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Study of Thermodynamic and Transport Properties of Binary Liquid Mixtures of Methyl Acrylate with Alkoxy Ethanols at 308.15 K

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Abstract: ***Densities (ρ) and Viscosities (η) of Binary mixtures of Methyl Acrylate (MA) with Alkoxy Ethanols [2-Methoxy Ethanol (2ME), 2-Ethoxy Ethanol (2EE), 2-Butoxy Ethanol (2BE), 2-(2-Methoxy Ethoxy) Ethanol (22MEE), 2-(2-Ethoxy Ethoxy) Ethanol (22EEE), 2-(2-Butoxy Ethoxy) Ethanol (22BEE)] have been measured at 308.15K. These measured data have been utilised to calculate excess molar volumes (V^E), Excess Viscosity (η^E), excess Gibbs free energy for activation of viscous flow (G^{*E}). The viscosity data were correlated with the Gruenberg-Nissan equations. The values of these excess functions are fitted to the Redlich Kister equation. The results were discussed in terms of the existence of intermolecular interactions between the components in the liquid mixtures.***

Keywords: Density, Viscosity, Methyl Acrylate (MA), Alkoxy Ethanols, Excess molar volumes, Gruenberg-Nissan Equation

1. Introduction

Studies of excess thermodynamic functions are useful tool in understanding the nature of molecular interactions in binary liquid mixtures. In chemical industry, knowledge of the properties of binary liquid mixtures is essential in designs involving chemical separations, heat transfer, mass transfer, and fluid flow [1]. The mixing of two solvents has been reported to result in specific interactions such as hydrogen bonding, dipole-dipole and charge transfer reactions. Strong and weak interactions between unlike molecules in mixtures lead to deviations from ideality. Deviations from ideality in binary liquid mixtures are usually associated with synergism and are attributed to differences in the chemistry and molecular architecture of the mixing solvent as well as the experimental conditions such as temperature and the mixing ratios of the binary liquids [2-5].

Methyl acrylate is an organic compound, colour less liquid with a characteristic acrid odour, which is used to weave synthetic carpets. It is a highly polar (dipole moment, μ = 1.77 D at 298.15 K) [6] and strongly associated aprotic solvent due to polar >C=O group in the molecule. Alcohols also several applications as reagents, hand sanitisers, antifreeze and antiseptic as well as preservatives in science and industry [7].

Some alcohols are bifunctional in nature, like Alkoxy propanols, have demonstrated excellent cleaning properties as a result of their dual molecular architecture [8]. In general, bifunctional alcohols, like Alkoxy Ethanols, are hydroxyethers which are widely used for various analytical and industrial purposes [9-14].

The present investigation is concerned with the study of the methyl acrylate with Alkoxy Ethanols. This study is aimed at providing mixing data in terms of the excess molar volumes of binary mixtures of methyl acrylate with Alkoxy Ethanols to see the effect of the chain length of solvent solute system and the excess molar volumes of the binary solvent solute system. The excess molar volume data obtained from the measured densities of the binary mixtures at 308.15 K over the entire range of solvent-solute composition have been used to interpret the types and strengths of intermolecular interactions in the binary mixtures of the solvent solute system investigated. Our findings on the volumetric behavior of these binary mixtures are reported here under.

The present study of excess thermodynamic functions such as excess viscosity, excess volume, excess Gibbs free energy of activation of viscous flow and Gruenberg-Nissan interaction parameter (d^l) of binary liquid mixtures are useful in understanding the nature of intermolecular interactions between the Methyl Acrylate with 2-Methoxy Ethanol (2ME), 2-Ethoxy Ethanol (2EE), 2-Butoxy Ethanol (2BE)), 2-(2-Methoxy Ethoxy) Ethanol (22MEE), 2-(2-Ethoxy Ethoxy) Ethanol (22EEE), 2-(2-Butoxy Ethoxy) Ethanol (22BEE) at the temperature 308.15K.

2. Materials and Methods

Methyl acrylate (MA) with 2-Methoxy Ethanol (2ME), 2-Ethoxy Ethanol (2EE), 2-Butoxy Ethanol (2BE), 2-(2-Methoxy Ethoxy) Ethanol (22MEE), 2-(2-Ethoxy Ethoxy) Ethanol (22EEE), 2-(2-Butoxy Ethoxy) Ethanol (22BEE) were purchased from Merck and used. Mixtures were prepared by mixing weighed amounts of the pure liquids adopting the method of closed system. The weightings were done by using Mettler balance with the precision of ± 0.1 mg. The uncertainty in the mole function was estimated to be less than ± 1×10^{-4}. Mixtures were allowed to stand for some time before every measurement so as to avoid air bubbles.
The densities of pure liquids and their binary mixtures were measured by using a single-capillary pycnometer (made of Borosil glass) having a bulb capacity of ≈ 10 mL. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triply distilled water. The uncertainty in density measurements was within ± 2×10^{-5} g cm-3.

