



Thermo acoustic study of acrylates with decane-1-ol

Patil Sujata S. and Mirgane Sunil R.*

PG Dept. of Chemistry, J.E.S. College, Jalna 431 203, MS, INDIA

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Abstract

Thermodynamic data involving viscosity of binary liquid mixture methyl acrylate, ethyl acrylate and butyl acrylate with decane-1-ol at 298.15 and 308.15 K temperatures and at atmospheric pressure have been measured. Values of viscosity further used to calculate deviation in viscosity of binary systems and were fitted to Redlich-Kister polynomial equation. Experimental viscosity data used to correlate with different semi-empirical equations such as Hind, Grunberg-Nissan, Tamura-Kurata, Choudhary-Katti, Heric-Brewer and McAllister three and four body model equations. Calculated deviations in viscosity were found to be negative for all binary liquid mixtures at both temperatures.

Keywords Redlich-Kister equation, Hind, Grunberg-Nissan, Tamura-Kurata, McAllister three and four body model, binary liquid mixtures.

Introduction

In the recent years, much importance has been given to the behavior of mixed solvents rather than a single solvent because of their wide range of applications in many chemical, industrial and biological processes. The physico-chemical data are often required in many industrial processes (flow, mass transfer or heat transfer calculation, polymerization, solvolysis, etc.) and also leads to the formulations of a large number of methods for correlating or predicting the physical properties. Therefore in view of practical importance of mixed solvents, a deeper knowledge of their solution structure and intermolecular interactions between component molecules at molecular level thus becomes essential. Recently researchers in this field have been focusing their interest more sharply on the molecular structure along with some representative macroscopic property that serves to characterize it. The composition and temperature dependence of volumetric, acoustic, transport and surface properties of associated liquid system provides substantial information of the molecular influence on the intensity of the intermolecular interactions among component molecules and can be used as a powerful tool for studying intermolecular interactions in these systems.

Thus, keeping both industrial and scientific interests in mind, here we report measured densities (ρ) and ultrasonic velocity (u) of binary liquid mixtures of acrylic esters with decane-1-ol at 298.15 and 308.15 K temperatures.

Material and Methods

All chemicals decane-1-ol, methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA) used of mass fraction purities > 0.998 (E-Merck) were double distilled, middle fraction collected of all liquids was stored over 0.4 nm molecular sieves. Masses were recorded on a Mettler balance, with an accuracy of ± 0.01 mg. Estimated uncertainty in mole fraction was $<1 \times 10^{-4}$. The

temperature was controlled using a constant temperature controlled water bath (Gemini Scientific Instruments, Chennai, India) having accuracy $\pm 0.02^\circ\text{C}$.

The dynamic viscosities were measured¹ using an Ubbelohde suspended level viscometer, calibrated with conductivity water. An electronic digital stop watch with readability of ± 0.01 s was used for the flow time measurements. At least three repetitions of each data reproducible to ± 0.05 s were obtained and the 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, the kinetic energy and end corrections, respectively, were found to be negligible. The accuracy in dynamic viscosities were of the order of ± 0.003 mPa.s. A comparison of measured values of viscosities of pure components with literature values in table 1 shows a good agreement.

The viscosity deviations ($\Delta\eta$) were calculated using equation,
$$\Delta\eta = \eta_{12} - x_1\eta_1 - x_2\eta_2 \quad (1)$$

where η_{12} is the viscosity of the mixture and x_1 , x_2 and η_1 , η_2 are the mole fraction and the viscosity of pure components 1 and 2 respectively.

Deviations in viscosity were fitted to Redlich-Kister² equation of the type,

$$Y = x_1x_2 \sum_i^n a_i (x_1 - x_2)^i \quad (2)$$

Where Y is $\Delta\eta$ and n is the degree of polynomial. Coefficient a_i was obtained by fitting equation (2) to experimental results using a least-squares regression method. In each case, the optimum number of coefficients is ascertained from an examination of the variation in standard deviation (σ). σ was calculated using the relation,

$$\sigma(Y) = \left[\frac{\sum (Y_{\text{exp}} - Y_{\text{calc}})^2}{N - n} \right]^{1/2} \quad (3)$$

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 the standard deviations (σ) are given in table 3.

