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Theoretical evaluation of density and viscosity of binary liquid mixture of acrylic esters with dodecane-1-ol at 308.15 K

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ABSTRACT

New experimental thermodynamic data involving density and viscosity of binary liquid mixture containing methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate with dodecane-1-ol at 308.15 K temperature and at atmospheric pressure have been measured. These experimental values were correlated using Jouyban-Acree model. These basic parameters further used to evaluate excess molar volume and deviation in viscosity of binary systems and these values were fitted to Redlich-Kister polynomial equation. The mixture viscosities were correlated by Hind, Choudhary-Katti, Grunberg-Nissan, Tamura and Kurata, Heric-Brewer two body model, McAllister three and four body model equations. Graphical presentation of excess molar volumes was found to be positive and deviations in viscosity were found to be negative for all the binary liquid mixtures 308.15 K.

Keywords: Acrylates, Alkanol, Choudhary-Katti, Heric-Brewer, Hind, Tamura and Kurata

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1. Introduction

Thermodynamic properties are also important in designing industrial equipments with better precision. There has been an increasing interest in study of molecular interactions and a number of experimental techniques have been used to investigate interactions between components of binary liquid mixtures. Traditional theories of solutions dwell exclusively on two aspects of liquid mixtures. One of these is the entropy associated with dispersion of two molecular species or of their constituent elements in case of complex molecules, among one another. A lattice model often serves as device for estimating this “combinational entropy”.

The other aspect relates to interactions between unlike and like neighbors. Treatment of properties of liquid mixtures has progressed little beyond level of interpretation possible within framework supported by these two considerations alone [1, 2]. There are two principal reasons for great amount of experimental and theoretical work on properties of liquid mixtures. The first is that they provide one way of studying physical forces acting between two molecules of different species, and second for study of mixtures, is appearance of new phenomenon (interactions) which are not present in pure liquids. The most interesting of these are, new types phase equilibrium which arise from extra degree of freedom introduced by possibility of varying properties of components.

The equilibrium properties of a liquid mixture are strongly dependent on its local structure, often expressed in terms such 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

2. 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.

The 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 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 ± 0.01 mg. Care was taken to avoid evaporation and contamination during mixing. The estimated uncertainty in mole fraction was $< 1 \times 10^{-4}$. Densities of solutions were measured using a single capillary pycnometer made up of borosil glass with a bulb

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 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].

The 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 and 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. In view of these considerations, it is planned to study liquid-liquid binary systems containing polar and hydrogen bonded or nonpolar liquids in association with industrially as well as biologically important solvent at 308.15 K temperature over entire range of compositions.

of 8 cm³ and capillary with an 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/cm³.

Dynamic viscosities were measured using an Ubbelohde suspended level viscometer calibrated with conductivity water. An electronic digital stop watch with readability of ± 0.01 s was used for flow time measurements. At least three repetitions of each data reproducible to ± 0.05 s were obtained and results were averaged. Since all flow times were greater than 300 s and capillary radius (0.1 mm) was far less than its length (50 to 60) mm, kinetic energy and end corrections, respectively, were found to be negligible. The uncertainties in dynamic viscosities were of the order of ± 0.003 m Pa.s. A comparison of measured values of pure components with literature values as presented in Table 1 shows a good agreement.

Table 1: Densities (ρ) and Viscosities (η) for Pure Components at 308.15 K.

Component	ρ / (g.m ⁻³)		η / (mPa.s)	
	Expt	Lit.	Expt	Lit.
Dodecane-1-ol	0.82309	0.82170 [3]	11.621	11.315 [3]
Methyl Acrylate	0.93561	0.93560 [3]	0.390	0.391 [3]
Ethyl Acrylate	0.90400	0.90460 [3]	0.456	0.455 [3]
Butyl Acrylate	0.88546	0.88460 [3]	0.684	0.684 [3]
Methyl Methacrylate	0.92571	0.92574 [4]	0.514	---

3. Results and Discussion

Density and viscosity measurements were performed with repetitions 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 308.15 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 ρ_{12} is density of mixture and x_1, M_1, ρ_1 , and x_2, M_2, ρ_2 are mole fraction, molecular weight and density of pure components 1 and 2, respectively. The 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 $100 \text{ cm}^3 \text{ mol}^{-1}$) their difference is usually smaller by two to three orders of magnitude and thus may carry a significantly larger error.

