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Densities, Viscosities, Sound Speeds, and Excess Properties of Binary Mixtures of Methyl Methacrylate with Alkoxyethanols and 1-Alcohols at 298.15 and 308.15 K

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The densities, viscosities, and sound speeds were measured for six binary mixtures of methyl methacrylate (MMA) + 2-methoxyethanol (ME), + 2-ethoxyethanol (EE), + 2-butoxyethanol (BE), + 1-butanol (1-BuOH), + 1-pentanol (1-PeOH), and + 1-heptanol (1-HtOH) at 298.15 and 308.15 K. The mixture viscosities were correlated by Grunberg–Nissan, McAllister, and Auslander equations. The sound speeds were predicted by using free length and collision factor theoretical formulations, and Junjie and Nomoto equations. The excess viscosities and excess isentropic compressibilities were also calculated. A qualitative analysis of both of these functions revealed that structure disruptions are more predominant in MMA + 1-alcohol than in MMA + alkoxyethanols mixtures. The estimated relative associations are found to become less in MMA + alcohol mixtures than in pure alcohols. The solvation numbers derived from the isentropic compressibility of the mixtures, considering MMA as a solvent, showed that structure making interactions are also present in MMA + alkoxyethanols in addition to the structure disruptions.

KEY WORDS: density; methyl methacrylate + alcohol binary liquid mixtures; molecular interactions; relative association; solvation number; sound speed; viscosity.

1. INTRODUCTION

The study of binary mixtures containing acrylic ester and 1-alcohols is of considerable interest and importance not only because of the wide use of

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the former as monomers in the production of polymer and emulsion formulations and the latter as industrial solvents, but also from a theoretical point of view. Acrylic esters of higher homologues are produced by transesterification reactions in which methyl or ethyl acrylate is reacted with an 1-alcohol of desired carbon chain length in an inert solvent media [1, 2]. Thus, the study and knowledge of thermodynamic, volumetric, transport, acoustic, and dielectric properties of the binary and ternary mixtures of acrylic esters such as methyl acrylate or methyl methacrylate with different types of polar associating and nonpolar solvents is expected to provide useful and vital process parameters for efficient design of transesterification processes of industrial interest. The results from such studies are also useful in solving many problems associated with heat flow and fluid flow. The qualitative and quantitative analysis of excess functions also provide information on the nature of molecular interactions in the binary mixtures. Alkoxyethanols are also of considerable interest for studying the heteroproximity effects of etheric oxygen on the –O-H bond and, hence, its influence on the associated nature of the species in these molecules.

In spite of the above mentioned potential industrial applications and considerable theoretical interest of acrylic esters, 1-alcohols, and alkoxyethanols, there are only a few experimental thermodynamic studies on binary mixtures consisting of these components. In particular, for mixtures of acrylic esters with 1-alcohols, data exist only for isothermal vapor–liquid equilibria for methyl methacrylate + methanol or + ethanol [3, 4]; excess enthalpies, excess volumes, and excess molar isobaric heat capacities of methyl methacrylate + methanol or + ethanol [5]; and densities and viscosities of butyl acrylate + 1-butanol [6]. Our laboratory has reported systematic measurements of various thermophysical properties on binary mixtures consisting of acrylic ester + 1-alcohols [7–11].

The present study is a continuation of the ongoing work on the thermodynamic behavior of acrylic ester-containing mixtures. This paper presents the experimental values for densities, viscosities, and sound speeds for binary systems of methyl methacrylate + alkoxyethanols (2-methoxy-, 2-ethoxy- and 2-butoxyethanol) and methyl methacrylate + 1-alcohols (1-butanol, 1-pentanol, and 1-heptanol) at 298.15 and 308.15 K. The 1-alcohols are chosen such that they represent homomorphic analogues of respective alkoxyethanols, with the difference being the presence of an etheric oxygen in the latter molecules in place of a $–CH_2$-group of 1-alcohols. Thus, we hope to study the influence of etheric oxygen on the molecular interactions between acrylic ester and alcohol species. We could not find any previous investigations on the binary systems of acrylic ester + alkoxyethanols, in particular, and aliphatic ester + alkoxyethanols, in general. The mixture viscosities were also correlated by several semiempirical approaches. The sound speeds of mixtures were predicted by various theoretical formulations.

