons and tendency of ester molecules to form hydrogen bonds with alkane-1-ols via participation of carbonyl group and hydrogen of -OH group have attracted attention of investigation in this field and hence present study of methyl methacrylate (MMA) with octane-1-ol, decane-1-ol, octane-2-ol and decane-2-ol have been successfully carried by us.

## MATERIALS AND METHODS

All chemicals used, of mass fraction purities > 0.997 (E-Merck) were double distilled, middle fraction collected of all liquids was stored over 0.4 nm molecular sieves. Masses were recorded on a Mettlar one pan balance, which can read up to fifth place of decimal, with an accuracy of ± 0.01 mg. The temperature was controlled using a constant temperature controlled water bath (Gemini Scientific Instruments, Chennai, India) having accuracy ± $0.02^0$ C.

***Experimental Part:***

Densities of solutions were measured [8] using a single capillary pycnometer made up of borosil glass with a bulb of 8 $cm^3$ and capillary with internal diameter of 0.1 cm. Accuracy in density measurement was ± $5x10^{-5}$ $g/cm^3$.

Dynamic viscosities were measured [8] using an Ubbelhode suspended level viscometer, calibrated with conductivity water. An electronic digital stop watch with readability of ± 0.01 s used for the flow time measurements. Accuracy in dynamic viscosity was ± $3x10^{-3}$ mPa.s. Comparison of measured values of pure components with literature values are given in Table 1.

**Table 1. Densities (ρ) and viscosities (η) for pure components at 298.15 and 308.15 K.**

| Property | T = 298.15 K | | T = 308.15 K | |
|---|---|---|---|---|
| | Expt. | Lit. | Expt. | Lit. |
| | | | Methyl Methacrylate | |
| $\rho$ / (g.$cm^{-3}$) | 0.93765 | 0.93763 [9] | 0.92571 | 0.92574 [9] |
| $\eta$ / (mPa.s) | 0.584 | 0.584 [7] | 0.514 | --- |
| | | | Octane-1-ol | |
| $\rho$ / (g.$cm^{-3}$) | 0.82160 | 0.82152 [10] | 0.81453 | 0.81467 [12] |
| $\eta$ / (mPa.s) | 7.362 | 7.596 [11] | 5.520 | 5.250 [13] |
| | | | Decane-1-ol | |
| $\rho$ / (g.$cm^{-3}$) | 0.82630 | 0.82637 [12] | 0.81944 | 0.81957 [12] |
| $\eta$ / (mPa.s) | 11.793 | 11.790 [13] | 8.116 | 8.124 [13] |
| | | | Octane-2-ol | |
| $\rho$ / (g.$cm^{-3}$) | 0.81705 | 0.81710 [14] | 0.80981 | --- |
| $\eta$ / (mPa.s) | 6.490 | 6.490 [14] | 4.361 | --- |
| | | | Decane-2-ol | |
| $\rho$ / (g.$cm^{-3}$) | 0.82096 | --- | 0.81174 | --- |
| $\eta$ / (mPa.s) | 10.744 | --- | 6.848 | --- |

***Computational Part:***

The density values have been used to calculate excess molar volume using equation,

$$V^E / cm^3.mol^{-1} = (x_1M_1+x_2M_2)/\rho_{12} - (x_1M_1/\rho_1)-( x_2M_2/\rho_2) \qquad (1)$$

where $\rho_{12}$ is the density of the mixture and $x_1$, $M_1$, $\rho_1$ and $x_2$, $M_2$, $\rho_2$ are mole fractions, molecular weights and densities of pure components 1 and 2, respectively. The first term on the right-hand side of above (Eq 1) represents the 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 $cm^3mol^{-1}$) their difference is usually smaller by two to three orders of magnitude and thus may carry a significantly larger error.

The viscosity deviation was calculated using equation,

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

where $\eta_{12}$ is the viscosity of the mixture and $x_1$, $x_2$ and $\eta_1$, $\eta_2$ are mole fractions and viscosities of pure components 1 and 2, respectively.

Experimental values of densities, viscosities, excess molar volumes and deviation in viscosities of mixtures at 298.15 and 308.15 K are listed as function of mole fraction in Table 2.

