

Thermodynamic and Acoustical Studies on Binary Mixtures of Methyl Acrylate with 2-(2-Alkoxy Ethoxy) Ethanols at 308.15K

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ABSTRACT: Densities and ultrasonic velocities of binary liquid mixtures of Methyl Acrylate with 2-(2-Alkoxy Ethoxy) Ethanols [2-(2-Methoxy Ethoxy) Ethanol, 2-(2-Ethoxy Ethoxy) Ethanol, 2-(2-Butoxy Ethoxy) Ethanol] have been measured at 308.15 K. With the observed data, various acoustical parameters like isentropic compressibility, Intermolecular free length, Acoustic impedance and Relative association and various excess properties like Excess ultrasonic velocity, Excess acoustic impedance, Excess isentropic compressibility and Excess Inter molecular free-length were calculated and fitted to the Redlich Kister equation.

KEYWORDS: Ultrasonic velocity, Methyl acrylate, 2-(2-Alkoxy Ethoxy) Ethanols, Excess isentropic compressibility, Excess acoustic impedance and Redlich Kister equation.

I. INTRODUCTION

Thermodynamic and acoustic properties are very essential for understanding the physical and chemical behaviour of the binary liquid mixtures [1]. Methyl acrylate (MA) is an organic compound, colour less liquid, which is used to weave synthetic carpets. It is a versatile compound having a wide range of applications as a solvent in chemical and biological processes involving both plants and animals [2]. It is a highly polar (dipole moment, $\mu = 1.77$ D at 298.15 K) and strongly associated aprotic solvent due to polar $>C=O$ group in the molecule [3]. It has excellent solvating power; MA is frequently used as a solvent for chemical reactions. Thus, a study of physical properties data on the binary mixture containing MA has attracted considerable interest in the literature. Thus, 2-(2-Alkoxy Ethoxy) Ethanol in MA mixed solvent would enable us to have a large number of solvents with appropriate physico-chemical properties, which can be used for a particular chemical process.

This paper aims to measure densities and ultrasonic velocity of binary liquid mixtures of methyl acrylate (MA) with 2-(2-Alkoxy Ethoxy) Ethanols [2-(2-Methoxy Ethoxy) Ethanol (22MEE), 2-(2-Ethoxy Ethoxy) Ethanol (22EEE), 2-(2-Butoxy Ethoxy) Ethanol (22BEE)] at 308.15 K, by using this data various acoustical parameters like Acoustic impedance (Z), Isentropic compressibility (K_s), Inter molecular free-length (L_f) and Relative association (R_A) and also various excess properties like excess ultrasonic velocity (u^E), excess acoustic impedance (Z^E), excess isentropic compressibility (K_s^E) and excess inter molecular free-length (L_f^E) were calculated and fitted to the Redlich Kister equation and the results are presented.

II. MATERIALS AND METHOD

Methyl acrylate, 2-(2-Methoxy Ethoxy) Ethanol, 2-(2-Ethoxy Ethoxy) Ethanol, 2-(2-Butoxy Ethoxy) Ethanol of E-Merck make was used in the present investigation. Mixtures were prepared by mixing weighed amounts of the pure liquids adopting the method of closed system by using Mettler balance with the precision of ± 0.1 mg. Mixtures were allowed to stand for some time before every measurement so as to avoid air bubbles.

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The measurements were made with proper care in an Air Conditioned room to avoid evaporation loss. The densities of liquids and their mixtures were measured using bicapillary pycnometer having a capillary diameter of 0.85 mm, which was calibrated using double distilled water. The necessary buoyancy corrections were applied. The density values were reproducible within $\pm 0.2 \text{ Kg m}^{-3}$. The ultrasonic velocity measurements were made by a single frequency (2 MHz) variable path interferometer with an accuracy of $\pm 0.03\%$. A thermostatically controlled, well stirred constant temperature water bath, Schott Gerrate (Model CT 050/2 made in Germany) whose temperature was controlled to $\pm 0.02 \text{ K}$ was used for all the measurements.