2. EXPERIMENTAL

2.1. Materials

The methyl methacrylate was a purum grade chemical from Fluka. It was stabilized with 2.5×10^{-5} mass fraction of hydroquinone and used as such without further treatment. 2-methoxy- and 2-ethoxyethanols were of locally acquired analytical reagent grade chemicals. They were purified by fractional distillation in a closed system in an adiabatic 1 m column packed with glass helices at a reflux ratio of 25:1. The 90 to 95 % constant boiling fraction was used. Commercial 2-butoxyethanol was purified by repeated distillation under vacuum in a 1.2 m column (packed with glass helices) with nitrogen bubbling into the flask. The mid-fraction of the fourth distillate was collected for measurements. 1-butanol was a BDH reagent grade chemical that was further purified by keeping it over un-slaked lime overnight and then distilling. The central portion was further digested over barium oxide, then dried over sodium, and finally fractionally distilled. 1-pentanol from Riedel and 1-heptanol from Merck were used as obtained without any treatment. The mole fraction purity of all chemicals was assessed with a Waters HPLC equipped with a multi-solvent delivery system, 46 K injector, micro-bondapak C18 column and 991-photodiode array detector. Tetrahydrofuran of HPLC grade was used as solvent. The purity of the chemicals is better than 0.995.

2.2. Methods

2.2.1. Binary Mixtures

The binary mixtures of varying compositions were prepared by mass in hermetically sealed glass vials. The MMA component was introduced first. The evaporation loss, if any, was kept to a minimum by adjusting the total volume in the glass vial in such a way that minimum free space is available over the binary solution. Fresh solutions were prepared for each mixture just prior to the measurements. The compositions of the binary mixtures are given in mole fractions and the uncertainity in the calculated mole fractions is estimated to be ± 0.0001 units.

2.2.2. Densities

Densities, ρ, of pure components and mixtures required for converting kinematic viscosities to absolute viscosities and for calculating isentropic compressibilities from the sound speed data were estimated by using a double stem Lypkin's-type pyknometer. The pyknometer was calibrated by using double-distilled cyclohexane and triple-distilled water. The calibration involves the estimation of two pyknometer constants, namely, the volume of the pyknometer up to the zero mark and the volume corresponding to a unit scale on the capillaries, from the known densities of the calibration liquids at different temperatures and the observed height of the liquid miniscus in the capillaries by using a cathetometer (Scientific Instruments, W. G. Pye and Co., Ltd. U.K.) with a resolution of ± 0.001 cm. The pyknometer was placed vertically in an electronically controlled thermostated water bath. The temperature of the bath during the measurements was maintained to ± 0.02°C by circulating the water through sealed copper tubes placed in the bath using an INSREF, India circulator. The densities are accurate to $\pm 0.0001\ \mathrm{g \cdot cm^{-3}}$.

2.2.3. Viscosities

The viscosity, η of pure liquids and binary mixtures was determined with a modified Ubbelohde suspended-level viscometer. The thoroughly cleaned and dried viscometer was calibrated by using calibration liquids, cyclohexane and triple- distilled water. The viscometer was suspended in the thermostatted water bath (maintained to ± 0.02°C, as described earlier). The arithmetic mean of four or five successive readings of flow times, t, was recorded with a Racer stop watch which can measure time within an uncertainty of ± 0.1 s. Using the flow times and viscosities of calibration liquids at respective temperatures, the values of the viscometer constants A and B in the following equation;

$$v = (At - B/t) \tag{1}$$

were determined. The kinematic viscosities obtained for the experimental pure liquids or binary mixtures were converted to absolute viscosities by using the densities. The estimated uncertainty in the measured viscosities is $\pm 0.2\%$.

2.2.4. Sound Speeds

The sound speeds were measured using an ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at a fixed frequency of 2 MHz. The temperature within the measuring cell was maintained to ± 0.02°C by circulating water through the input and output jacket chutes. The measured sound speeds have an uncertainty of $\pm 0.15\%$.

Table I. Densities, Viscosities (η), and Sound Speeds (υ) of Pure Components at 298.15 K

	ρ (g·cm^{-3})		η (mPa·s)		υ (m·s^{-1})	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
MMA	0.9376	0.93766 [28]	0.584	—	1182	—
ME	0.9600	0.9602 [29]	1.595	1.5414 [29]	1340	1339.39 [38]
EE	0.9254	0.9253 [30]	1.792	1.784 [30]	1300	1300.40 [38]
BE	0.8966	0.8962 [31]	2.795	2.786 [37]	1304	1304.40 [38]
1-BuOH	0.8062	0.8060 [32]	2.570	2.571 [32]	1244	1240.00 [36]
1-PeOH	0.8109	0.81097 [33]	3.514	3.5128 [32]	1274	1277.00 [36]
1-HtOH	0.8187	0.8187 [34]	5.770	5.774 [35]	1330	1330.00 [36]

The measured densities, viscosities, and sound speeds of pure components at the temperature of 298.15 K are compared with literature values in Table I.

3. RESULTS

The experimental values of densities, viscosities, and sound speeds of the six binary mixtures at 298.15 and 308.15 K are listed in Table II. No published data on viscosities and sound speeds for these mixtures are found in the literature. The experimental mixture viscosities are also plotted as a function of MMA mole fraction in Figs. 1a–d.