The 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 η_{12} is viscosity of mixture and x_1, x_2 and η_1, η_2 are mole fraction and viscosity of pure components 1 and 2, respectively [5]. Experimental values of densities (ρ), excess molar volumes (V^E), viscosities (η) and viscosity deviations ($\Delta \eta$) of these mixtures at 308.15 K are listed in Table 2.

Table 2: Densities (ρ), Excess Molar Volumes (V^E), Viscosities (η) and Viscosity Deviation ($\Delta \eta$) for Acrylates (1) + Dodecane-1-ol (2) at 308.15 K.

x_1	V^E			
	(g.cm ⁻³)	(cm ³ mol ⁻¹)	(mPa.s)	(mPa.s)
	MA (1) + Dodecane-1-ol (2)			
0	0.82309	0.000	11.621	0.000
0.0554	0.82506	0.173	9.627	-1.371
0.1000	0.82714	0.209	8.277	-2.221
0.1555	0.82970	0.304	6.855	-3.020
0.1998	0.83191	0.370	5.898	-3.479
0.2554	0.83495	0.439	4.883	-3.869
0.2999	0.83759	0.485	4.199	-4.054
0.3554	0.84120	0.529	3.478	-4.152
0.3999	0.84436	0.554	2.990	-4.140
0.4553	0.84869	0.572	2.477	-4.030

0.5000	0.85252	0.576	2.129	-3.877
0.5557	0.85779	0.569	1.762	-3.618
0.5999	0.86242	0.554	1.517	-3.367
0.6546	0.86878	0.521	1.260	-3.010
0.6999	0.87464	0.484	1.080	-2.681
0.7553	0.88268	0.427	0.895	-2.243
0.7999	0.88999	0.369	0.769	-1.868
0.8555	0.90026	0.286	0.637	-1.377
0.8999	0.90964	0.208	0.548	-0.966
0.9555	0.92311	0.099	0.453	-0.436
1	0.93561	0.000	0.390	0.000
EA (1) + Dodecane-1-ol (2)				
0	0.82309	0.000	11.621	0.000
0.0555	0.82503	0.085	9.710	-1.292
0.0998	0.82664	0.159	8.412	-2.095
0.1555	0.82884	0.234	7.024	-2.861
0.1997	0.83072	0.286	6.087	-3.304
0.2554	0.83328	0.340	5.082	-3.687
0.2998	0.83546	0.376	4.402	-3.872
0.3555	0.83843	0.410	3.675	-3.977
0.3998	0.84098	0.429	3.183	-3.973
0.4554	0.84443	0.443	2.659	-3.877
0.4999	0.84739	0.451	2.303	-3.737
0.5554	0.85147	0.440	1.924	-3.496
0.5999	0.85500	0.427	1.665	-3.257
0.6550	0.85977	0.400	1.393	-2.914
0.6999	0.86401	0.371	1.205	-2.602
0.7554	0.86975	0.324	1.006	-2.180
0.8000	0.87482	0.278	0.871	-1.818
0.8555	0.88177	0.211	0.728	-1.342
0.9000	0.88794	0.149	0.630	-0.943
0.9555	0.89665	0.041	0.527	-0.427