Viscosity measurements were carried out with a precision of ± 0.2% using calibrated Schott-Gerate AVS 400 viscometer, whose flow time for doubly distilled water was found to be

375 seconds at 25^{0}C. The temperature of the test liquids during the measurements was maintained within an uncertainty of ± 0.01 K in an electronically controlled thermostatic water bath.

The measurements were made with proper care in an AC room to avoid evaporation loss. The purities of the liquids were checked by comparing the values of densities and viscosities with literature data (Table 1) and found in good agreement in general.

Table 1: Comparison of experimental density (ρ) and viscosity (η) of pure liquids with Literature at 308.15 K

LIQUID	Density (ρ) x 10^{-3} Kg m^{-3}		Viscosity (η) x 10^{3} Kg m^{-1} s^{-1}	
	EXP	LIT	EXP	LIT
Methyl Acrylate	0.9367	0.93565[15]	0.3920	0.3900[15]
2-methoxy ethanol (2ME)	0.9529	0.9511[16]	1.2560	1.2540[16]
2-ethoxy ethanol (2EE)	0.9163	0.9164[16]	1.4890	1.4870[16]
2-butoxyethanol (2BE)	0.8887	0.8887[16]	2.2880	2.288[16]
2-(2-Methoxyethoxy) ethanol(22MEE)	1.0073	1.0098[17]	2.546	2.547[17]
2-(2-Ethoxyethoxy)ethanol(22EEE)	0.9751	0.9838[18]	2.766	2.839[18]
2-(2-Buthoxyethoxy)ethanol(22BEE)	0.9399	0.9456[19]	3.481	3.582[18]

3. Results and Discussion

The experimental results of measured densities and viscosities of binary mixtures are presented in Table 2. The molar volume (V), excess volume (V^E), excess viscosity (η^E), excess Gibbs energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter (d^l) were calculated from the measured data using the following equations 1 to 5 respectively.

$$V = (X_1M_1 + X_2M_2) / \rho \ldots (1)$$
$$V^E = V - (X^1 V_1 + X_2 V_2) \ldots (2)$$
$$\eta^E = \eta - (X_1 \eta_1 + X_2 \eta_2) \ldots (3)$$
$$G^{*E} = RT [\ln \eta V - (X_1 \ln \eta_1 V_1 + X_2 \ln \eta_2 V_2)] \ldots (4)$$
$$d^l = \ln \eta / [X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1 X_2] \ldots (5)$$

Where ρ, η and V are the density, viscosity and molar volume of the mixture, M_1 and M_2 are the molar masses, η_1 and η_2 are the viscosities V_1 and V_2 are the molar volumes of the methyl acrylate and Alkoxy Ethanols respectively d^1 is a constant [20, 21] and x is the mole fraction of MA. The above calculated values are also included in Table 2.

The dependence of η^E, V^E and G^{*E} on the mole fraction of methyl acrylate (X_{MA}) for all the six systems were fitted to the following Redlich-Kister equation by the least-squares method and the values are given in Table 3.

$$Y^E = X(1-X)\sum_i A_i(2X-1)^i \quad \ldots (6)$$

Where Y^E is η^E, V^E and G^{*E} parameters.

The parameters A_i, obtained by a non-linear least squares polynomial fitting procedure, are also given in Table 3 together with the standard deviations (σ) values.

The variation of the parameters V^E, η^E and G^{*E} with mole fraction of methyl acrylate (X_{MA}) for the systems under study are shown graphically in Figs. 1 to 3 respectively.

It is clear from the Fig. 1 that the negative V^E values are obtained over the entire composition range for all these systems which indicates the presence of strong molecular interactions between the unlike components of the mixtures. It is also observed from Fig. 1 and Tables 2 that the negative values fall in the sequence.