Several semi-empirical relations have been proposed to evaluate the 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.

The expression for Hind³ equation is,

$$\eta_{12} = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2H_{12} \quad (4)$$

where H_{12} is the interaction parameter.

The expression for Choudhary-Katti⁴ equation is,

$$\ln(\eta_n V_m) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1 x_2 [W_{vis}/(RT)] \quad (5)$$

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

The expression for Grunberg-Nissan⁵ equation is,

$$\ln\eta_{12} = x_1 \ln\eta_1 + x_2 \ln\eta_2 + x_1 x_2 G_{12} \quad (6)$$

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

Tamura and Kurata⁶ developed expression for viscosity of binary mixtures as,

$$\eta = x_1\phi_1\eta_1 + x_2\phi_2\eta_2 + 2(x_1x_2\phi_1\phi_2)^{1/2}T_{12} \quad (7)$$

where T_{12} is the interaction parameter, ϕ_1 and ϕ_2 are the volume fractions. The calculated values of adjustable parameters H_{12} , W_{vis} , G_{12} and T_{12} with standard deviations (σ) calculated by equation (11) are given in table 4.

Heric-Brewer⁷ proposed two parameter model of the form,

$$\ln\eta = x_1 \ln\eta_1 + x_2 \ln\eta_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln(x_1 M_1 + x_2 M_2) + x_1 x_2 [\alpha_{12} + \alpha_{21}(x_1 - x_2)] \quad (8)$$

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 the least square method and other terms involved have their usual meaning.

McAllister's multibody interaction model⁸ was widely used to correlate kinematic viscosity (ν) data. 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 the relation,

$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3x_1^2 x_2 \ln Z_{12} + 3x_1 x_2^2 \ln Z_{21} - \ln[x_1 + (x_2 M_2/M_1)] + 3x_1^2 x_2 \ln[(2/3) + (M_2/3M_1)] + 3x_1 x_2^2 \ln[(1/3) + (2M_2/3M_1)] + x_2^3 \ln(M_2/M_1) \quad (9)$$

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

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

$$\ln[(3+M_2/M_1)/4] + 6x_1^2 x_2^2 \ln[(1+M_2/M_1)/2] + 4x_1 x_2^3 \ln[(1+3M_2/M_1)/4] + x_2^4 \ln(M_2/M_1) \quad (10)$$

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

To perform a numerical comparison of the correlating capability of above equation (4 to 10) we have calculated the standard percentage deviation (σ %) using the relation,

$$\sigma \% = [1/(\eta_{\text{expt}} - k) \times \sum (100(\eta_{\text{expt}} - \eta_{\text{cal}}) / \eta_{\text{expt}})^2]^{1/2} \quad (11)$$

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

The interaction parameters H_{12} , W_{vis} , G_{12} , T_{12} , α_{12} , α_{21} , Z_{12} , Z_{21} , Z_{1112} , Z_{1122} and Z_{2221} in the above Eq (4 to 10) have been considered as adjustable parameters, estimated by a non-linear regression analysis based on a least-squares method⁹. The parameters α_{12} , α_{21} , Z_{12} , Z_{21} , Z_{1112} , Z_{1122} and Z_{2221} are presented with their standard percentage deviation (σ %) in table 5.