**Table 2. Densities (ρ), viscosities (η), excess molar volumes ($V^E$) and viscosity deviation (Δη) for MMA (1) + Alkane-1-ols (2) and MMA (1) + Alkane-2-ols (2) at 298.15 and 308.15 K.**

| $x_1$ | T = 298.15 K | | | | T = 308.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| | ρ ($g.cm^{-3}$) | η (mPa.s) | $V^E$ ($cm^3mol^{-1}$) | Δη (mPa.s) | ρ ($g.cm^{-3}$) | η (mPa.s) | $V^E$ ($cm^3mol^{-1}$) | Δη (mPa.s) |
| | | | | MMA (1) + Octane-1-ol (2) | | | | |
| 0 | 0.82160 | 7.362 | 0 | 0 | 0.81453 | 5.520 | 0 | 0 |
| 0.0555 | 0.82554 | 6.396 | 0.089 | -0.590 | 0.81841 | 4.839 | 0.071 | -0.403 |
| 0.0999 | 0.82877 | 5.715 | 0.167 | -0.970 | 0.82158 | 4.355 | 0.135 | -0.665 |
| 0.1555 | 0.83304 | 4.964 | 0.246 | -1.344 | 0.82576 | 3.816 | 0.199 | -0.926 |
| 0.1998 | 0.83661 | 4.437 | 0.301 | -1.571 | 0.82924 | 3.435 | 0.243 | -1.085 |
| 0.2556 | 0.84132 | 3.852 | 0.359 | -1.778 | 0.83383 | 3.009 | 0.290 | -1.232 |
| 0.2997 | 0.84523 | 3.444 | 0.397 | -1.886 | 0.83763 | 2.709 | 0.321 | -1.310 |
| 0.3551 | 0.85036 | 2.993 | 0.434 | -1.962 | 0.84261 | 2.376 | 0.351 | -1.367 |
| 0.3999 | 0.85474 | 2.672 | 0.455 | -1.980 | 0.84684 | 2.136 | 0.368 | -1.382 |
| 0.4551 | 0.86039 | 2.323 | 0.470 | -1.954 | 0.85228 | 1.874 | 0.381 | -1.368 |
| 0.4998 | 0.86518 | 2.074 | 0.475 | -1.900 | 0.85690 | 1.685 | 0.385 | -1.333 |
| 0.5555 | 0.87149 | 1.801 | 0.469 | -1.796 | 0.86296 | 1.476 | 0.380 | -1.263 |
| 0.5998 | 0.87677 | 1.610 | 0.456 | -1.687 | 0.86802 | 1.329 | 0.369 | -1.189 |
| 0.6550 | 0.88367 | 1.400 | 0.430 | -1.523 | 0.87462 | 1.166 | 0.348 | -1.076 |
| 0.6999 | 0.88961 | 1.249 | 0.400 | -1.369 | 0.88028 | 1.048 | 0.324 | -0.969 |
| 0.7555 | 0.89734 | 1.085 | 0.353 | -1.156 | 0.88764 | 0.918 | 0.285 | -0.820 |
| 0.7998 | 0.90385 | 0.970 | 0.306 | -0.971 | 0.89382 | 0.826 | 0.247 | -0.690 |
| 0.8554 | 0.91248 | 0.842 | 0.238 | -0.722 | 0.90200 | 0.724 | 0.191 | -0.513 |
| 0.8999 | 0.91977 | 0.752 | 0.174 | -0.510 | 0.90889 | 0.652 | 0.140 | -0.363 |
| 0.9550 | 0.92931 | 0.654 | 0.088 | -0.235 | 0.91790 | 0.572 | 0.068 | -0.168 |
| 1 | 0.93765 | 0.584 | 0 | 0 | 0.92571 | 0.514 | 0 | 0 |
| | | | | MMA (1) + Decane-1-ol (2) | | | | |
| 0 | 0.82630 | 11.793 | 0 | 0 | 0.81944 | 8.116 | 0 | 0 |
| 0.0555 | 0.82942 | 9.983 | 0.091 | -1.189 | 0.82249 | 6.965 | 0.075 | -0.730 |
| 0.0999 | 0.83193 | 8.734 | 0.189 | -1.939 | 0.82499 | 6.160 | 0.149 | -1.196 |
| 0.1555 | 0.83534 | 7.394 | 0.281 | -2.658 | 0.82834 | 5.287 | 0.222 | -1.649 |
| 0.1998 | 0.83825 | 6.469 | 0.344 | -3.085 | 0.83119 | 4.676 | 0.272 | -1.921 |
| 0.2556 | 0.84214 | 5.471 | 0.412 | -3.458 | 0.83499 | 4.009 | 0.325 | -2.164 |
| 0.2997 | 0.84544 | 4.788 | 0.456 | -3.644 | 0.83820 | 3.547 | 0.359 | -2.289 |
| 0.3551 | 0.84985 | 4.052 | 0.499 | -3.757 | 0.84248 | 3.043 | 0.393 | -2.371 |
| 0.3999 | 0.85363 | 3.544 | 0.524 | -3.766 | 0.84613 | 2.691 | 0.412 | -2.384 |
| 0.4551 | 0.85866 | 3.000 | 0.542 | -3.688 | 0.85098 | 2.309 | 0.427 | -2.344 |
| 0.4998 | 0.86297 | 2.624 | 0.550 | -3.565 | 0.85513 | 2.042 | 0.432 | -2.273 |
| 0.5555 | 0.86876 | 2.221 | 0.540 | -3.346 | 0.86067 | 1.753 | 0.426 | -2.141 |
| 0.5998 | 0.87373 | 1.943 | 0.526 | -3.125 | 0.86542 | 1.550 | 0.414 | -2.005 |
| 0.6550 | 0.88041 | 1.644 | 0.495 | -2.801 | 0.87178 | 1.330 | 0.390 | -1.803 |
| 0.6999 | 0.88616 | 1.439 | 0.460 | -2.509 | 0.87723 | 1.176 | 0.364 | -1.619 |
| 0.7555 | 0.89392 | 1.217 | 0.405 | -2.107 | 0.88459 | 1.009 | 0.321 | -1.364 |
| 0.7998 | 0.90060 | 1.065 | 0.351 | -1.762 | 0.89091 | 0.893 | 0.278 | -1.143 |
| 0.8554 | 0.90968 | 0.901 | 0.271 | -1.303 | 0.89946 | 0.766 | 0.216 | -0.847 |