III. RESULTS AND DISCUSSIONS

From the measured density (ρ) and ultrasonic velocity (u) the various acoustical parameters such as K_S , Z , L_f and R_A were calculated using the following equations 1, 2, 3 & 4 respectively and are incorporated in Table 2 for the binary systems under study.

$$K_S = 1/u^2 \rho \quad \dots (1)$$

$$Z = \rho u \quad \dots (2)$$

$$L_f = K(K_S)^{1/2} \quad \dots (3)$$

Where 'K' is Jacobson's constant [4].

$$R_A = \rho / \rho_o (u_o/u)^{1/3} \quad \dots (4)$$

The excess functions Y^E have being calculated using the relation:

$$Y^E = Y_{mix} - (X_1 Y_1 + X_2 Y_2) \quad \dots (5)$$

Where Y denotes u, Z, K_S and L_f respectively, X is the mole fraction and a suffix 1 & 2 denotes the components 1 & 2 in binary mixture and the values are given in Table 1.

Table 1: Values of ρ , u, Z, K_S , L_f and R_A for the binary liquid mixtures of MA with 2-(2-Alkoxy Ethoxy) Ethanols at 308.15 K.						
Mole fraction of MA (X_{MA})	$\rho \times 10^{-3} \text{ Kg m}^{-3}$	u m s ⁻¹	Z x 10 ⁻⁴ Kg m ⁻² s ⁻¹	$K_S \times 10^{11} \text{ m}^2 \text{ N}^{-1}$	$L_f \times 10^{12} \text{ m}$	Relative association (R_A)
MA + 22MEE						
0.0000	1.0073	1413.5	1.4238	49.6878	4.6684	1.0000
0.1343	1.0002	1386.4	1.3867	52.0176	4.7766	0.9994
0.2587	0.9932	1359.2	1.3499	54.5011	4.8893	0.9989
0.3743	0.9861	1332.1	1.3136	57.1517	5.0068	0.9985
0.4820	0.9791	1304.9	1.2776	59.9841	5.1293	0.9982
0.5826	0.9720	1277.8	1.2420	63.0147	5.2573	0.9980
0.6767	0.9649	1250.6	1.2068	66.2617	5.3910	0.9979
0.7651	0.9579	1223.5	1.1719	69.7455	5.5309	0.9978
0.8481	0.9508	1196.3	1.1375	73.4889	5.6774	0.9979
0.9263	0.9438	1169.2	1.1034	77.5172	5.8310	0.9981
1.0000	0.9367	1142.0	1.0697	81.8592	5.9920	0.9984
MA + 22EEE						
0.0000	0.9751	1384.0	1.3495	53.5400	4.8460	1.0000
0.1476	0.9713	1359.8	1.3207	55.6819	4.9420	1.0019
0.2804	0.9674	1335.6	1.2890	58.2271	5.0536	1.0048
0.4005	0.9636	1311.4	1.2609	60.6057	5.1558	1.0068
0.5096	0.9597	1287.2	1.2307	63.3661	5.2719	1.0096
0.6092	0.9559	1263.0	1.2033	66.0168	5.3811	1.0118
0.7004	0.9521	1238.8	1.1747	68.9956	5.5011	1.0145
0.7843	0.9482	1214.6	1.1456	72.2501	5.6294	1.0175

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0.8618	0.9444	1190.4	1.1189	75.4379	5.7522	1.0200
0.9335	0.9405	1166.2	1.0938	78.6134	5.8721	1.0222
1.0000	0.9367	1142.0	1.0697	81.8592	5.9920	1.0242
MA + 2BEE						
0.0000	0.9399	1355.5	1.2740	57.9054	5.0397	1.0000
0.1731	0.9396	1334.2	1.2505	60.0882	5.1338	1.0058
0.3202	0.9393	1312.8	1.2236	62.7357	5.2456	1.0126
0.4468	0.9389	1291.5	1.1989	65.3196	5.3526	1.0191
0.5568	0.9386	1270.1	1.1763	67.8335	5.4546	1.0251
0.6533	0.9383	1248.8	1.1533	70.5412	5.5624	1.0314
0.7387	0.9380	1227.4	1.1329	73.0882	5.6619	1.0371
0.8147	0.9377	1206.1	1.1156	75.3413	5.7485	1.0419
0.8829	0.9373	1184.7	1.0992	77.5720	5.8330	1.0466
0.9443	0.9370	1163.4	1.0836	79.8037	5.9163	1.0511
1.0000	0.9367	1142.0	1.0697	81.8592	5.9920	1.0552

The dependence of u^E , Z^E , K_S^E and L_f^E on the mole fraction of methyl acrylate (X_{MA}) for all the three systems were fitted to the following Redlich-Kister equation by the least-squares polynomial method and the values are given in Table 2.