3.1. Correlation of Mixture Viscosities as a Function of Composition

The correlation of viscosities of liquid mixtures in terms of pure component data using semiempirical approaches is desirable for industrial applications. The following equations were used to describe the compositional dependence of the viscosities.

(a) Grunberg–Nissan Equation—one parameter [11]:

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \tag{2}$$

(b) McAllister Equation—two parameters [12]:

$$\begin{aligned} \ln v_{12} = {} & x_1^3 \ln v_1 + 3x_1^2 x_2 \ln M_{12} + 3x_1 x_2^2 \ln M_{21} + x_2^3 \ln v_2 \\ & - \ln(x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln(2/3 + M_2/3M_1) \\ & + 3x_1 x_2^2 \ln(1/3 + 2M_2/3M_1) + x_2^3 \ln(M_2/M_1) \end{aligned} \tag{3}$$

Table II. Densities, Viscosities (η), and Sound Speeds (υ) of Methyl Methacrylate + Alkoxyethanols and +1-Alcohols at 298.15 and 308.15 K

$x_1{}^a$	ρ ($g \cdot cm^{-3}$)	η ($mPa \cdot s$)	υ ($m \cdot s^{-1}$)	$x_1{}^a$	ρ ($g \cdot cm^{-3}$)	η ($mPa \cdot s$)	υ ($m \cdot s^{-1}$)
			298.15 K				
	MMA + ME				MMA + EE		
0.0557	0.9579	1.449	1330	0.0533	0.9259	1.640	1294
0.1541	0.9546	1.237	1313	0.1540	0.9269	1.402	1283
0.2554	0.9517	1.068	1296	0.2467	0.9278	1.225	1273
0.3538	0.9491	0.941	1281	0.3554	0.9289	1.059	1261
0.4561	0.9466	0.836	1263	0.4551	0.9300	0.937	1249
0.4992	0.9456	0.799	1256	0.4993	0.9305	0.890	1244
0.5530	0.9445	0.759	1248	0.5543	0.9312	0.838	1238
0.6543	0.9425	0.696	1233	0.6547	0.9324	0.758	1226
0.7542	0.9408	0.650	1218	0.7547	0.9338	0.693	1214
0.8539	0.9393	0.616	1203	0.8858	0.9357	0.628	1198
0.9543	0.9381	0.592	1189	0.9532	0.9368	0.603	1188
	MMA + BE				MMA + 1-BuOH		
0.0589	0.8985	2.450	1299	0.0500	0.8132	2.220	1238
0.1467	0.9015	2.063	1291	0.1489	0.8269	1.700	1229
0.2571	0.9054	1.682	1280	0.2479	0.8403	1.341	1220
0.3556	0.9092	1.416	1270	0.3487	0.8537	1.086	1213
0.4555	0.9132	1.201	1259	0.4499	0.8668	0.906	1207
0.5016	0.9152	1.117	1253	0.5024	0.8736	0.835	1204
0.5559	0.9175	1.028	1247	0.5479	0.8794	0.783	1202
0.6734	0.9227	0.868	1232	0.6441	0.8916	0.699	1197
0.7556	0.9264	0.778	1221	0.7437	0.9042	0.639	1192
0.8570	0.9311	0.686	1206	0.8469	0.9174	0.602	1187
0.9547	0.9355	0.613	1190	0.9453	0.9303	0.585	1183
	MMA + 1-PeOH				MMA + 1-HtOH		
0.0449	0.8156	3.018	1267	0.0526	0.8224	4.782	1320
0.1463	0.8267	2.195	1254	0.1258	0.8281	3.728	1308
0.2463	0.8381	1.658	1243	0.2484	0.8389	2.538	1288
0.3476	0.8500	1.290	1233	0.3455	0.8483	1.926	1273
0.4311	0.8601	1.077	1225	0.4471	0.8588	1.483	1258
0.5019	0.8687	0.941	1219	0.5009	0.8647	1.307	1250
0.5439	0.8740	0.876	1215	0.5615	0.8716	1.143	1241
0.6459	0.8862	0.753	1206	0.6456	0.8817	0.965	1228
0.7431	0.8997	0.674	1198	0.7444	0.8946	0.811	1215
0.8477	0.9143	0.619	1190	0.8476	0.9098	0.695	1200
0.9445	0.9287	0.591	1184	0.9438	0.9264	0.618	1188