| 0.8999 | 0.91755 | 0.789 | 0.197 | -0.918 | 0.90686 | 0.677 | 0.158 | -0.598 |
| 0.9550 | 0.92830 | 0.667 | 0.090 | -0.416 | 0.91690 | 0.581 | 0.079 | -0.271 |
| 1 | 0.93765 | 0.584 | 0 | 0 | 0.92571 | 0.514 | 0 | 0 |
| | | | | MMA (1) + Octane-2-ol (2) | | | | |
| 0 | 0.81705 | 6.490 | 0 | 0 | 0.80981 | 4.361 | 0 | 0 |
| 0.0555 | 0.82112 | 5.678 | 0.094 | -0.484 | 0.81380 | 3.873 | 0.080 | -0.275 |
| 0.0999 | 0.82454 | 5.102 | 0.160 | -0.798 | 0.81718 | 3.522 | 0.129 | -0.455 |
| 0.1555 | 0.82902 | 4.463 | 0.232 | -1.109 | 0.82156 | 3.127 | 0.190 | -0.636 |
| 0.1998 | 0.83275 | 4.011 | 0.282 | -1.299 | 0.82521 | 2.845 | 0.229 | -0.748 |
| 0.2556 | 0.83768 | 3.507 | 0.334 | -1.474 | 0.83001 | 2.525 | 0.273 | -0.853 |
| 0.2997 | 0.84176 | 3.153 | 0.369 | -1.567 | 0.83399 | 2.297 | 0.300 | -0.911 |
| 0.3551 | 0.84711 | 2.760 | 0.405 | -1.633 | 0.83919 | 2.041 | 0.328 | -0.954 |
| 0.3999 | 0.85167 | 2.477 | 0.423 | -1.651 | 0.84361 | 1.854 | 0.343 | -0.968 |
| 0.4551 | 0.85755 | 2.169 | 0.437 | -1.633 | 0.84928 | 1.648 | 0.357 | -0.962 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 0.4998 | 0.86256 | 1.948 | 0.438 | -1.590 | 0.85413 | 1.498 | 0.355 | -0.940 |
| 0.5555 | 0.86910 | 1.703 | 0.435 | -1.506 | 0.86042 | 1.329 | 0.354 | -0.895 |
| 0.5998 | 0.87457 | 1.530 | 0.425 | -1.417 | 0.86568 | 1.209 | 0.345 | -0.844 |
| 0.6550 | 0.88174 | 1.340 | 0.400 | -1.282 | 0.87255 | 1.075 | 0.326 | -0.766 |
| 0.6999 | 0.88789 | 1.203 | 0.373 | -1.153 | 0.87844 | 0.976 | 0.303 | -0.692 |
| 0.7555 | 0.89590 | 1.052 | 0.330 | -0.976 | 0.88609 | 0.867 | 0.269 | -0.587 |
| 0.7998 | 0.90264 | 0.945 | 0.287 | -0.821 | 0.89252 | 0.788 | 0.234 | -0.496 |
| 0.8554 | 0.91157 | 0.827 | 0.224 | -0.611 | 0.90100 | 0.700 | 0.184 | -0.370 |
| 0.8999 | 0.91911 | 0.743 | 0.168 | -0.432 | 0.90817 | 0.636 | 0.138 | -0.263 |
| 0.9550 | 0.92892 | 0.651 | 0.094 | -0.199 | 0.91743 | 0.566 | 0.082 | -0.121 |
| 1 | 0.93765 | 0.584 | 0 | 0 | 0.92571 | 0.514 | 0 | 0 |
| MMA (1) + Decane-2-ol (2) | | | | | | | | |
| 0 | 0.82096 | 10.744 | 0 | 0 | 0.81174 | 6.848 | 0 | 0 |
| 0.0555 | 0.82421 | 9.142 | 0.097 | -1.039 | 0.81497 | 5.932 | 0.085 | -0.565 |
| 0.0999 | 0.82690 | 8.032 | 0.183 | -1.696 | 0.81770 | 5.287 | 0.149 | -0.928 |
| 0.1555 | 0.83049 | 6.834 | 0.271 | -2.332 | 0.82132 | 4.580 | 0.214 | -1.284 |
| 0.1998 | 0.83356 | 6.004 | 0.335 | -2.708 | 0.82439 | 4.082 | 0.265 | -1.499 |
| 0.2556 | 0.83766 | 5.104 | 0.396 | -3.044 | 0.82848 | 3.533 | 0.311 | -1.696 |
| 0.2997 | 0.84113 | 4.485 | 0.438 | -3.212 | 0.83193 | 3.150 | 0.344 | -1.798 |
| 0.3551 | 0.84576 | 3.816 | 0.479 | -3.317 | 0.83653 | 2.728 | 0.374 | -1.869 |
| 0.3999 | 0.84973 | 3.351 | 0.502 | -3.329 | 0.84045 | 2.430 | 0.392 | -1.885 |
| 0.4551 | 0.85501 | 2.851 | 0.519 | -3.266 | 0.84565 | 2.105 | 0.406 | -1.858 |
| 0.4998 | 0.85953 | 2.505 | 0.525 | -3.160 | 0.85011 | 1.876 | 0.408 | -1.805 |
| 0.5555 | 0.86559 | 2.131 | 0.520 | -2.969 | 0.85603 | 1.625 | 0.407 | -1.704 |
| 0.5998 | 0.87079 | 1.872 | 0.505 | -2.777 | 0.86112 | 1.448 | 0.394 | -1.600 |
| 0.6550 | 0.87778 | 1.592 | 0.476 | -2.492 | 0.86794 | 1.254 | 0.370 | -1.442 |
| 0.6999 | 0.88378 | 1.399 | 0.444 | -2.233 | 0.87377 | 1.118 | 0.347 | -1.296 |
| 0.7555 | 0.89190 | 1.190 | 0.385 | -1.880 | 0.88165 | 0.968 | 0.300 | -1.096 |
| 0.7998 | 0.89889 | 1.046 | 0.340 | -1.570 | 0.88842 | 0.863 | 0.266 | -0.918 |
| 0.8554 | 0.90838 | 0.889 | 0.261 | -1.164 | 0.89757 | 0.747 | 0.206 | -0.683 |
| 0.8999 | 0.91661 | 0.781 | 0.191 | -0.820 | 0.90550 | 0.666 | 0.151 | -0.482 |
| 0.9550 | 0.92780 | 0.665 | 0.095 | -0.371 | 0.91624 | 0.577 | 0.078 | -0.219 |
| 1 | 0.93765 | 0.584 | 0 | 0 | 0.92571 | 0.514 | 0 | 0 |