Table 2: Values of u^E , Z^E , K_S^E and L_f^E for the binary liquid mixtures of MA + 2-(2-Alkoxy Ethoxy) Ethanol at 308. 15 K.				
Mole fraction of MA (X_{MA})	u^E m s ⁻¹	$Z^E \times 10^{-4}$ Kg m ⁻² s ⁻¹	$K_S^E \times 10^{11}$ m ² N ⁻¹	$L_f^E \times 10^{12}$ m
MA + 22MEE				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1343	9.2994	1.0404	-1.9893	-0.6951
0.2587	15.9261	1.7705	-3.4081	-1.2149
0.3743	20.1638	2.2274	-4.3307	-1.5703
0.4820	22.2572	2.4429	-4.9006	-1.7704
0.5826	22.4188	2.4448	-5.0526	-1.8222
0.6767	20.8339	2.2573	-4.7976	-1.7311
0.7651	17.6648	1.9014	-4.1554	-1.5012
0.8481	13.0545	1.3960	-3.0483	-1.1352
0.9263	7.1289	0.7573	-1.6958	-0.6347
1.0000	0.0000	0.0000	0.0000	0.0000
MA + 22EEE				
0.0000	0.0000	0.0000	0	0.0000
0.1476	11.5227	1.2487	-2.38398	-0.7319
0.2804	19.4555	2.1010	-3.82334	-1.2585
0.4005	24.3136	2.6163	-4.65903	-1.6021
0.5096	26.5183	2.8433	-5.08483	-1.7806
0.6092	26.4171	2.8223	-5.14095	-1.8082
0.7004	24.2994	2.5867	-4.83138	-1.6961

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0.7843	20.4081	2.1647	-4.26505	-1.4532
0.8618	14.9487	1.5799	-3.2194	-1.0863
0.9335	8.0961	0.8525	-1.79808	-0.6007
1.0000	0.0000	0.0000	0	0.0000
MA + 22BEE				
0.0000	0.0000	0.0000	0	0.0000
0.1731	15.6133	1.4881	-2.90426	-0.8337
0.3202	25.6711	2.4458	-4.30075	-1.3930
0.4468	31.3382	2.9848	-4.99078	-1.7286
0.5568	33.4753	3.1872	-5.24985	-1.8776
0.6533	32.7317	3.1154	-5.17363	-1.8672
0.7387	29.6069	2.8170	-4.81819	-1.7184
0.8147	24.4909	2.3295	-4.21905	-1.4466
0.8829	17.6932	1.6823	-3.20829	-1.0639
0.9443	9.4623	0.8994	-1.87021	-0.5794
1.0000	0.0000	0.0000	0	0.0000

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

Where Y^E is u^E , Z^E , K_S^E and L_f^E are excess parameters.