Table II. *(Continued)*

x_1[a]	ρ $(\mathrm{g \cdot cm^{-3}})$	η $(\mathrm{mPa \cdot s})$	υ $(\mathrm{m \cdot s^{-1}})$	x_1[a]	ρ $(\mathrm{g \cdot cm^{-3}})$	η $(\mathrm{mPa \cdot s})$	υ $(\mathrm{m \cdot s^{-1}})$
308.15 K							
MMA + ME				MMA + EE			
0.0000	0.9530	1.242	1328	0.0000	0.9174	1.402	1264
0.0557	0.9503	1.149	1295	0.0533	0.9175	1.305	1257
0.1541	0.9462	1.010	1274	0.1540	0.9181	1.146	1244
0.2554	0.9427	0.892	1254	0.2467	0.9187	1.022	1232
0.3538	0.9396	0.799	1236	0.3554	0.9194	0.900	1219
0.4561	0.9368	0.720	1219	0.4551	0.9201	0.807	1207
0.4992	0.9357	0.691	1212	0.4993	0.9205	0.770	1202
0.5530	0.9343	0.658	1204	0.5543	0.9209	0.727	1196
0.6543	0.9319	0.606	1190	0.6547	0.9217	0.658	1185
0.7542	0.9298	0.564	1177	0.7547	0.9226	0.600	1175
0.8539	0.9279	0.529	1166	0.8858	0.9240	0.537	1162
0.9543	0.9263	0.502	1156	0.9532	0.9250	0.517	1156
1.0000	0.9257	0.492	1152				
MMA + BE				MMA + 1-BuOH			
0.0000	0.8889	2.228	1280	0.0000	0.7981	1.970	1212
0.0589	0.8906	1.998	1273	0.0500	0.8050	1.726	1206
0.1467	0.8932	1.704	1263	0.1489	0.8184	1.355	1197
0.2571	0.8967	1.408	1250	0.2479	0.8314	1.092	1188
0.3556	0.9001	1.196	1236	0.3487	0.8444	0.900	1181
0.4555	0.9038	1.021	1226	0.4499	0.8572	0.761	1175
0.5016	0.9056	0.952	1220	0.5024	0.8637	0.705	1172
0.5559	0.9077	0.878	1213	0.5479	0.8694	0.664	1169
0.6734	0.9123	0.742	1197	0.6441	0.8813	0.596	1166
0.7556	0.9157	0.664	1186	0.7437	0.8937	0.546	1162
0.8570	0.9198	0.583	1172	0.8469	0.9065	0.513	1158
0.9547	0.9239	0.518	1158	0.9453	0.9188	0.496	1154
MMA + 1-PeOH				MMA + 1-HtOH			
0.0000	0.8035	2.660	1240	0.0000	0.8120	4.200	1292
0.0449	0.8081	2.317	1233	0.0526	0.8156	3.544	1282
0.1463	0.8188	1.733	1219	0.1258	0.8211	2.828	1269
0.2463	0.8300	1.340	1208	0.2484	0.8313	1.991	1250
0.3476	0.8413	1.064	1197	0.3455	0.8402	1.546	1236
0.4311	0.8510	0.900	1189	0.4471	0.8504	1.213	1222
0.5019	0.8595	0.793	1183	0.5009	0.8561	1.078	1214
0.5439	0.8645	0.740	1179	0.5615	0.8629	0.950	1206
0.6459	0.8765	0.641	1171	0.6456	0.8728	0.810	1194
0.7431	0.8896	0.575	1164	0.7444	0.8855	0.685	1181
0.8477	0.9037	0.527	1157	0.8476	0.9002	0.588	1168
0.9445	0.9174	0.501	1153	0.9438	0.9157	0.522	1157

[a] Mole fraction of MMA.

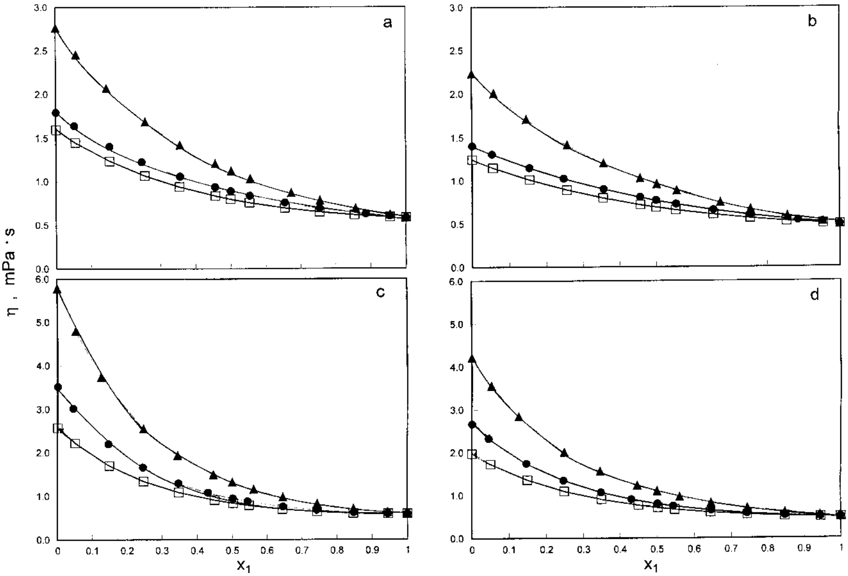

Fig. 1. Mixture viscosities as a function of MMA mole fraction at (a) 298.15 K and (b) 308.15 K for MMA + alkoxyethanols (□, ME; ●, EE; and ▲, BE) and (c) at 298.15 K and (d) 308.15 K for MMA + 1-alcohols (□, 1-BuOH; ●, 1-PeOH; and ▲, 1-HtOH); — (Grunberg–Nissan equation correlated values).