The other required values were taken from literature [14-15].

Excess molar volume and viscosity deviation were fitted to Redlich Kister [15] equation,

$$Y = x_1 x_2 \sum_{i}^{n} a_i (x_1 - x_2)^i \tag{3}$$

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

$\sigma$ was calculated using the relation,

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

where N is the number of data points and n is the number of coefficients. The calculated values of the coefficients $a_i$ along with standard deviations ($\sigma$) are given in Table 3.

**Table 3. Adjustable parameters of Eq (3) and (4) for excess functions for MMA (1) + Alkane-1-ols (2) and MMA (1) + Alkane-2-ols (2) at 298.15 and 308.15 K.**

| Property | T / K | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | σ |
|---|---|---|---|---|---|---|---|
| MMA (1) + Octane-1-ol (2) | | | | | | | |
| $V^E/(cm^3mol^{-1})$ | 298.15 | 1.8975 | -0.0505 | 0.0259 | 0.2409 | -0.0584 | 0.00291 |
| | 308.15 | 1.5338 | -0.0410 | 0.0815 | 0.1810 | -0.1937 | 0.00252 |
| $\Delta\eta$ / (mPa.s) | 298.15 | -7.5999 | 3.0487 | -0.9288 | 0.2383 | -0.0793 | 0.00023 |
| | 308.15 | -5.3306 | 2.0151 | -0.5949 | 0.1384 | -0.0107 | 0.00027 |
| MMA (1) + Decane-1-ol (2) | | | | | | | |
| $V^E/(cm^3mol^{-1})$ | 298.15 | 2.1747 | -0.0636 | 0.2912 | 0.2877 | -0.6661 | 0.00549 |
| | 308.15 | 1.7207 | -0.0620 | 0.1082 | 0.2911 | -0.2269 | 0.00419 |
| $\Delta\eta$ / (mPa.s) | 298.15 | -14.2602 | 6.6332 | -2.3668 | 0.7365 | -0.2265 | 0.00103 |
| | 308.15 | -9.0924 | 5.9326 | -1.2962 | 0.3581 | -0.1005 | 0.00067 |
| MMA (1) + Octane-2-ol (2) | | | | | | | |
| $V^E/(cm^3mol^{-1})$ | 298.15 | 1.7768 | -0.0653 | -0.2398 | 0.2709 | 0.5794 | 0.00440 |
| | 308.15 | 1.4532 | -0.0677 | -0.3364 | 0.2748 | 0.7652 | 0.00555 |
| $\Delta\eta$ / (mPa.s) | 298.15 | -6.3616 | 2.4311 | -0.7197 | 0.1869 | -0.0337 | 0.00031 |
| | 308.15 | -3.7618 | 1.2892 | -0.3443 | 0.0781 | -0.0099 | 0.00028 |
| MMA (1) + Decane-2-ol (2) | | | | | | | |
| $V^E/(cm^3mol^{-1})$ | 298.15 | 2.0963 | -0.0678 | 0.0577 | 0.2855 | -0.1578 | 0.00430 |
| | 308.15 | 1.6418 | -0.0413 | -0.0868 | 0.1491 | 0.2224 | 0.00319 |
| $\Delta\eta$ / (mPa.s) | 298.15 | -12.6392 | 5.7206 | -1.9993 | 0.6023 | -0.1512 | 0.00109 |
| | 308.15 | -7.2213 | 2.9442 | -0.9136 | 0.2526 | -0.0658 | 0.00068 |