Table-1
Viscosities (η) for Pure Components at T = (298.15 and 308.15) K

Property	T = 298.15 K		T = 308.15 K	
	Expt.	Lit.	Expt	Lit.
Decane-1-ol				
η (mPa.s)	11.793	11.790 ¹²	8.116	8.124 ¹²
Methyl Acrylate				
η (mPa.s)	0.449	0.449 ¹³	0.390	0.391 ¹³
Ethyl Acrylate				
η (mPa.s)	0.518	0.517 ¹³	0.456	0.455 ¹³
Butyl Acrylate				
η (mPa.s)	0.787	0.786 ¹³	0.684	0.684 ¹³

Table-2
Viscosities (η) and Viscosity Deviation ($\Delta\eta$) for Acrylates (1) + Decane-1-ol (2) at T= (298.15 and 308.15) K

X ₁	T = 298.15 K		T = 308.15 K	
	η	$\Delta\eta$	η	$\Delta\eta$
	(mPa.s)	(mPa.s)	(mPa.s)	(mPa.s)
MA (1) + Decane-1-ol (2)				
0	11.793	0	8.116	0
0.0552	9.846	-1.317	6.864	-0.823
0.0997	8.514	-2.148	5.997	-1.349
0.1555	7.095	-2.935	5.063	-1.852
0.1999	6.137	-3.389	4.424	-2.148
0.2554	5.118	-3.778	3.738	-2.405
0.3000	4.424	-3.966	3.265	-2.534
0.3555	3.689	-4.071	2.758	-2.611
0.3999	3.192	-4.065	2.411	-2.616
0.4538	2.676	-3.970	2.047	-2.563
0.4999	2.301	-3.820	1.779	-2.474
0.5554	1.919	-3.573	1.503	-2.322
0.5999	1.660	-3.327	1.313	-2.167
0.6550	1.386	-2.977	1.111	-1.945
0.6999	1.197	-2.656	0.970	-1.738
0.7555	0.998	-2.224	0.819	-1.460
0.7999	0.863	-1.856	0.716	-1.220
0.8555	0.720	-1.369	0.605	-0.902
0.8999	0.623	-0.962	0.528	-0.635
0.9555	0.519	-0.434	0.446	-0.287
1	0.449	0	0.390	0
EA (1) + Decane-1-ol (2)				
0	11.793	0	8.116	0
0.0554	9.917	-1.251	6.918	-0.773
0.0999	8.630	-2.036	6.087	-1.263
0.1553	7.257	-2.785	5.189	-1.737
0.1998	6.315	-3.223	4.565	-2.019
0.2556	5.305	-3.607	3.888	-2.270
0.2999	4.619	-3.793	3.422	-2.397
0.3554	3.883	-3.903	2.916	-2.477
0.4000	3.378	-3.905	2.565	-2.487
0.4555	2.840	-3.818	2.187	-2.440
0.4999	2.472	-3.684	1.924	-2.362
0.5554	2.078	-3.451	1.640	-2.221
0.5999	1.808	-3.221	1.442	-2.079
0.6555	1.520	-2.882	1.229	-1.865
0.6999	1.323	-2.578	1.082	-1.672
0.7556	1.112	-2.162	0.921	-1.407
0.7999	0.968	-1.805	0.811	-1.177
0.8555	0.814	-1.334	0.691	-0.872
0.8999	0.708	-0.939	0.608	-0.615
0.9555	0.595	-0.425	0.518	-0.279
1	0.518	0	0.456	0
BA (1) + Decane-1-ol (2)				
0	11.793	0	8.116	0
0.0555	10.148	-1.034	7.075	-0.629
0.0998	9.000	-1.694	6.340	-1.034
0.1556	7.740	-2.341	5.523	-1.437
0.1998	6.865	-2.729	4.950	-1.681
0.2554	5.906	-3.076	4.314	-1.904
0.3000	5.235	-3.257	3.864	-2.023
0.3556	4.503	-3.377	3.368	-2.106
0.3998	3.995	-3.398	3.018	-2.127
0.4555	3.436	-3.344	2.630	-2.101
0.5000	3.046	-3.244	2.356	-2.044
0.5555	2.621	-3.058	2.053	-1.934
0.5999	2.324	-2.866	1.840	-1.817
0.6555	1.999	-2.580	1.603	-1.641
0.6999	1.773	-2.317	1.437	-1.477
0.7554	1.525	-1.954	1.252	-1.250
0.7999	1.352	-1.637	1.122	-1.049
0.8545	1.167	-1.222	0.980	-0.786
0.8999	1.032	-0.857	0.876	-0.552
0.9550	0.889	-0.393	0.764	-0.255
1	0.787	0	0.684	0