(c) Auslander Equation—three parameters [13]:

$$x_1(x_1+B_{12}x_2)(\eta_{12}-\eta_1)+A_{21}x_2(B_{21}x_1+x_2)(\eta_{12}-\eta_2)=0 \qquad (4)$$

where G_{12}, M_{12}, M_{21}, B_{12}, A_{21}, and B_{21} are adjustable parameters, and x and M are the mole fraction and molar mass of MMA (1) and alcohol (2) components. η and ν are the dynamic and kinematic viscosities of pure MMA (1), alcohol (2), and mixture (12) components. The values of the adjustable parameters of all three equations were determined from experimental data using nonlinear least squares. Table III lists the values of the parameters along with the standard deviations. The mixture viscosities calculated from the Grunberg–Nissan equation are also shown as curves in Figs. 1a–d. The standard deviation values listed in Table III show that both the Grunberg–Nissan and McAllister equations fit the mixture viscosities to within the experimental precision. However, the Grunberg–Nissan equation, which has only one adjustable parameter, provides the smallest standard deviation.

Table III. Adjustable Parameters and Standard Deviations (σ) (in mPa · s) for the Correlation of Viscosities of Methyl Methacrylate + Alkoxyethanols and + 1-Alcohols at 298.15 and 308.15 K

	G_{12} [a]	σ	M_{12} [b]	M_{21} [b]	σ	B_{12} [c]	A_{21} [c]	B_{21} [c]	σ
					298.15 K				
MMA +									
ME	−0.7570	0.001	0.6823	0.9252	0.001	1.2077	0.4331	0.3726	0.006
EE	−0.5647	0.001	0.7632	1.0895	0.005	1.5006	0.5948	0.4271	0.002
BE	−0.5018	0.001	0.7789	2.0294	0.001	0.6266	1.1935	1.1935	0.002
1-BuOH	−1.5189	0.001	0.6292	1.1346	0.002	1.1131	0.2856	0.0775	0.001
1-PeOH	−1.6665	0.001	0.6852	1.3152	0.001	0.8885	0.2135	0.2342	0.001
1-HtOH	−1.3521	0.001	0.9127	2.0308	0.001	0.6422	0.1586	0.6826	0.001
					308.15 K				
MMA +									
ME	−0.4959	0.001	0.6272	0.8146	0.001	1.4252	0.6026	0.4502	0.003
EE	−0.3162	0.001	0.6862	0.9686	0.009	1.1997	0.5707	0.6854	0.003
BE	−0.3722	0.001	0.6678	1.8270	0.001	0.5784	0.2419	1.3669	0.013
1-BuOH	−1.3210	0.001	0.5563	0.9679	0.003	1.1284	0.3117	0.1603	0.001
1-PeOH	−1.4545	0.001	0.6067	1.1138	0.001	0.8915	0.2312	0.3252	0.001
1-HtOH	−1.1444	0.001	0.7511	1.8550	0.001	0.6797	0.1825	0.7336	0.001

[a] Grunberg–Nissan equation.
[b] McAllister equation.
[c] Auslander equation.

3.2. Prediction of Sound Speeds

The sound speeds of binary mixtures are often predicted by free length theory (FLT), collision factor theory (CFT), the Junjie equation (J), and the Nomoto equation (N). The theoretical basis and details of the calculations have been described elsewhere [14–18]. The following final relations were used for calculating sound speeds:

$$\upsilon_{\mathrm{FLT}} = 1/K_{\mathrm{s(FLT)}}\,\rho_{12} \tag{5}$$

$$\log K_{\mathrm{s(FLT)}} = \log k + p \log L_{\mathrm{f12}} \tag{6}$$

$$L_{\mathrm{f12}} = \frac{2(V_{12} - x_1 V_{0.1} + x_2 V_{0.2})}{x_1 Y_1 + x_2 Y_2} \tag{6a}$$

and

$$\upsilon_{\mathrm{CFT}} = \upsilon_{\alpha}[x_1 S_1 + x_2 S_2][(x_1 B_1 + x_2 B_2)/V_{12}] \tag{7}$$