1	0.90400	0.000	0.456	0.000
BA (1) + Dodecane-1-ol (2)				
0	0.82309	0.000	11.621	0.000
0.0554	0.82509	0.070	9.932	-1.083
0.0997	0.82679	0.112	8.761	-1.770
0.1555	0.82903	0.163	7.481	-2.440
0.1998	0.83090	0.198	6.597	-2.838
0.2555	0.83336	0.235	5.634	-3.192
0.2999	0.83542	0.260	4.969	-3.372
0.3555	0.83814	0.284	4.245	-3.488
0.3998	0.84043	0.297	3.744	-3.504
0.4555	0.84345	0.308	3.198	-3.442
0.4999	0.84601	0.307	2.820	-3.334
0.5555	0.84934	0.308	2.409	-3.137
0.6000	0.85218	0.300	2.123	-2.935
0.6554	0.85592	0.283	1.815	-2.638
0.6999	0.85908	0.265	1.600	-2.366
0.7553	0.86325	0.235	1.368	-1.993
0.8000	0.86682	0.206	1.205	-1.667
0.8555	0.87152	0.163	1.030	-1.235
0.8999	0.87552	0.122	0.908	-0.871
0.9555	0.88073	0.083	0.776	-0.395
1	0.88546	0.000	0.684	0.000
MMA (1) + Dodecane-1-ol (2)				
0	0.82309	0.000	11.621	0.000
0.0555	0.82553	0.095	9.774	-1.230
0.0998	0.82758	0.175	8.514	-1.999
0.1555	0.83036	0.257	7.156	-2.738
0.1997	0.83272	0.315	6.235	-3.169
0.2554	0.83594	0.375	5.240	-3.544

0.2998	0.83869	0.415	4.563	-3.729
0.3555	0.84242	0.453	3.835	-3.838
0.3998	0.84562	0.475	3.340	-3.840
0.4554	0.84996	0.492	2.808	-3.755
0.4999	0.85372	0.496	2.444	-3.624
0.5554	0.85882	0.491	2.056	-3.396
0.5999	0.86327	0.478	1.789	-3.168
0.6550	0.86927	0.450	1.507	-2.839
0.6999	0.87462	0.419	1.310	-2.537
0.7554	0.88188	0.370	1.102	-2.129
0.8000	0.88829	0.321	0.959	-1.777
0.8555	0.89711	0.250	0.806	-1.313
0.9000	0.90495	0.184	0.702	-0.923
0.9555	0.91581	0.097	0.590	-0.418
1	0.92571	0.000	0.514	0.000

Excess molar volumes and deviations in viscosity were then fitted to Redlich- Kister equation of type,

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

Where Y is either V^E or η 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 (σ).

σ Was calculated using relation,

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

Where N is number of data points and n is number of coefficients [6]. The calculated values of coefficients a_i along with standard deviations (σ) are given in Table 3.

Table 3: Adjustable parameters of Eq 3 and 4 for Excess Functions for Acrylates (1) + Dodecane-1-ol (2) at 308.15 K.

Property	a_0	a_1	a_2	a_3	a_4	σ
MA (1) + Dodecane-1-ol (2)						
$V^E/(\text{cm}^3 \text{mol}^{-1})$	2.3471	0.2754	-0.7298	-0.8226	1.4766	0.01588
$\eta/(\text{mPa.s})$	-15.5081	7.9980	-3.2148	1.1397	-0.3549	0.00069
EA (1) + Dodecane-1-ol (2)						
$V^E/(\text{cm}^3 \text{mol}^{-1})$	1.7493	0.1175	0.6278	-0.4648	-1.3558	0.01009
$\eta/(\text{mPa.s})$	-14.9466	7.4138	-2.8996	0.9632	-0.2168	0.00049
BA (1) + Dodecane-1-ol (2)						

$V^E/(\text{cm}^3\text{mol}^{-1})$	1.2720	-0.1070	-0.4902	0.4466	1.0722	0.00889
$\eta/(\text{mPa}\cdot\text{s})$	-13.3350	5.8993	-2.0166	0.5897	-0.1397	0.00042
MMA (1) + Dodecane-1-ol (2)						
$V^E/(\text{cm}^3\text{mol}^{-1})$	1.9919	-0.0737	-0.1007	0.3214	0.1975	0.00406
$\eta/(\text{mPa}\cdot\text{s})$	-14.4969	6.9648	-2.5930	0.8362	-0.2418	0.00037

Several relations have been proposed to evaluate dynamic viscosity (η) 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.