Several semi-empirical relations have been proposed to evaluate and correlate dynamic viscosity and to check the suitability of the equation for experimental data fits by taking into account the number of empirical adjustable coefficients. The equations of Hind, Choudhary-Katti, Grunberg-Nissan and Tamura-Kurata have one adjustable parameter.

Hind [16] proposed following equation,

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

where $H_{12}$ is the interaction parameter.

Choudhary-Katti [17] proposed following equation,

$$\ln(\eta_n V_m) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1x_2[Wvis/(RT)] \qquad (6)$$

where Wvis is the interaction energy for activation of viscous flow.

Grunberg-Nissan [18] provided following empirical equation,

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1x_2G_{12} \qquad (7)$$

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

Tamura and Kurata [19] developed expression for viscosity of binary mixtures as,

$$\eta = x_1\phi_1 \eta_1 + x_2\phi_2 \eta_2 + 2(x_1x_2\phi_1\phi_2)^{1/2}T_{12} \qquad (8)$$

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

Terms $H_{12}$, Wvis, $G_{12}$ and $T_{12}$ were estimated by a non-linear regression analysis based on least-squares method and represented with standard percentage deviation (σ %) in Table 4.

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**Table 4. Adjustable parameters of Eq (5), (6), (7), (8) and (12) for MMA (1) + Alkane-1-ols (2) and MMA (1) + Alkane-2-ols (2) at 298.15 and 308.15 K.**

| T / K | $H_{12}$ | σ | Wvis | σ | $G_{12}$ | σ | $T_{12}$ | σ |
|---|---|---|---|---|---|---|---|---|
| MMA (1) + Octane-1-ol (2) | | | | | | | | |
| 298.15 | 0.078 | 15.252 | 0.091 | 0.092 | -0.001 | 0.028 | -0.564 | 23.632 |
| 308.15 | 0.292 | 11.918 | 0.087 | 0.084 | -0.001 | 0.026 | -0.174 | 18.733 |
| MMA (1) + Decane-1-ol (2) | | | | | | | | |
| 298.15 | -1.185 | 29.768 | 0.184 | 0.249 | -0.001 | 0.033 | -2.771 | 51.594 |
| 308.15 | -0.363 | 21.179 | 0.179 | 0.254 | 0.000 | 0.032 | -1.418 | 37.520 |
| MMA (1) + Octane-2-ol (2) | | | | | | | | |
| 298.15 | 0.284 | 12.576 | 0.093 | 0.091 | -0.001 | 0.020 | 0.280 | 19.870 |
| 308.15 | 0.522 | 8.117 | 0.088 | 0.083 | -0.001 | 0.028 | 0.163 | 13.242 |
| MMA (1) + Decane-2-ol (2) | | | | | | | | |
| 298.15 | -0.859 | 26.221 | 0.187 | 0.259 | -0.001 | 0.035 | -2.307 | 46.096 |
| 308.15 | -0.023 | 16.544 | 0.183 | 0.257 | 0.000 | 0.026 | -0.906 | 30.146 |

Heric–Brewer [20] proposed two parameter model of the following form,

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln(x_1M_1+x_2M_2) + x_1x_2[\alpha_{12} + \alpha_{21}(x_1-x_2)] \qquad (9)$$

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 the least square method.