Table-3
Adjustable parameters of Eq (2) and (3) for Viscosity Deviation ($\Delta\eta$) for binary liquid mixture of Acrylates (1) + Decane-1-ol (2) at T = (298.15 and 308.15) K

Property	T (K)	a_0	a_1	a_2	a_3	a_4	σ
MA (1) + Decane-1-ol (2)							
$\Delta\eta$ (mPa.s)	298.15	-15.2734	7.6920	-3.1350	0.8481	0.0227	0.00281
	308.15	-9.8918	4.6871	-1.7917	0.4135	0.0539	0.00203
EA (1) + Decane-1-ol (2)							
$\Delta\eta$ (mPa.s)	298.15	-14.7384	7.0946	-2.6375	0.8462	-0.2441	0.00095
	308.15	-9.4514	4.2371	-1.4541	0.4356	-0.1340	0.00083
BA (1) + Decane-1-ol (2)							
$\Delta\eta$ (mPa.s)	298.15	-12.9774	5.5119	-1.8073	0.5129	-0.1183	0.00043
	308.15	-8.1779	3.2097	-0.9600	0.2375	-0.0672	0.00033

Table-4
Adjustable parameters of Eq (4), (5), (6), (7) and (11) for binary liquid mixture of Acrylates (1) + Decane-1-ol (2) at T = (298.15 and 308.15) K

T (K)	H_{12}	σ	W_{vis}	σ	G_{12}	σ	T_{12}	σ
MA (1) + Decane-1-ol (2)								
298.15	-1.826	42.088	0.294	0.518	-0.001	0.032	-3.899	80.003
308.15	-0.868	31.002	0.288	0.506	-0.001	0.040	-2.254	60.118
EA (1) + Decane-1-ol (2)								
298.15	-1.484	34.942	0.170	0.229	0.000	0.024	-3.027	58.839
308.15	-0.589	25.056	0.163	0.207	-0.001	0.036	-1.616	43.010
BA (1) + Decane-1-ol (2)								
298.15	-0.382	19.667	0.049	0.037	-0.001	0.014	1.158	27.121
308.15	0.214	13.913	0.047	0.034	-0.001	0.023	0.305	19.538

Table-5
Adjustable parameters of Eq (8), (9), (10) and (11) for binary liquid mixture of Acrylates (1) + Decane-1-ol (2) at T = (298.15 and 308.15) K

T (K)	α_{12}	α_{21}	σ	Z_{12}	Z_{21}	σ	Z_{1112}	Z_{1122}	Z_{2221}	σ
MA (1) + Decane-1-ol (2)										
298.15	0.297	0.070	0.115	1.595	4.763	0.115	1.177	1.909	6.282	10.345
308.15	0.290	0.066	0.105	1.292	3.573	0.105	0.972	1.492	4.616	4.406
EA (1) + Decane-1-ol (2)										
298.15	0.170	0.029	0.040	1.730	4.988	0.040	1.304	2.268	6.478	11.515
308.15	0.163	0.026	0.039	1.414	3.758	0.039	1.089	1.784	4.778	4.765
BA (1) + Decane-1-ol (2)										
298.15	0.050	0.006	-0.021	2.258	5.693	0.021	1.785	3.201	7.166	16.963
308.15	0.046	0.003	-0.023	1.828	4.273	0.023	1.472	2.504	5.266	7.032