MA + 2BE > MA + 2EE > MA +2ME, MA + 22BEE > MA + 22EEE > MA +22MEE

From Fig. 1, it is further observed that the negative V^E Vs X_{MA} plots were found to be large and symmetrical showing a maximum between 0.5 to 0.7 mole fractions of MA. (X_{MA})

According to several effects may contribute to the sign and values of V^E and the following three effects may be considered as being important. Vijaya Lakshmi *et al.*, [15]

- Break up of hydrogen bonds and dipolar interactions in unlike molecules.
- The possible intermolecular interactions like hydrogen bonding interactions between unlike molecules.
- Interstitial accommodation of one component molecules into the other unlike Component molecules due to their differences in size and shape.

The change of actual volume depends on the relative strength of these three opposing effects.

In the present investigation, the interactions between MA and Alkoxy Ethanols may be due to the formation of strong intermolecular hydrogen bonded complexes which are responsible for the negative excess volume.

The self-association of Alkoxy Ethanols through hydrogen bonding leads to the formation of polymeric form of Alkoxy Ethanols, the addition of MA would contribute to expansion in volume. The difference in molecular size, skeletal shape conformations and steric hinderance (Geometrical effects) between the components in the solvents mixtures.

Table 2: Values of density (ρ), viscosity (η), excess viscosity (η^E), molar volume (V), excess volume (V^E), excess Gibbs free energy of activation of viscous flow (G^{*E}) and Gruenberg-Nissan equation (d^1) for the binary liquid mixtures of Methyl Acrylate (MA) + Alkoxy Ethanols at 308.15 K.

Mole fraction of MA (X_{MA})	ρ x 10^{-3} Kg m^{-3}	η x 10^3 Kg m^{-1} s^{-1}	η^E x 10^3 Kg m^{-1} s^{-1}	V x 10^6 m^3 mol-1	V^E x 10^6 m^3 mol^{-1}	G^{*E} x 10^3 N mol^{-1}	d^1
Methyl Acrylate (MA) + 2-Methoxy Ethanol (2ME)							
0.0000	0.9529	1.2560	0.0000	79.8510	0.0000	0.0000	---
0.0894	0.9513	1.1696	-0.0091	80.9270	-0.0002	20.6195	0.4036
0.1810	0.9497	1.0832	-0.0164	82.0291	-0.0003	39.3077	0.4232
0.2747	0.9480	0.9968	-0.0218	83.1582	-0.0003	55.5570	0.4456
0.3708	0.9464	0.9104	-0.0253	84.3152	-0.0004	68.7102	0.4713
0.4692	0.9448	0.8240	-0.0266	85.5014	-0.0003	77.9001	0.5012
0.5700	0.9432	0.7376	-0.0259	86.7176	-0.0003	81.9548	0.5365
0.6734	0.9416	0.6512	-0.0229	87.9652	-0.0003	79.2443	0.5790
0.7795	0.9399	0.5648	-0.0177	89.2452	-0.0002	67.4168	0.6312
0.8883	0.9383	0.4784	-0.0101	90.5589	-0.0001	42.9142	0.6972
1.0000	0.9367	0.3920	0.0000	91.9078	0.0000	0.0000	---
Methyl Acrylate (MA) + 2-Ethoxy Ethanol (2EE)							
0.0000	0.9163	1.4890	0.0000	98.3521	0.0000	0.0000	---
0.1042	0.9183	1.3793	0.0046	97.6764	-0.0021	38.3983	0.6700
0.2074	0.9204	1.2696	0.0081	97.0079	-0.0039	72.0964	0.7144
0.3097	0.9224	1.1599	0.0106	96.3465	-0.0051	100.4023	0.7651
0.4110	0.9245	1.0502	0.0121	95.6921	-0.0059	122.4140	0.8240
0.5114	0.9265	0.9405	0.0125	95.0447	-0.0063	136.9259	0.8931
0.6109	0.9285	0.8308	0.0120	94.4041	-0.0061	142.2785	0.9757
0.7095	0.9306	0.7211	0.0104	93.7702	-0.0054	136.0996	1.0766
0.8072	0.9326	0.6114	0.0079	93.1429	-0.0042	114.8311	1.2032
0.9040	0.9347	0.5017	0.0044	92.5221	-0.0024	72.7826	1.3683
1.0000	0.9367	0.3920	0.0000	91.9078	0.0000	0.0000	---
Methyl Acrylate (MA) + 2-Butoxy Ethanol (2BE)							
0.0000	0.8887	2.2880	0.0000	119.2793	0.0000	0.0000	---
0.1323	0.8935	2.0984	0.0613	115.5497	-0.0043	94.2444	1.2802
0.2555	0.8983	1.9088	0.1052	112.1046	-0.0075	172.2791	1.4173
0.3704	0.9031	1.7192	0.1335	108.9142	-0.0098	234.2046	1.5767
0.4779	0.9079	1.5296	0.1476	105.9525	-0.0111	279.6003	1.7651
0.5785	0.9127	1.3400	0.1489	103.1971	-0.0115	307.3516	1.9921
0.6731	0.9175	1.1504	0.1386	100.6284	-0.0110	315.3219	2.2724
0.7621	0.9223	0.9608	0.1177	98.2293	-0.0095	299.7054	2.6300
0.8459	0.9271	0.7712	0.0871	95.9848	-0.0072	253.6374	3.1074
0.9251	0.9319	0.5816	0.0476	93.8816	-0.0040	163.7886	3.7889
1.0000	0.9367	0.3920	0.0000	91.9078	0.0000	0.0000	---
Methyl Acrylate (MA) + 2-(2-Methoxy Ethoxy) Ethanol (22MEE)							
0.0000	1.0073	2.5469	0.0000	132.9808	0.0000	0.0000	---
0.1343	1.0002	2.3314	0.0738	127.5133	-0.0190	101.7067	1.4012
0.2587	0.9932	2.1159	0.1264	122.4323	-0.0322	186.2225	1.5578
0.3743	0.9861	1.9004	0.1600	117.6987	-0.0404	253.7170	1.7408
0.4820	0.9791	1.6849	0.1767	113.2787	-0.0443	303.7705	1.9581
0.5826	0.9720	1.4695	0.1779	109.1425	-0.0443	335.1792	2.2219
0.6767	0.9649	1.2540	0.1654	105.2642	-0.0409	345.5739	2.5505
0.7651	0.9579	1.0385	0.1402	101.6208	-0.0345	330.6491	2.9748
0.8481	0.9508	0.8230	0.1036	98.1920	-0.0254	282.4566	3.5506
0.9263	0.9438	0.6075	0.0566	94.9596	-0.0138	185.0257	4.3940
1.0000	0.9367	0.3920	0.0000	91.9078	0.0000	0.0000	---
Methyl Acrylate (MA) + 2-(2-Ethoxy Ethoxy) Ethanol (22EEE)							
0.0000	0.9751	2.7664	0.0000	137.6064	0.0000	0.0000	---
0.1476	0.9713	2.5290	0.1131	130.8416	-0.0318	127.3162	1.3237
0.2804	0.9674	2.2915	0.1909	124.7605	-0.0322	229.5155	1.5134
0.4005	0.9636	2.0541	0.2386	119.2651	-0.0404	308.3155	1.7131
0.5096	0.9597	1.8166	0.2602	114.2750	-0.0443	364.4566	1.9100
0.6092	0.9559	1.5792	0.2592	109.7243	-0.0443	397.5735	2.0994
0.7004	0.9521	1.3418	0.2384	105.5577	-0.0409	405.8324	2.4123
0.7843	0.9482	1.1043	0.2002	101.7290	-0.0345	385.1053	2.7773
0.8618	0.9444	0.8669	0.1467	98.1992	-0.0254	327.0307	3.2652