Choudhary-Katti [8] proposed following equation,

$$\ln(\eta_{12}/\eta_m) = x_1 \ln(\eta_1/\eta_m) + x_2 \ln(\eta_2/\eta_m) + x_1x_2[W_{vis}/(RT)] \quad (6)$$

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

Grunberg-Nissan [9] provided following empirical equation containing one adjustable parameter. The expression is,

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

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

Tamura and Kurata [10] developed expression for viscosity of binary mixtures as,

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

Where T_{12} is interaction parameter, ϕ_1 and ϕ_2 are volume fractions. These are presented with their standard percentage deviation (%) in Table 4.

Table 4: Adjustable parameters of Eq 5, 6, 7, 8 and 12 for Acrylates (1) + Dodecane-1-ol (2) at 308.15 K

H_{12}	W_{vis}	G_{12}	T_{12}
MA (1) + Dodecane-1-ol (2)			
-2.081	49.411	0.415	0.887
0.000	0.040	-4.582	2.725
EA (1) + Dodecane-1-ol (2)			
-1.731	40.504	0.263	0.438
-0.001	0.027	3.683	75.554
BA (1) + Dodecane-1-ol (2)			
-0.720	23.500	0.106	0.125
0.000	0.021	-1.903	37.027
MMA (1) + Dodecane-1-ol (2)			
-1.448	34.633	0.281	0.489
-0.001	0.028	-3.441	66.442

Heric – Brewer [11] proposed two parameter model of following form,

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln(x_1 M_1 + x_2 M_2) + x_1x_2[\alpha_{12} + \alpha_{21}(x_1 - x_2)]$$

Where M_1 and M_2 are molecular weights of components of 1 and 2, α_{12} and α_{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 [12] was widely used to correlate kinematic viscosity (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,

$$\ln \eta_{12} = x_1^3 \ln \eta_1 + x_2^3 \ln \eta_2 + 3x_1^2x_2 \ln Z_{12} + 3x_1x_2^2 \ln Z_{21} - \ln [x_1 + (x_2M_2/M_1)] + 3x_1^2x_2 \ln [(2/3) + (M_2/3M_1)] + 3x_1x_2^2 \ln [(1/3) + (2M_2/3M_1)] + x_2^3 \ln (M_2/M_1) \quad (10)$$

Similarly, four body models was defined by relation,

$$\ln \eta_{12} = x_1^4 \ln \eta_1 + 4x_1^3x_2 \ln Z_{1112} + 6x_1^2x_2^2 \ln Z_{1122} + 4x_1x_2^3 \ln Z_{2221} + x_2^4 \ln \eta_2 - \ln [x_1 + x_2(M_2/M_1)] + 4x_1^3x_2 \ln [(3+M_2/M_1)/4] + 6x_1^2x_2^2 \ln [1 + M_2/M_1]/2 + 4x_1x_2^3 \ln [(1+3M_2/M_1)/4] + x_2^4 \ln (M_2/M_1) \quad (11)$$

Where Z_{12} , Z_{21} , Z_{1112} , Z_{1122} and Z_{2221} are model parameters and M_i and η_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 (%) using relation,

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

Where k represents number of numerical coefficients in respective equations.

The terms H_{12} , W_{vis} , G_{12} , T_{12} , α_{12} , α_{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 [13]. These are presented with their standard percentage deviation (%) in Table 5.

Table 5: Adjustable parameters of Eq 9, 10, 11 and 12 for Acrylates (1) + Dodecane-1-ol (2) at 308.15 K.