Results and Discussion

A graphical representations of the viscosity deviations ($\Delta\eta$) for the binary mixtures of acrylic esters with decane-1-ol at 298.15 and 308.15 K are shown in figure 1 and figure 2, respectively. It is known that the strength of the intermolecular electric donor-acceptor interaction is not the only factor that influences the viscosity deviation in liquid mixtures. The molecular size and shape of the components and average degree of association of the mixture are equally important factors. In the present investigation the negative values of $\Delta\eta$ may be attributed to the same effect. Weak specific interaction may be present or dispersion forces may be operating in the systems. The observed large negative values of $\Delta\eta$ in general indicate a high dilution of

1-alkanol viscosities in the presence of the ester species. The decrease in viscosity values can be ascribed to the breaking up of decane-1-ol associates by unlike acrylic ester molecules. This type of interaction seems to be dominant when the share of ester in the mixture is small. In the ester-rich mixtures dispersion interactions are expected to be replaced by ester-ester like interactions indicated by the closeness of the viscosity values.

Table 3 shows that the standard deviations are very close to each other at 298.15 and 308.15 K. The Redlich-Kister equation was originally developed to correlate the excess Gibb's energy function and to calculate the values of the activity coefficients. It turned out to be such a powerful and versatile correlating tool that its use has been extended to other properties, particularly

excess molar volumes and excess enthalpies of mixing. It suffers from the important drawback that the values of the adjustable parameters change as the number in the series is increased, so that no physical interpretation can be attached to them¹⁰. Redlich-Kister regressor is very powerful and frequently used to correlate vapor-liquid equilibrium data and excess properties¹¹.

Experimental viscosity data used to correlate with different semi-empirical equations. Their parameters with standard errors are summarized in table 4. All these equations are having single parameter. From the equations such as Hind (H_{12}), Choudhary-Katti (W_{vis}), Grunberg-Nissan (G_{12}), Tamura and Kurata (T_{12}); the least standard error is observed for Grunberg-Nissan equation parameter. Therefore the order of correlating ability of these equations will be $G_{12} > W_{vis} > H_{12} > T_{12}$. The interaction parameter derived from the Tamura-Kurata equation shows

highest values of the standard errors in all the binary liquid mixtures in all the sections.

Parameters evaluated from the equations proposed by Heric-Brewer, McAllister three and four body models are summarized with their standard percentage deviations in Table 5. The values of standard errors of Heric-Brewer and McAllister three body model are exactly equal and higher as compared to standard error of McAllister four body model for the binary liquid mixtures of methyl acrylate and ethyl acrylate with decane-1-ol at both temperatures. Therefore the order of correlating ability of these equations in the form of their parameters is, $(\alpha_{12}, \alpha_{21}) = (Z_{12}, Z_{21}) > (Z_{1112}, Z_{1122}, Z_{2221})$. For butyl acrylate + decane-1-ol the correlating ability of the Heric-Brewer equation is good as compared to the McAllister three body models. Hence, in this system the order of the correlating ability of various models can be given as, $(\alpha_{12}, \alpha_{21}) > (Z_{12}, Z_{21}) > (Z_{1112}, Z_{1122}, Z_{2221})$.