0.9335	0.9405	0.6294	0.0794	94.9350	-0.0138	213.8030	4.1274
1.0000	0.9367	0.3920	0.0000	91.9078	0.0000	0.0000	---
Methyl Acrylate (MA) + + 2-(2-Butoxy Ethoxy) Ethanol (22BEE)							
0.0000	0.9399	3.4811	0.0000	172.6035	0.0000	0.0000	---
0.1731	0.9396	3.1722	0.2259	158.6324	-0.0549	189.7815	1.9923
0.3202	0.9393	2.8633	0.3714	146.7613	-0.0948	332.9366	2.3155
0.4468	0.9389	2.5544	0.4534	136.5496	-0.1208	436.9459	2.6957
0.5568	0.9386	2.2455	0.4843	127.6723	-0.1343	506.4342	3.1513
0.6533	0.9383	1.9366	0.4736	119.8838	-0.1363	543.5853	3.7106
0.7387	0.9380	1.6276	0.4284	112.9953	-0.1276	548.0345	4.4193
0.8147	0.9377	1.3187	0.3544	106.8595	-0.1090	515.9904	5.3569
0.8829	0.9373	1.0098	0.2560	101.3593	-0.0811	437.6363	6.6784
0.9443	0.9370	0.7009	0.1369	96.4008	-0.0446	289.1822	8.7411
1.0000	0.9367	0.3920	0.0000	91.9078	0.0000	0.0000	---