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

Table 3: Parameters of Eq. (6) and Standard deviations						
Excess Property	A₀	A₁	A₂	A₃	A₄	σ
MA + 22MEE						
$U^E \text{ m s}^{-1}$	0.00314	77.23924	-57.36855	-9.86016	-10.00118	0.00782
$Z^E \times 10^{-4} \text{ Kg m}^{-2} \text{ s}^{-1}$	-0.000171	8.67728	-6.70551	-1.29798	-0.67326	0.000437
$K_S^E \times 10^{11} \text{ m}^2 \text{ N}^{-1}$	-0.00973	-16.11283	11.54636	-1.11371	5.70854	0.03417
$L_f^E \times 10^{12} \text{ m}$	0.000215	-4.74853	0.64902	3.29345	0.80467	0.00747
MA + 22EEE						
$U^E \text{ m s}^{-1}$	0.00314	77.23924	-57.36855	-9.86016	-10.00118	0.00782
$Z^E \times 10^{-4} \text{ Kg m}^{-2} \text{ s}^{-1}$	-0.000171	8.67728	-6.70551	-1.29798	-0.67326	0.000437
$K_S^E \times 10^{11} \text{ m}^2 \text{ N}^{-1}$	-0.00973	-16.11283	11.54636	-1.11371	5.70854	0.03417
$L_f^E \times 10^{12} \text{ m}$	0.000215	-4.74853	0.64902	3.29345	0.80467	0.00747
MA + 22BEE						
$U^E \text{ m s}^{-1}$	-0.0172	103.09277	-74.41506	25.06383	53.6679	0.06384
$Z^E \times 10^{-4} \text{ Kg m}^{-2} \text{ s}^{-1}$	-0.00161	9.82469	-7.08143	2.32093	-5.05731	0.00597
$K_S^E \times 10^{11} \text{ m}^2 \text{ N}^{-1}$	0.01913	-23.92158	49.1164	-61.65877	36.36376	0.08681
$L_f^E \times 10^{12} \text{ m}$	0.000786	-6.29176	7.53143	-7.72183	6.47835	0.00314

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From the Table 1, it is clear that the values of u , Z , K_s , L_f and R_A varied with the mole fraction of MA (X_{MA}). This indicates the presence of interactions between the components in these binary liquid mixtures. The variations of ultrasonic velocity for the mixtures depend on the values of L_f . It observed that decrease in ultrasonic velocity and the corresponding increase in L_f with mole fraction of MA (Table 1) all the systems are in accordance with the view proposed by Eyring and Kincaid [5]. However, the excess functions which are a measure of the deviations from the ideal behaviour are relatively more sensitive to the intermolecular interactions between the unlike molecules of the mixture than the pure acoustical parameters as explained above.

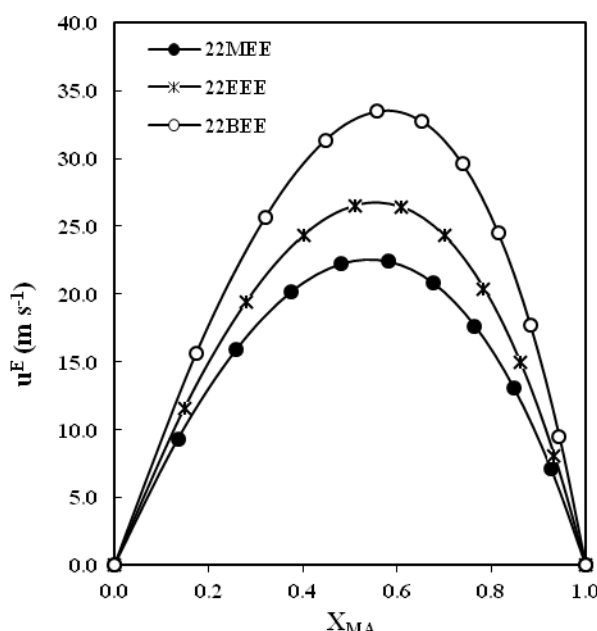


Fig: 1: Plots of u^E vs Binary mixtures of X_{MA} with 22MEE, 22EEE and 22BEE at 308.15 K.

The positive deviations in u^E and Z^E (Figs. 1 to 2) for all the systems of MA and 2-(2-Alkoxy Ethoxy) Ethanol are observed over the entire range of composition. These trends for these systems again support the view that, the interactions between unlike molecules are quite possible and these values are in the following order.

$$MA+22BEE > MA+22EEE > MA+22MEE$$

In common, for denser media, the values of ultrasonic velocity shall be more and for lesser dense media, the ultrasonic velocity value will be less. The ultrasonic velocity value will be positive, When two liquids are mixed and if they condense or compress more [6]. From Fig. 1 it is evident that u^E values are positive for all the systems, which indicates that the mixtures are compressed more and it is natural to get positive u^E values and if mixtures are less compressed the u^E values are negative. In Fig. 2, Excess acoustic impedance values show positive deviations as per the equation 2. A similar observation was reported by Eswari Bai et al [7] and Vijaya lakshmi et al [8].