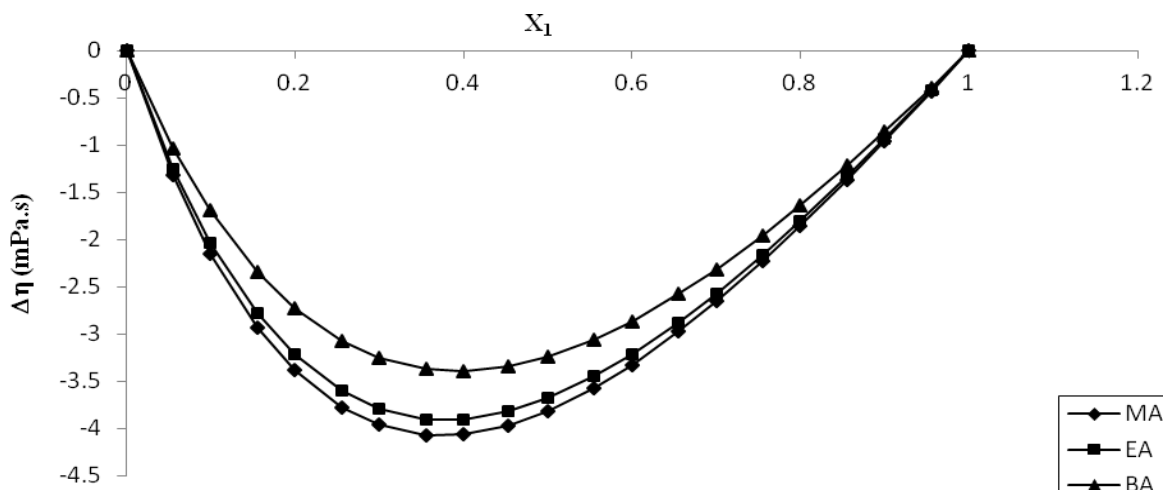


Figure-1
 Variation of deviation in viscosity for Acrylates (1) + Decane-1-ol (2) at 298.15 K

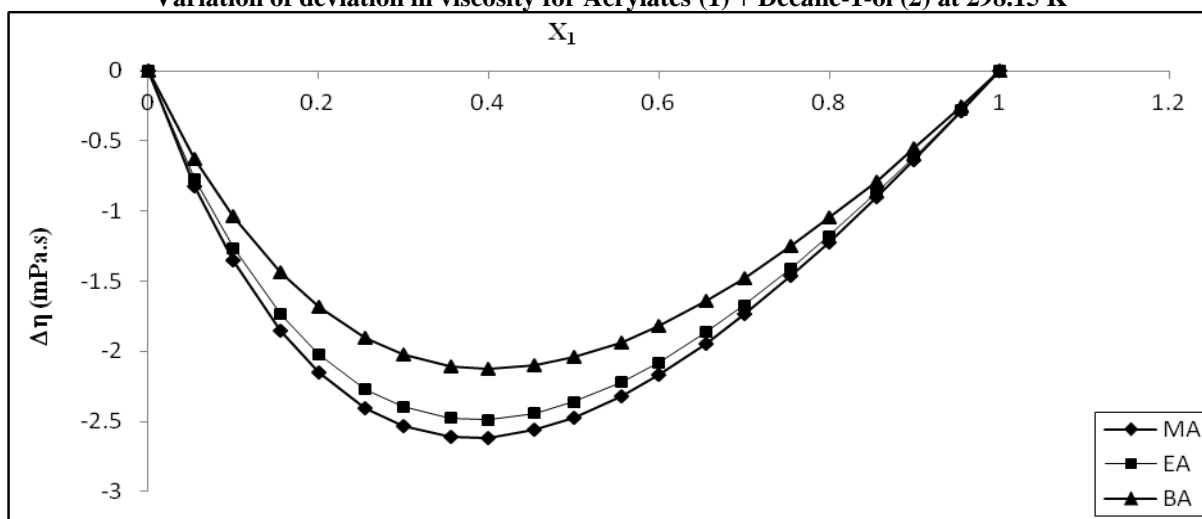


Figure-2
 Variation of deviation in viscosity for Acrylates (1) + Decane-1-ol (2) at 308.15 K

Conclusion

The main effect in viscosity deviation of binary liquid mixtures is breaking of self interactions in compounds during mixing process, in this, H-bonding and dipole-dipole interactions. The presence of new OH-O interactions in mixture increases viscosity, but according to experimental result, effect is not as important as breaking of self interactions. Negative viscosity deviations means system has an easier flow than pure liquids.

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