	Z_{12}	Z_{21}	Z_{1112}	Z_{1122}	Z_{2221}					
MA (1) + Dodecane-1-ol (2)										
0.418	0.123	0.171	1.505	4.536	0.171	1.088	1.615	6.039	9.352	
EA (1) + Dodecane-1-ol (2)										
0.265	0.064	-0.071	1.633	4.780	0.071	1.214	1.928	6.270	10.256	
BA (1) + Dodecane-1-ol (2)										
0.107	0.018	0.034	2.088	5.439	0.034	1.627	2.733	6.905	14.287	
MMA (1) + Dodecane-1-ol (2)										
0.283	0.067	0.069	1.754	4.958	0.069	1.311	2.040	6.437	10.994	

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

$$\ln y_{mT} = f_1 \ln y_{1T} + f_2 \ln y_{2T} + f_3 f_2 [A_j (f_1 - f_2)^j / T] \quad (13)$$

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 proposed model provides reasonably accurate calculations for density and viscosity of binary liquid mixtures and model could be used in data modeling [14, 15]. 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	APD	
MA (1) + Dodecane-1-ol (2)							
$\rho / (\text{g} \cdot \text{m}^{-3})$	-35.8822	-14.4987	-4.7883	-1.6088	-3.1256	8.0418	0.0355
$\eta / (\text{mPa} \cdot \text{s})$	-0.3910	1.2563	4.4627	-4.1517	-8.5936	4.7799	0.0249
EA (1) + Dodecane-1-ol (2)							
$\rho / (\text{g} \cdot \text{m}^{-3})$	-22.1031	-7.5597	-3.6048	0.4497	2.3879	5.2287	0.0453
$\eta / (\text{mPa} \cdot \text{s})$	-0.1873	0.0605	-0.5018	-1.7158	-0.9880	4.9217	0.0158
BA (1) + Dodecane-1-ol (2)							
$\rho / (\text{g} \cdot \text{m}^{-3})$	-11.4653	-2.1140	0.4519	-1.0777	-2.1107	3.0751	0.0216

/ (mPa.s)	-0.1818	0.2020	-0.0970	-1.2300	-0.9196	5.3158	0.0145
/ (g.m ⁻³)	-27.6933	-9.0012	-2.8447	-1.8270	-0.8159	6.3393	0.0335
/ (mPa.s)	-0.2253	0.1431	0.4657	-1.4437	-1.9474	5.0259	0.0138

A graphical comparison of dependence of excess molar volume (V^E) at 308.15 K for binary mixtures of each acrylic ester with dodecane-1-ol is represented in Fig. 1.

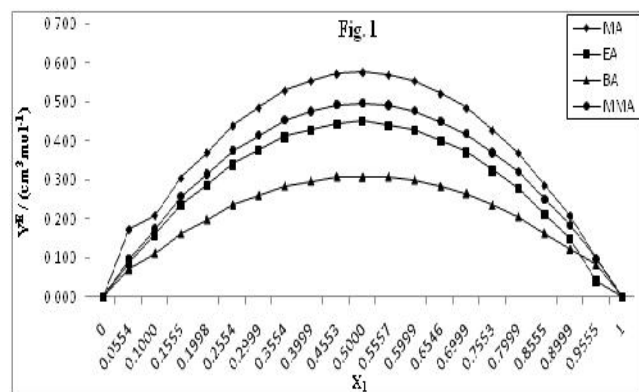


Figure 1: Variation of excess molar volumes (V^E) for Acrylates (1) + Dodecane-1-ol (2) at 308.15 K.

The values of excess molar volumes (V^E) are found to be positive for all systems, where dispersion, induction and dipolar forces are operating, whereas existence of specific interactions between mixing components of various binary systems tends to make excess molar volumes negative [16]. Since, normally dispersive interaction between unlike molecules is weaker than those between like molecules, it is reasonable that they contribute positively [17, 18] to excess molar volumes. In these systems, excess molar volumes decrease with increase in carbon atom of alkanols, which results in solute-solvent interaction between mixing components. Changes in excess molar volume takes place during mixing which is result of several effects that operate in same or opposite directions. The most important ones are:

1. A positive effect caused by break-up of structure of one or both components originating from nonchemical or chemical interactions, such as, hydrogen bonding or complex formatting interactions; such as, self-association.