$$\upsilon_{\mathrm{J}} = [(x_1 M_1/\rho_1) + (x_2 M_2/\rho_2)]/\{(x_1 M_1 + x_2 M_2)^{1/2} \times [(x_1 M_1/\rho_1 \upsilon_1^2) + (x_2 M_2/\rho_2 \upsilon_2^2)]^{1/2}\} \tag{8}$$

$$\upsilon_{\mathrm{N}} = [(x_1 R_1 + x_2 R_2)/(x_1 V_1 + x_2 V_2)]^3 \tag{9}$$

where K_{S}, L_{f}, V, V_0, B, S, ρ, and R are the isentropic compressibility, free length, molar volume, molar volume at absolute zero, actual volume of the molecule per mole, collision factor, density, and molar sound, respectively, for pure MMA (1), alcohol (2), and the binary mixture (12). υ_{α} is a constant value taken as 1600 $\mathrm{m \cdot s^{-1}}$.

The $\log k$ and p are constants ($\log k = 7.274$ and 7.629 and $p = 2.106$ and 2.148 at 298.15 and 308.15 K, respectively [14]). The basic parameters that are needed for estimating the sound speeds using Eqs. (5)–(9) are L_{f}, V_0, V_{a}, Y, B, S, and r_i. These parameters for the pure components, as summarized in Table IV, were calculated in the following manner:

$$\log L_{\mathrm{f}} = (\log K_{\mathrm{S}} - \log k)/p \tag{6b}$$

The internal surface area per mole, Y, is then estimated from $Y_i = 2V_{\mathrm{a}.i}/L_{\mathrm{f}.i}$, where $V_{\mathrm{a}.i} = V_{\mathrm{T}.i} - V_{0.i}$ and V_{T} and V_0 are the molar volume at a given temperature T and the molar volume at absolute zero, respectively. The V_0 value for each pure component is obtained from the fit of experimental molar volumes at different temperatures using the equation

$$V_0 = V_{\mathrm{T}}(1 - T/T_{\mathrm{c}})^{0.3} \tag{10}$$

where T_{c} is the critical temperature. The actual volume of the molecule per mole, B, and collision factor, S, for the pure components were calculated from the relations [19], $B_i = (4\pi/3)\, r_i^3 N_{\mathrm{A}}$ and $S = \upsilon V_i/\upsilon_{\infty} B_i$, where r_i is the molecular radius and N_{A} = Avogadro's number. The molar sound velocities of the pure components were calculated using, $R_i = \upsilon_i^{1/3} V_i$.

The compositional dependence of the experimental and calculated sound speeds for binary mixtures of MMA + 2-methoxyethanol and MMA + 1-butanol are shown at 298.15 K in Figs. 2a and b. Similar variations were noted for all other mixtures. The sound speeds vary nonlinearly with an increase in the MMA mole fraction. The decrease in sound speeds is sharp at low MMA mole fractions, while it is smooth in the ester-rich region. All four approaches predicted the dependence in sound speed on composition adequately. Table V summarizes the deviations for different

Table IV. Molar Volume (V_T), Molar Volume at Absolute Zero (V_0), Available Volume (V_a), Free Length (L_f), Surface Area Factor (Y), Collision Factor (S), Actual Volume (B), Molecular Radius (r_i), and Molar Heat Capacities (C_p) for Pure Components at 298.15 and 308.15 K

	V_T ($cm^3 \cdot mol^{-1}$)	V_0 ($cm^3 \cdot mol^{-1}$)	V_a ($cm^3 \cdot mol^{-1}$)	L_f (Å)	Y (Å^2)	S	B ($cm^3 \cdot mol^{-1}$)	r_i (Å)	C_p ($J \cdot K^{-1} \cdot mol^{-1}$)
					298.15 K				
MMA	106.7833	84.459	22.324	0.5680	78.604	2.968	26.582	2.411	191.1
ME	79.2646	63.702	15.563	0.4779	65.131	3.361	19.753	3.361	175.4
EE	97.3849	78.973	18.412	0.4900	75.163	3.261	24.265	3.261	209.8
BE	131.8091	109.328	22.481	0.4817	93.363	3.270	32.851	3.270	273.8
1-BuOH	91.9375	73.234	18.704	0.5234	71.476	3.123	22.889	2.588	177.2
1-PeOH	108.7064	87.868	20.838	0.5165	80.706	3.211	26.961	2.034	208.1
1-HtOH	141.9323	117.197	24.735	0.5060	97.792	3.347	35.253	1.391	272.1
					308.15 K				
MMA	108.156		23.697	0.6029		2.890	26.947	2.515	198.2
ME	79.8468		16.145	0.4959		3.285	19.872	3.285	178.5
EE	98.2341		19.261	0.5126		3.171	24.471	3.171	214.0
BE	132.9508		23.623	0.5061		3.221	33.019	3.221	278.2
1-BuOH	92.8706		19.637	0.5495		3.056	23.021	2.782	184.6
1-PeOH	109.7075		21.840	0.5413		3.124	27.218	2.209	216.5
1-HtOH	143.1035		25.907	0.2990		3.250	35.561	1.533	273.9