McAllister [21] proposed multibody interaction model is widely used to correlate kinematic viscosity (υ) 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 is defined by the relation,

$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3 x_1^2 x_2 \ln Z_{12} + 3 x_1 x_2^2 \ln Z_{21} - \ln [x_1+(x_2M_2/M_1)] + 3 x_1^2 x_2 \ln[(2/3)+(M_2/3M_1)] + 3x_1x_2^2 \ln[(1/3)+(2M_2/3M_1)] + x_2^3 \ln(M_2/M_1) \qquad (10)$$

Similarly, the four body model is defined by the relation,

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3x_2 \ln Z_{1112} + 6 x_1^2x_2^2 \ln Z_{1122} + 4 x_1x_2^3 \ln Z_{2221} + x_2^4 \ln \nu_2 - \ln [x_1+x_2 (M_2/M_1)] + 4 x_1^3x_2 \ln [(3+M_2/M_1)/4] + 6 x_1^2 2x_2^2 \ln[1+M_2/M_1)/2] + 4 x_1x_2^3 \ln [(1+ 3M_2/M_1)/4] + x_2^4 \ln (M_2/M_1) \qquad (11)$$

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

To perform a numerical comparison of the correlating capability of above Eqs 5 to 11, we have calculated the standard percentage deviation (σ %) using the relation,

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

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

The terms $\alpha_{12}$, $\alpha_{21}$, $Z_{12}$, $Z_{21}$, $Z_{1112}$, $Z_{1122}$ and $Z_{2221}$ were also estimated by a non-linear regression analysis based on a least-squares method and presented with standard percentage deviation (σ %) in Table 5.

The proposed equation is,

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

where $y_{mT}$, $y_{1T}$ and $y_{2T}$ is density or viscosity of the mixture and solvents 1 and 2 at temperature T, respectively, $f_1$ and $f_2$ are the volume fractions of solvents in case of density, mole fraction in case of viscosity and Aj are the model constants.

The correlating ability of the Jouyban-Acree model was tested by calculating the average percentage deviation (APD) between the experimental and calculated density and viscosity as,

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

Where N is the number of data points in each set. The optimum numbers of constants Aj, in each case, are determined from the examination of the average percentage deviation value.

**Table 5. Adjustable parameters of Eq (9), (10), (11) and (12) for MMA (1) + Alkane-1-ols (2) and MMA (1) + Alkane-2-ols (2) at 298.15 and 308.15 K.**

| T / K | $\alpha_{12}$ | $\alpha_{12}$ | $\sigma$ | $Z_{12}$ | $Z_{21}$ | $\sigma$ | $Z_{1112}$ | $Z_{1122}$ | $Z_{2221}$ | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | MMA (1) + Octane-1-ol (2) | | | | | | |
| 298.15 | 0.090 | 0.010 | 0.038 | 1.554 | 3.757 | 0.038 | 1.234 | 2.106 | 4.659 | 4.517 |
| 308.15 | 0.087 | 0.012 | 0.026 | 1.311 | 2.996 | 0.026 | 1.057 | 1.719 | 3.673 | 1.618 |
| | | | | MMA (1) + Decane-1-ol (2) | | | | | | |
| 298.15 | 0.184 | 0.033 | 0.037 | 1.856 | 5.169 | 0.037 | 1.408 | 2.394 | 6.652 | 12.433 |
| 308.15 | 0.179 | 0.034 | 0.044 | 1.520 | 3.892 | 0.044 | 1.179 | 1.876 | 4.912 | 5.190 |
| | | | | MMA (1) + Octane-2-ol (2) | | | | | | |
| 298.15 | 0.093 | 0.014 | 0.027 | 1.496 | 3.464 | 0.027 | 1.202 | 1.973 | 4.264 | 3.233 |
| 308.15 | 0.088 | 0.012 | 0.025 | 1.215 | 2.571 | 0.025 | 0.998 | 1.533 | 3.092 | 0.847 |
| | | | | MMA (1) + Decane-2-ol (2) | | | | | | |
| 298.15 | 0.188 | 0.037 | 0.048 | 1.808 | 4.879 | 0.048 | 1.383 | 2.286 | 6.244 | 10.507 |
| 308.15 | 0.185 | 0.038 | 0.055 | 1.445 | 3.500 | 0.055 | 1.137 | 1.728 | 4.363 | 3.425 |

Jouyban [22-23] proposed model for correlating the density and viscosity of liquid mixtures at various temperatures.

The constants Aj calculated from the least square analysis are presented in Table 6 along with the average percentage deviation (APD). The proposed model provides reasonably accurate calculations for density and viscosity of binary liquid mixtures and used in data modeling.