Table 3: Parameters of Eq. (6) and Standard deviations

Excess Property	A_0	A_1	A_2	A_3	A_4	σ
Methyl Acrylate (MA) + 2-Methoxy Ethanol (2ME)						
η^E x 10^3 Kg m^{-1} s^{-1}	0.00000783	-0.11319	0.12673	-0.01403	0.000476	0.0000319
V^E x 10^6 m^3 mol^{-1}	0.00000817	-0.02661	0.03002	-0.00417	0.000751	0.0000336
G^{*E} x 10^3N mol^{-1}	-0.15074	252.07429	-1999.24669	110.98376	-163.5048	0.026897
Methyl Acrylate (MA) + 2-Ethoxy Ethanol (2EE)						
η^E x 10^3 Kg m^{-1} s^{-1}	0.00000699	0.04864	-0.04516	-0.00465	0.00116	0.0000239
V^E x 10^6 m^3 mol^{-1}	-0.0000134	-0.04541	0.04408	0.00174	-0.000389	0.0000273
G^{*E} x 10^3N mol^{-1}	-0.50846	421.89473	-418.8714	477.53283	-479.31609	0.0106045
Methyl Acrylate (MA) + 2-Butoxy Ethanol (2BE)						
η^E x 10^3 Kg m^{-1} s^{-1}	0.0000143	0.51631	-0.38723	-0.06971	-0.05934	0.0000394
V^E x 10^6 m^3 mol^{-1}	0.00000158	-0.16209	0.13831	0.00634	0.01743	0.0000191
G^{*E} x 10^3N mol^{-1}	-2.4409	950.27241	-1636.1628	2837.14632	-2142.55366	0.0698146
Methyl Acrylate (MA) + 2-(2-Methoxy Ethoxy) Ethanol (22MEE)						
η^E x 10^3 Kg m^{-1} s^{-1}	0.0000230	.061284	-0.45449	-0.07934	-0.07893	0.0000681
V^E x 10^6 m^3 mol^{-1}	0.00008308	-0.19991	0.14143	0.02585	0.03319	0.0006876
G^{*E} x 10^3N mol^{-1}	-3.05285	1047.68458	-1978.0172	3550.35894	-2608.72981	0.09217
Methyl Acrylate (MA) + 2-(2-Ethoxy Ethoxy) Ethanol (22EEE)						
η^E x 10^3 Kg m^{-1} s^{-1}	0.00006268	0.85936	-0.60802	-0.0443	-0.20682	0.00019115
V^E x 10^6 m^3 mol^{-1}	0.00001818	-0.23916	0.15353	0.01574	0.06982	0.00005988
G^{*E} x 10^3N mol^{-1}	-3.80936	1266.61503	-12698.8773	4945.8626	-3496.9150	0.013343
Methyl Acrylate (MA) + 2-(2-Butoxy Ethoxy) Ethanol (22BEE)						
η^E x 10^3 Kg m^{-1} s^{-1}	0.0002474	1.49172	-1.07806	0.36535	-0.77826	0.00009128
V^E x 10^6 m^3 mol^{-1}	0.0000164	-0.36043	0.26862	-0.33857	0.42969	0.0005999
G^{*E} x 10^3N mol^{-1}	-5.56919	1845.28085	-4851.91052	9057.19281	-6016.54844	0.0262524

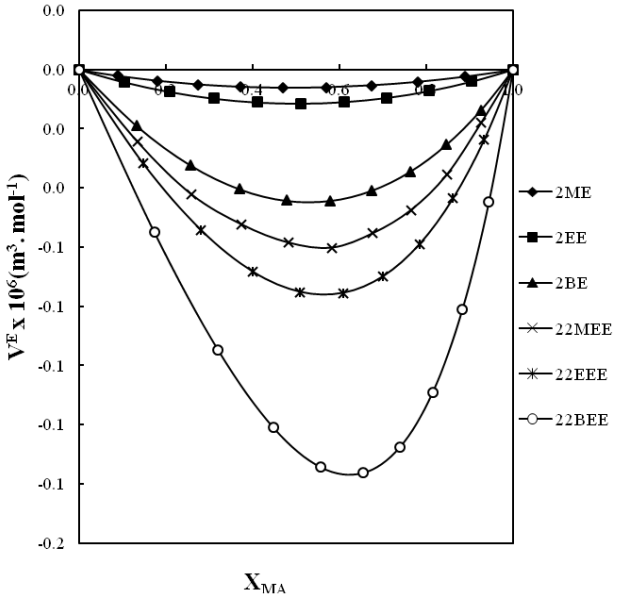


Figure 1: Plots of excess volumes (V^E) vs. mole fraction of Methyl Acrylate (X_{MA}) for binary mixtures of Methyl Acrylate (MA) with 2-Methoxy Ethanol (2ME, −♦−), 2-Ethoxy Ethanol (2EE, −■−), 2-Butoxy Ethanol (2BE, −▲−), 2-(2-Methoxy