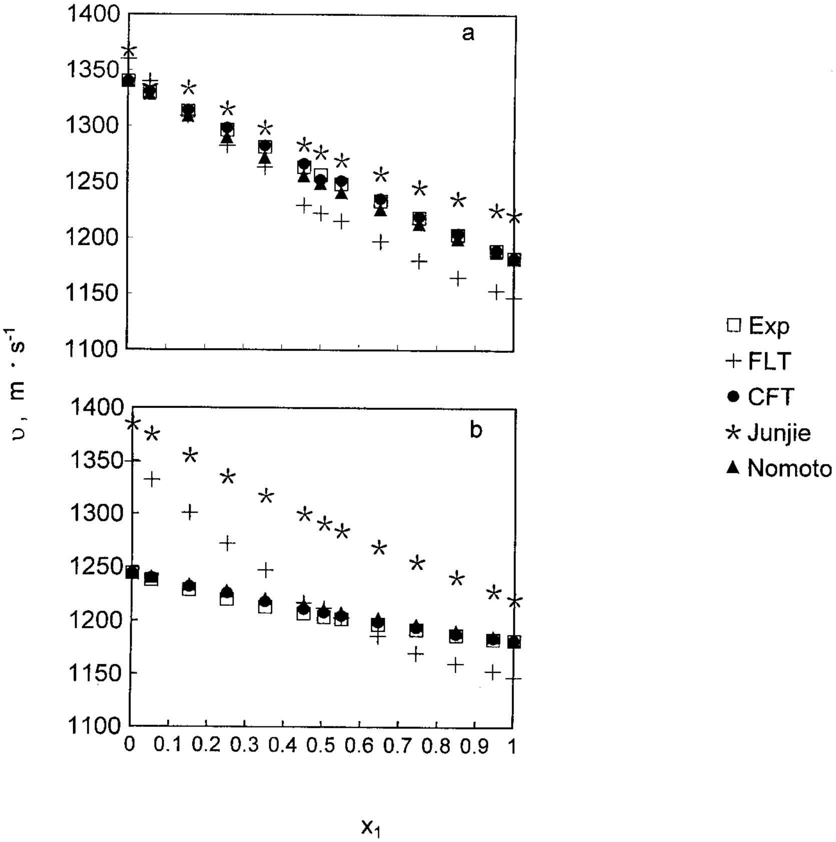

Fig. 2. Sound speeds as a function of MMA mole fraction at 298.15 K; (a) MMA + 2-methoxyethanol and (b) MMA + 1-butanol.

Table V. Values of Standard Deviation (%) for Sound Speeds by Various Methods

	σ (%)				σ (%)			
	FLT	CFT	Nomoto	Junjie	FLT	CFT	Nomoto	Junjie
	298.15 K				308.15 K			
MMA +								
ME	2.5	0.2	0.6	2.0	4.9	1.1	1.1	4.0
EE	2.2	0.3	0.5	3.2	3.3	0.3	0.2	4.3
BE	3.3	0.7	0.4	4.2	3.5	0.2	0.1	5.2
1-BuOH	3.7	0.3	0.4	8.1	4.3	0.4	0.5	8.7
1-PeOH	3.1	0.2	0.6	2.6	4.3	0.5	0.9	9.1
1-HtOH	2.5	0.2	1.0	8.4	4.6	0.5	1.1	9.1

prediction methods. The deviations are in general larger than the experimental uncertainty, i.e., 0.15%. The following order for the relative predictive capability for each of the methods was observed based on the deviations:

$$\text{CFT} \geqslant \text{Nomoto} > \text{FLT} > \text{Junjie}$$

3.3. Excess Viscosities and Isentropic Compressibilities

The excess viscosities, $\delta\eta$, and excess isentropic compressibilities, $K_{\mathrm{s}}^{\mathrm{E}}$, were calculated using the following relations:

$$\delta\eta = \eta_{12} - (x_1\eta_1 + x_2\eta_2) \tag{11}$$

$$K_{\mathrm{S}}^{\mathrm{E}} = K_{\mathrm{s}.12} - K_{\mathrm{s}}^{\mathrm{id}} \tag{12}$$

where $K_{\mathrm{s}.12}$ is the isentropic compressibility of the mixture and was calculated from the relation,