**Table 6. Adjustable parameters of Eq (13) and (14) for MMA (1) + Alkane-1-ols (2) and MMA (1) + Alkane-2-ols (2).**

| Property | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $\sigma$ | APD |
|---|---|---|---|---|---|---|---|
| | | | MMA (1) + Octane-1-ol (2) | | | | |
| $\rho$ / (g.cm$^{-3)}$ | -16.4802 | -2.7146 | -0.5244 | -0.5479 | 0.0619 | 4.0617 | 0.0212 |
| $\eta$ / (mPa.s) | -0.3227 | 0.3503 | 1.4463 | -2.1352 | -3.5058 | -2.7374 | 0.0183 |
| | | | MMA (1) + Decane-1-ol (2) | | | | |
| $\rho$ / (g.cm$^{-3)}$ | -22.8485 | -5.8312 | -1.7246 | -0.9070 | 0.2586 | 5.3388 | 0.0277 |
| $\eta$ / (mPa.s) | 1.1421 | -6.8746 | -22.1039 | 19.1150 | 41.4104 | 3.8039 | 0.1296 |
| | | | MMA (1) + Octane-2-ol (2) | | | | |
| $\rho$ / (g.cm$^{-3)}$ | -16.9505 | -2.7076 | 0.3434 | -0.8721 | -1.9710 | 4.1461 | 0.0192 |
| $\eta$ / (mPa.s) | -0.2333 | -0.6186 | -0.4581 | 0.7979 | 0.7709 | 2.3693 | 0.0189 |
| | | | MMA (1) + Decane-2-ol (2) | | | | |
| $\rho$ / (g.cm$^{-3)}$ | -24.0460 | -6.1348 | -1.3152 | -0.9964 | -0.8606 | 5.5675 | 0.0138 |
| $\eta$ / (mPa.s) | -0.1447 | -0.4685 | -0.0426 | 0.0230 | -0.0949 | 3.4120 | 0.0241 |

## RESULTS AND DISCUSSION

A systematic increase in $V^E$ is noted with the rise in the carbon chain length of 1-alcohols from octane-1-ol to decane-1-ol and octane-2-ol to decane-2-ol at both temperatures in all the binary mixtures. Table 2 reveals that the values of the excess molar volumes of alkane-2-ols are lower than the alkane-1-ols. As far as we are aware, there are no literature data on any of properties for the binary mixtures of MMA + octane-1-ol, decane-1-ol, octane-2-ol and decane-2-ol with which we can compare our results.

A graphical comparison of excess molar volume ($V^E$) results at 298.15 K for binary mixtures of each alkane-1-ols and alkane-2-ols with methyl methacrylate given in Fig. 1.

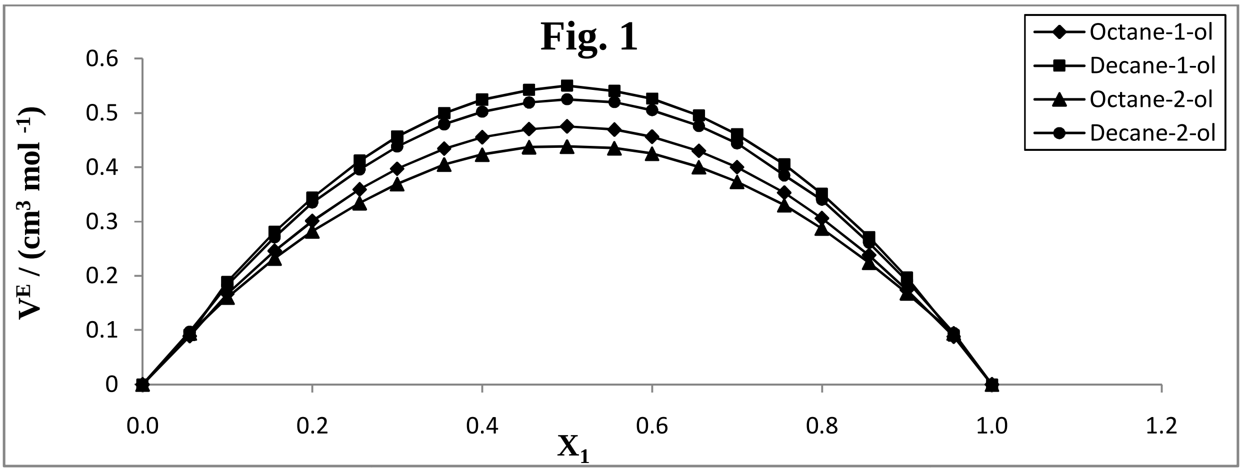

**Figure 1. Variation of excess molar volumes with MMA mole fraction for binary mixtures of MMA + alkane-1-ols and alkane-2-ols at 298.15 K.**

Excess molar volumes can be considered as arising from three types of interactions between the component molecules:- (a) Physical interaction consisting mainly of dispersion forces or weak dipole interaction and making a positive contribution, (b) Chemical or specific interactions which include charge transfer forming hydrogen bonds and other complex forming interactions resulting in a negative contribution, (c) Negative contribution is also possible due to difference in size and shapes of component molecules of mixtures. Positive values of excess molar volumes can be visualized as being due to a closer approach of unlike molecules having significantly different molecular size. Due to presence of nonpolar molecule like acrylic esters, H-bonding in alcohols breaks and system shows weak intermolecular interactions. Positive values of $V^E$ show volume expansion due to rupture of H-bonds in self associated alcohols.