Ethoxy) Ethanol (22MEE, −●−), 2-(2- Ethoxy Ethoxy) Ethanol (22EEE, −*−), 2-(2-Butoxy Ethoxy) Ethanol (22BEE, −○−) at 308.15 K.

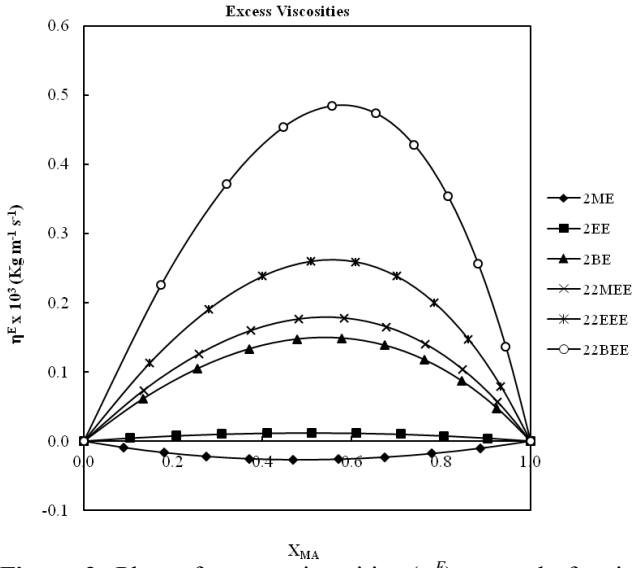


Figure 2: Plots of excess viscosities (η^E) vs. mole fraction of Methyl Acrylate (X_{MA}) for binary mixtures of Methyl Acrylate (MA) with 2-Methoxy Ethanol (2ME, −♦−), 2-Ethoxy Ethanol (2EE, −■−), 2-Butoxy Ethanol (2BE, −▲−), 2-(2- Methoxy Ethoxy) Ethanol (22MEE, −●−), 2-(2- Ethoxy Ethoxy) Ethanol (22EEE, −*−), 2-(2-Butoxy Ethoxy) Ethanol (22BEE, −○−) at 308.15 K.

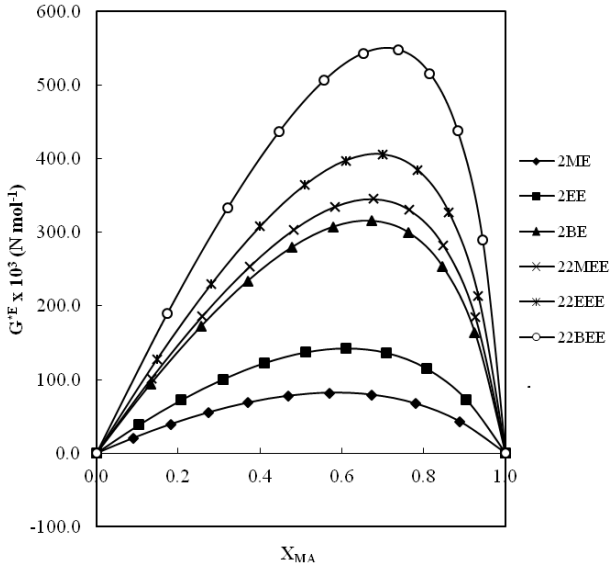
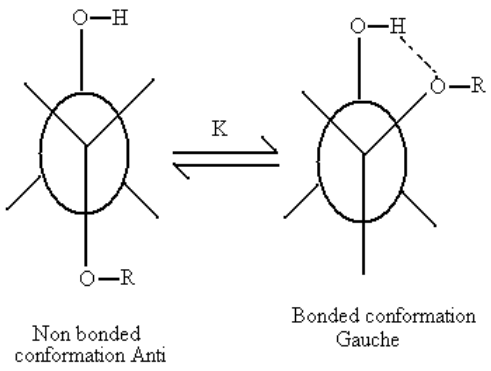
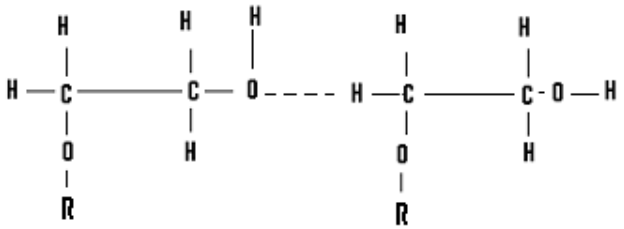