Viscosity deviations may be explained in terms of relative strength of molecular interactions between like and unlike molecules. The sign and magnitude of Δ depends on combined effect of factors like molecular size and shape of components in addition to operating, values of viscosity deviation are found to be negative, whereas existence of specific interactions between mixing components of various binary systems tends to make intermolecular forces [23]. For systems where dispersion, induction and dipolar forces are present shows viscosity deviations positive. Negative values of Δ over whole composition range suggest that, viscosities of associates formed between unlike molecules

2. A negative one, due to physical interactions (hetero association) or geometric fitting of on component into second, leading to a more compact packing (interstitial accommodation). The second contribution becomes more important with increasing sphericity of solute molecule and higher molar volume of solvent [19].

Excess thermodynamic properties reflect interactions that take place between solute-solute, solute-solvent and solvent-solvent species. Inspection of results indicates that excess molar volumes are positive for binary liquid systems (probably as a result of large dipole moments of solvents) and become smaller as solute becomes more branched or longer. The solutes studied differ from one another by molecular size, geometry, dipole moment, ability to form hydrogen bonds, etc. The excess molar volumes of a solution are sensitive to all of these factors, which may act in opposite directions [20]. The magnitude of density of a pure compound is a strong indication of attraction forces acting between and within its molecule [21]. Positive excess molar volumes may be due to compensation between strong like interactions such as those present in alkanols and equally strong unlike H-bond interactions such as those present between alkanols and esters (acrylates). Negative excess molar volumes will occur when unlike interactions prevail over self-association, particularly when packing effects such as free volume, interstitial accommodation, etc. may be neglected. Binary mixtures are an important class of solvents, solutions and behavior of some of their physical properties is not still clear. For example, a solution presents positive excess molar volumes and excess dynamic viscosity is negative, vice versa. Results indicates that increase in molar volume of mixture and positive contribution to excess volume is due to a disruption of pure component liquid [22].

are relatively less than those of pure components, which is exhibited by decreased values of viscosity with mole fraction. Decrease in viscosity attributed to breaking of dipolar association of alkanols 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 decrease trend of viscosity. In case of polar and non-polar binary liquid mixtures forces between pairs of unlike molecules are far less as compared to forces between pairs of like molecules and that is why mixture is more fluid that is less viscous. Negative deviations from rectilinear dependence on mole fraction may also occur

where dispersion forces are dominant, particularly for systems having different molecular size as in this case. This

More specifically, negative values can be explained by three factors:

- Breaking of associated molecules of alkanols.
- Formation of weak hydrogen bonding between acrylates and alkanols molecules.

explanation is also supported by large positive values of Δ reported by others for polar-polar mixtures.

- Dipole-dipole induced interactions between acrylates and alkanols

A graphical comparison of dependence of deviation in viscosity ($\Delta\eta$) at 308.15 K for binary mixtures of each acrylic ester with dodecane-1-ol is represented in Fig. 2.

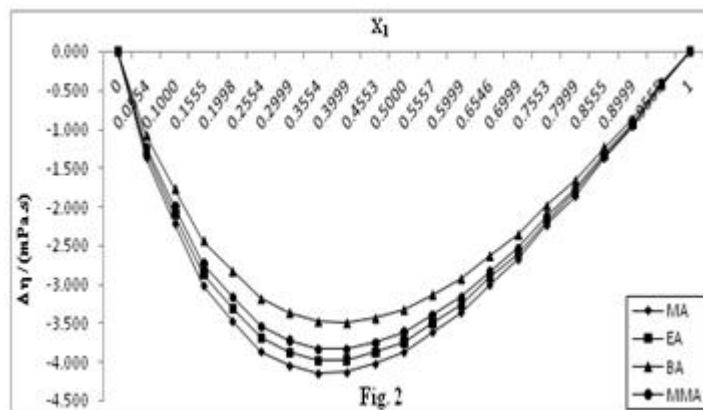


Figure 2: Variation of deviation in viscosity ($\Delta\eta$) for Acrylates (1) + Dodecane-1-ol (2) at 308.15 K.

4. Conclusion

Observed positive values of excess molar volume (V^E) and deviation in viscosity ($\Delta\eta$) 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 dodecane-1-ol.

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