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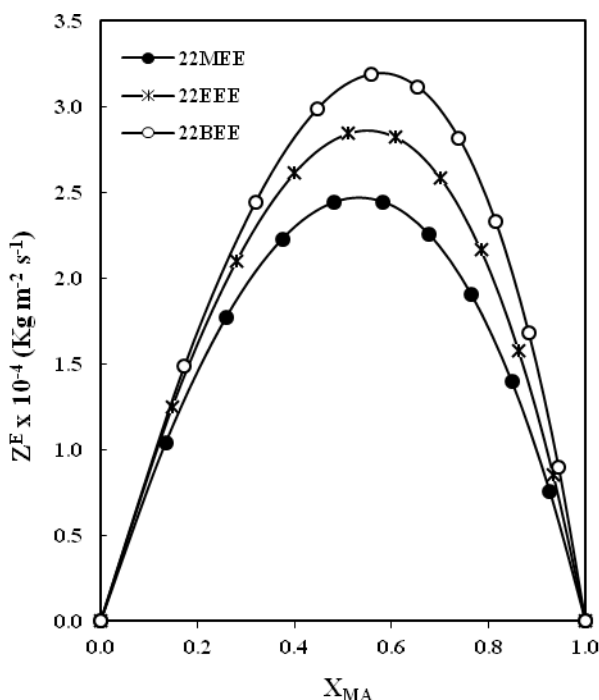


Fig. 2: Plots of Z^E vs Binary mixtures of X_{MA} with 22MEE, 22EEE and 22BEE at 308.15 K.

From the Figs. 3 & 4 that K_S^E and L_f^E are negative for all the systems over the whole mole fraction range. In general, K_S^E and L_f^E values depend upon three factors.

- (i) Mutual disruption of associated present in the pure liquids [4],
- (ii) Formation of weak H- bonding by dipole-induced dipole interaction between unlike molecules and
- (iii) Geometrical complex fitting formation between the component molecules [9].

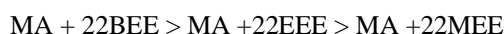
The first effect contributes to the increase in interspace between molecules in mixtures, as a result sound waves cover smaller distances in mixtures than in pure components and this would result to negative deviation in ultrasonic velocity and positive deviation in isentropic compressibility.

The second & third effects contribute to the decrease in interspace between molecules in mixtures as a result sound waves cover larger distances in mixtures than in pure components and this would result to positive deviation in ultrasonic velocity and negative deviation in isentropic compressibility.

K_S^E values are positive due to First factor, but the remaining two factors lead to negative K_S^E values. The resultant values of for the present mixtures are due to the net effect of above all the three factors [10].

Negative deviations of K_S^E and L_f^E values indicated that the presence of strong interactions between unlike molecules, which may be resulted in complex formation.

Polar nature of the two unlike molecules leads to formation of H-bonding between the oxygen atom of $>C=O$ group of MA with hydrogen atom of $-OH$ group of 2-(2-Alkoxy Ethoxy) Ethanol $[>C=O \cdots H-O]$ and also expected intermolecular H-bonding between 2-(2-Alkoxy Ethoxy) Ethanol molecules, which may be due to complex formation. 2-(2-Alkoxy Ethoxy) Ehanol with the interstitial accommodation of smaller sized MA molecules into interstitial space of bigger size 2-(2-Alkoxy Ethoxy) Ethanol molecules. Thus, the complex formation between the two components molecules lead to a decrease in the intermolecular distance thereby decreasing the isentropic compressibilities of the mixtures. The negative values obtained for the K_S^E and L_f^E are in the following order:



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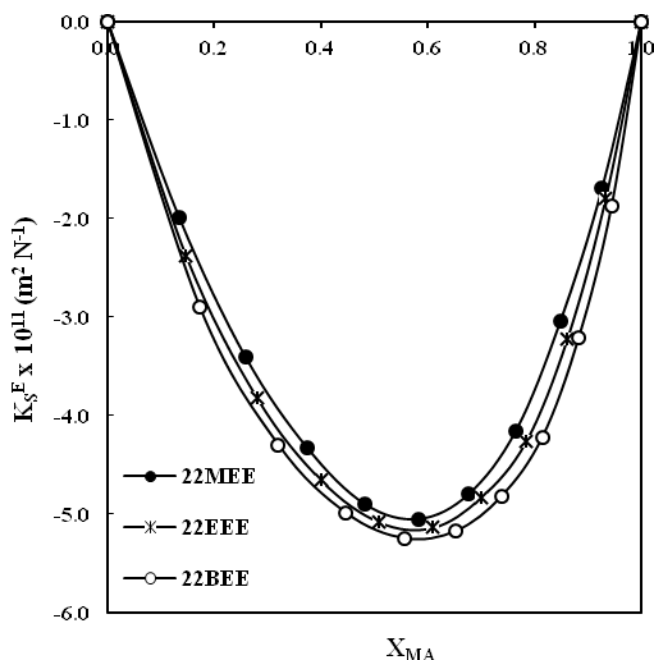


Fig: 3: Plots of K_s^E vs Binary mixtures of X_{MA} with 22MEE, 22EEE and 22BEE at 308.15 K.

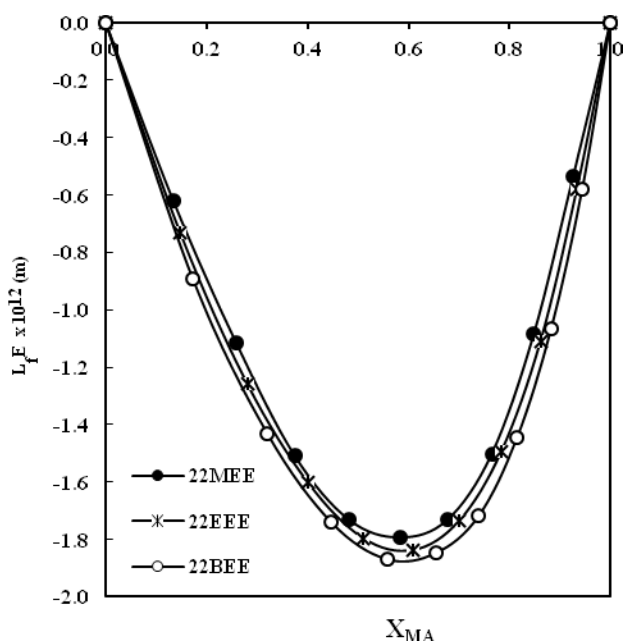


Fig: 4: Plots of L_f^E vs Binary mixtures of X_{MA} with 22MEE, 22EEE and 22BEE at 308.15 K.

Further, from the experimental results it is observed that, the negative contributions increase with increase in chain length of Alkoxy ethanols. The change in magnitude of negative values of K_s^E and L_f^E from 2-(2-Methoxy Ethoxy)

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Ethanol, 2-(2-Ethoxy Ethoxy) Ethanol, 2-(2-Butoxy Ethoxy) Ethanol revealed that, increase in chain length of 2-(2-Alkoxy Ethoxy) Ethanols lead to less compressibility in homologous series. Further the data suggests that the strength of complex formation between unlike molecules increase from 2-(2-Methoxy Ethoxy) Ethanol to 2-(2-Butoxy Ethoxy) Ethanol. This conclusion is supported by researchers like, Fort and Moore [11], Gerard Douhéreta et al [12], and A. S. Bahadur et al [13].

IV. CONCLUSIONS

From the experimental investigation and from the above discussions, following conclusions have been drawn.

1. The variation of the properties of the mixtures studied support that the interactions between unlike molecules is predominant and characterised by the positive u^E and Z^E and negative K_S^E and L_f^E for all the systems.
2. The negative contributions in K_S^E and L_f^E increase with increase in chain length of 2-(2-Alkoxy Ethoxy) Ethanols.
3. The hydrogen bonding between unlike molecules of Methyl Acrylate and 2-(2-Alkoxy Ethoxy) Ethanols and inter H-bonding between 2-(2-Alkoxy Ethoxy) Ethanols molecules lead to complex formations between the component molecules.
4. MA molecules are accommodated into the 2-(2-Alkoxy Ethoxy) Ethanol molecules, due to their differences in size and shape.

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