Figure 3: Plots of excess Gibbs free energy of activation of viscous flow (G^{*E}) vs. mole fraction of Methyl Acrylate (X_{MA}) for binary mixtures of Methyl Acrylate (MA) with 2-Methoxy Ethanol (2ME, −♦−), 2- EthoxyEthanol (2EE, −■−), 2-Butoxy Ethanol (2BE, −▲−), 2-(2- Methoxy Ethoxy) Ethanol (22MEE, −●−), 2-(2- Ethoxy Ethoxy) Ethanol (22EEE, −*−), 2-(2-Butoxy Ethoxy) Ethanol (22BEE, −○−) at 308.15 K.



Where R= $-CH_3$ or $-C_2H_5$ or $-C_4H_9$

A Schematic Representation of conformational structure of H-bonding in Alkoxy Ethanol molecule.

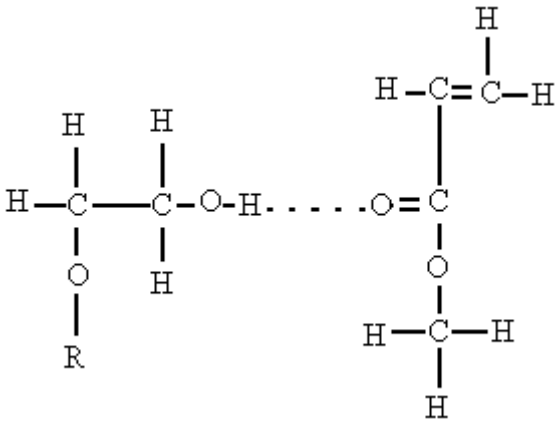


A Schematic Representation of Polymeric form of Alkoxy Ethanols

After depolymerisation the other two effects will come into force i.e intermolecular interactions and formation of H-bonding between unlike molecules which leads to negative V^E, thereby change of free volume in real mixtures.

At first, Self association of hydrogen bonding in Alkoxy Ethanols leads to the formation of polymeric form of Alkoxy Ethanols, second effect, interstitial accommodation i.e the of smaller size MA molecule accommodate in the molecules of bigger size Alkoxy Ethanols and third effect, formation of hydrogen bond between –OH groups of Alkoxy ethanol and >C=O group of MA molecule [>C=O----------H-O-]. Hence, the actual volume change depends upon the relative strength of all the above said three effects. The negative excess volumes of MA + Alkoxy Ethanols over the whole range of composition suggest that the 2nd and 3rd factors are responsible for this situation. The negative contributions get more and more importance when the alkyl group in the Alkoxy Ethanols become more and more branched. Hence the negative V^E volumes are in the following orders

MA + 2BE > MA + 2EE > MA +2ME, MA + 22BEE > MA + 22EEE > MA +22MEE



Where R= $-CH_3$ or $-C_2H_5$ or $-C_4H_9$

A Schematic Representation of H-bond formation between Alkoxy Ethanol and MA

The difference between molar volume of Methyl Acrylate has 91.9078 x 10^6 m^3 mol^{-1}, the molar volumes of Alkoxy Ethanols [2-Methoxy Ethanol (2ME), 2-Ethoxy Ethanol (2EE), 2-Butoxy Ethanol (2BE), 2-(2-Methoxy Ethoxy) Ethanol (22MEE), 2-(2-Ethoxy Ethoxy) Ethanol (22EEE), 2-(2-Butoxy Ethoxy) Ethanol (22BEE)] are 79.8510 x 10^6 m^3 mol^{-1}, 98.3521 x 10^6 m^3 mol^{-1}, 132.9808 x 10^6 m^3 mol^{-1}, 119.2793 x 10^6 m^3 mol^{-1}, 137.6064 x 10^6 m^3 mol^{-1}, 172.6035 x 10^6 m^3 mol^{-1}, respectively. The molar volume of Methyl Acrylate is smaller than the molar volume of Alkoxy Ethanols except Methoxy Ethanol (2ME). This situation can therefore result in the fitting the smaller MA molecules into the Alkoxy Ethanols and result in the negative excess volumes. The molar volumes of 2-(2-Butoxy Ethoxy) Ethanol (22BEE) are much greater than that of 2-(2-Ethoxy Ethoxy) Ethanol (22EEE). More molecules of Methyl Acrylate can therefore fit into 2-(2-Butoxy Ethoxy) Ethanol (22BEE) than into 2-(2-Ethoxy Ethoxy) Ethanol (22EEE). A similar observation was reported several Research authors [23-25].