The observed large negative values of viscosity deviation (Δη) in general indicate a high dilution of alkane-1-ol and alkane-2-ol viscosities in presence of acrylic esters in Fig. 2, which shows values of deviation in viscosities of alkane-2-ols are slightly higher than alkane-1-ols.

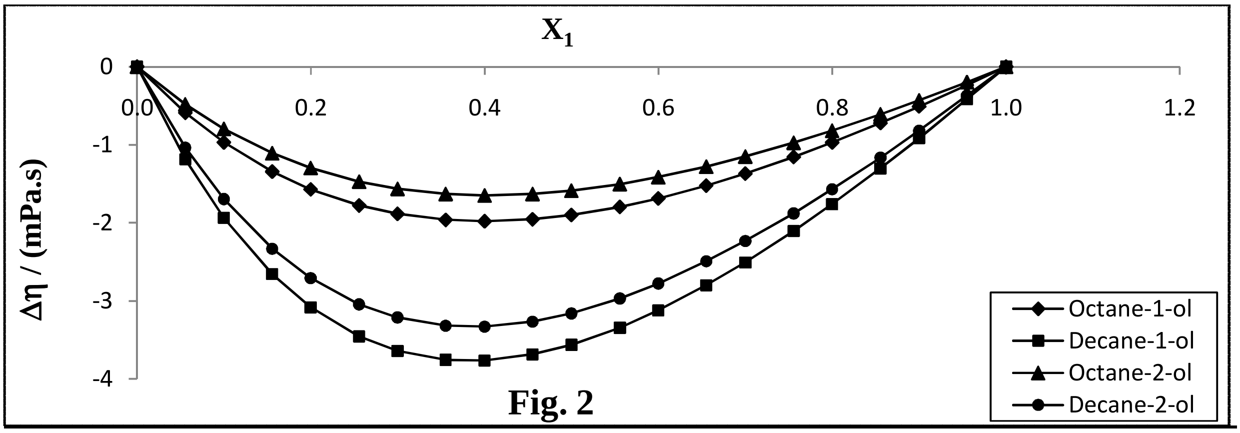

**Figure 2. Variation of deviation in viscosity with MMA mole fraction for binary mixtures of MMA + alkane-1-ols and alkane-2-ols at 298.15 K.**

The decrease in viscosity values can be ascribed to the structure breaking-up of these alkanols associates by unlike ester species. This result is also attributed to rupture of hydrogen bonds between alkane-1-ols and alkane-2-ols molecules by methyl methacrylate to be based on negative excess viscosities. This type of interaction seems to be dominant when the share of ester in the mixture is small. 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 is observed in binary liquid mixture of methyl methacrylate with branched alcohol.

The terms $H_{12}$, Wvis, $G_{12}$, $T_{12}$, $\alpha_{12}$, $\alpha_{21}$, $Z_{12}$, $Z_{21}$, $Z_{1112}$, $Z_{1122}$ and $Z_{2221}$ in above Eqs 5 to 11 have been considered as adjustable parameters and were estimated by a non-linear regression analysis based on a least-squares method. These equations are particularly selected because the characteristic constant parameter $G_{12}$ allows for the positive and negative deviations from the additivity rule. Table 4 and 5 includes models used to correlate mixture viscosity shows different values of their standard deviations. Table 4 shows that, out of all four different equations used to correlate experimental data of mixture viscosity standard deviation of $G_{12}$ parameter is lowest than any other equations. Hence, Grunberg-Nissan equation is more convenient and fits well. The order of their correlating ability is $T_{12} < H_{12} <$ Wvis $< G_{12}$. Table 4 also shows that the values of interaction parameters $H_{12}$, Wvis, $G_{12}$ and $T_{12}$ for alkane-1-ols are higher than alkane-2-ols.

In the similar way, in Table 5 among Heric–Brewer, McAllister's three and four body models the values of $\alpha_{12}$, $\alpha_{21}$, $Z_{12}$, $Z_{21}$, $Z_{1112}$, $Z_{1122}$ and $Z_{2221}$ adjustable parameters positive, supporting weak type of molecular interactions for all the four binary liquid mixtures. In these three types of models, Heric–Brewer and McAllister's three body models shows lower and equal values of their standard deviations and hence convenient than McAllister's four body model.

## CONCLUSION

Positive excess molar volumes explain systematic variations of methyl methacrylate with alkane-1-ols and alkane-2-ols species suggests the dominance of non-specific interactions. As the carbon chain length of the alkane-1-ols and alkane-2-ols increases, the steric factors prevent geometrical fitting and thus the excess molar volumes are found to be positive. The free volume difference and interstitial accommodation of smaller molecules are chief factors for negative excess molar volumes. In higher alcohols, geometrical fitting of one into other is negligibly small; therefore association decreases with increase in chain length of alcohols. Negative values of deviations in viscosities 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.

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