Sastry et al., Patil and Peralta [26-28] have reported negative excess volumes for the mixtures of Acrylate with polar components, this observation is supported by the present work where V^E values are negative for the entire MA with Alkoxy Ethanols. The negative excess volumes reported by Subha et al. [29] for propionic acid and alcohol binary liquid mixtures and concluded that this is due to the interaction between the oxygen atom of propionic acid and hydrogen atom of alcohols.

This type of behavior was supported by the work of Jayachandra *et.al*, [17] who measured the excess volumes of some Alkoxy Ethanols with Amines. In the same lines the present increase of negative V^E values from 2ME to 2BE and 22MEE to 22BEE can be explained as follows.

From Fig.1 it is clear that the negative excess volumes increase in magnitude as the alkyl group of the normal Alkoxy Ethanols become large and they fall in the following orders:

MA + 2BE > MA + 2EE > MA +2ME, MA + 22BEE > MA + 22EEE > MA +22MEE

The effect of interaction between the two components becomes more and more predominant as the alkyl group of the normal Alkoxy Ethanols becomes more due to their electron donation ability. And also the size of Alkoxy Ethanols molecules increases from 2ME to 2BE and 22MEE to 22BEE, this in turn makes a larger difference in size of MA and Alkoxy Ethanol molecules. This gives more possibilities for the more interstitial accommodation resulting in negative V^E values.

Thus, in the present investigation the negative V^E values for MA + Alkoxy Ethanols indicate the predominance of the formation of hydrogen bonding and interstitial accommodation between them over the other effect.

Fig. 2 shows that η^E values are positive for the whole composition range in all the systems under study. A correlation between signs of η^E and V^E has been observed for a number of binary solvent systems [30], η^E being positive where V^E is negative or vice-versa. In general for systems, where dispersion and dipolar interactions are operating η^E values are found to be negative, whereas charge transfer and hydrogen bonding interactions lead to the formation of complex species between unlike molecules there by resulting in positive η^E values.

The algebraic values of η^E for all the mixtures of MA + Alkoxy Ethanols fall in the orders.

MA + 2BE > MA + 2EE > MA +2ME, MA + 22BEE > MA + 22EEE > MA +22MEE

This order suggests that the presence of charge transfer and hydrogen bonding between unlike molecules increase with increase in chain length in Alkoxy Ethanols. A similar observation was reported by Jayachandra *et al*., [19]. The variation of excess Gibbs free energy of activation of viscous flow (G^{*E}) with X_{MA} for all the systems under study are shown graphically in Fig. 3.

Reed and Taylor [31] reported that G^{*E} parameter can be considered as a reliable criterion to detect or exclude the presence of interactions between unlike molecules. According to these authors, the magnitude of the positive values is an excellent indicator of the strength of specific interactions. G^{*E} values for the systems under study suggest the following orders.

MA + 2BE > MA + 2EE > MA +2ME, MA + 22BEE > MA + 22EEE > MA +22MEE

Fort and Moore [32] & Meyer *et al*. [33] reported that for any binary liquid mixture, the positive value of d^l indicates the presence of strong interactions and the negative value of d^l indicates the presence of weak interactions between the components. On this basis the positive d^1 values obtained in the present study for the six systems (Tables 2) confirms the presence of strong interactions between the component molecules. A similar observation was made by Subha et. al., [29] from the d^1 values of the binary liquid mixtures of propionic acid with alcohols.

4. Conclusion

1) It is evident that, the observed variation of the properties of the mixtures studied support the view that the interactions between unlike molecules is predominant and

characterised by the negative V^E and positive η^E, G^{*E} and d^l values.

2) The overall sign and magnitude of V^E depends on the resultant of the Breakup of hydrogen bonds and dipolar interactions in MA and intermolecular interactions in Alkoxy Ethanols.
3) The possible intermolecular interactions hydrogen bonding between unlike molecules of MA and Alkoxy Ethanols.
4) Interstitial accommodation of MA molecules into the Alkoxy Ethanol molecules is due to their differences in size and shape.
5) The overall excess volumes are negative in sign.

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