$$K_{\mathrm{s}.12} = 1/\upsilon_{12}^2 \rho_{12} \tag{12a}$$

$K_{\mathrm{s}}^{\mathrm{id}}$ is calculated from the relation,

$$K_{\mathrm{s}}^{\mathrm{id}} = \sum_{i=1}^{2} \phi_i [K_{\mathrm{s}.i} + TV_i(\alpha_i)^2/C_{\mathrm{p}.i}] - T\left(\sum_{i=1}^{2} x_i V_i\right)\left(\sum_{i=1}^{2} \phi_i \alpha_i\right)^2 \Bigg/ \sum_{i=1}^{2} x_i C_{\mathrm{p}.i} \tag{12b}$$

where ϕ_i is the ideal state volume fraction defined by the relation,

$$\phi_i = x_i V_i \Bigg/ \left(\sum_{i=1}^{2} x_i V_i\right) \tag{12c}$$

α_i is the isobaric thermal expansion coefficient and is calculated from the measured densities by the relation, $\alpha = [(\rho_1/\rho_2) - 1]/\Delta t$, where $\Delta t = T_2 - T_1$, and T_2 and T_1 are two different temperatures corresponding to densities ρ_2 and ρ_1.

The $\delta\eta$ and $K_{\mathrm{S}}^{\mathrm{E}}$ functions were fitted to a Redlich–Kister-type equation,

$$A^{\mathrm{E}} = x_1(1 - x_1) \sum_{j=0}^{n} a_j (2x_1 - 1)^j \tag{13}$$

where $A^{\mathrm{E}} = \delta\eta$ (mPa · s) or $K_{\mathrm{S}}^{\mathrm{E}}$ (T · Pa^{-1}), x_1 is the MMA mole fraction, and a_j's are the fitting coefficients. The values of a_j were estimated by unweighted least squares. The values of the coefficients along with the standard deviation, σ, are summarized in Table VI.

Table VI. Values of Coefficients a_j of Eq. (13) for Excess Viscosities ($\delta\eta$) and Excess Isentropic Compressibilities (K_S^E) of MMA + Alkoxyethanols, + 1-Alcohols at 298.15 and 308.15 K

	$\delta\eta$ (mPa · s)				K_S^E $(T \cdot Pa)^{-1}$			
	a_0	a_1	a_2	σ	a_0	a_1	a_2	σ
				298.15 K				
MMA +								
ME	−1.1633	0.4534	−0.1640	0.002	−120.78	11.70	−3.69	0.6
EE	−1.1899	0.4513	−0.1647	0.003	−51.18	0.04	−8.31	0.3
BE	−2.2082	0.9231	−0.2962	0.003	−1.66	−18.1	4.94	0.2
1-BuOH	−2.9459	1.6880	−0.8842	0.008	18.09	4.31	11.70	0.8
1-PeOH	−4.3941	2.8701	−1.5761	0.017	56.03	2.63	44.43	0.7
1-HtOH	−7.4442	5.0472	−2.6618	0.027	119.99	33.79	42.19	0.7
				308.15 K				
MMA +								
ME	−0.7059	0.2295	−0.0691	0.002	−64.49	25.89	18.40	0.3
EE	−0.7134	0.2548	−0.0205	0.004	−1.99	16.18	18.69	0.4
BE	−1.6231	0.6081	−0.1891	0.001	5.40	−2.87	2.47	0.1
1-BuOH	−2.0887	1.1150	−0.5407	0.005	30.25	−26.60	−1.44	0.8
1-PeOH	−3.1095	1.8879	−0.9728	0.010	80.66	4.41	43.30	0.5
1-HtOH	−5.0524	3.1547	−1.5434	0.015	123.48	23.57	28.93	0.9

The variation of $\delta\eta$ as a function of the MMA mole fraction for all the binary mixtures is presented in Figs. 3a and b. A definite trend in the $\delta\eta$ vs x_1 curves is noted. The $\delta\eta$ values are negative over the complete composition range for all mixtures. The curves are skewed towards the low MMA mole fractions. The $\delta\eta_{0.5}$ are found to increase monotonically with the rise in carbon chain length from ME, to EE, and to BE and 1-BuOH, to 1-PeOH, and to 1-HtOH at both temperatures. The $\delta\eta$ values for binary mixtures of MMA + ME, and + EE are approximately the same. However, the $\delta\eta$ values for MMA + 1-alcohol mixtures are unevenly spread. Another striking feature of Figs. 3a and b is that the $\delta\eta$ values are almost 3 to 4 times more negative for MMA + 1-alcohol mixtures than for corresponding MMA + homomorphic alkoxyethanols. The $\delta\eta_{0.5}$ values increase sharply with temperature, i.e., the values become less negative.

The negative $\delta\eta$ values mean that the mixture viscosities are less than the mole fraction average of the pure component values. The decrease of mixture viscosities indicates the weakening of self association of 1-alcohols in presence of MMA. The sharp fall in viscosities in the ester-dilute region as shown in Fig. 1 supports the above observation. The increase in amount

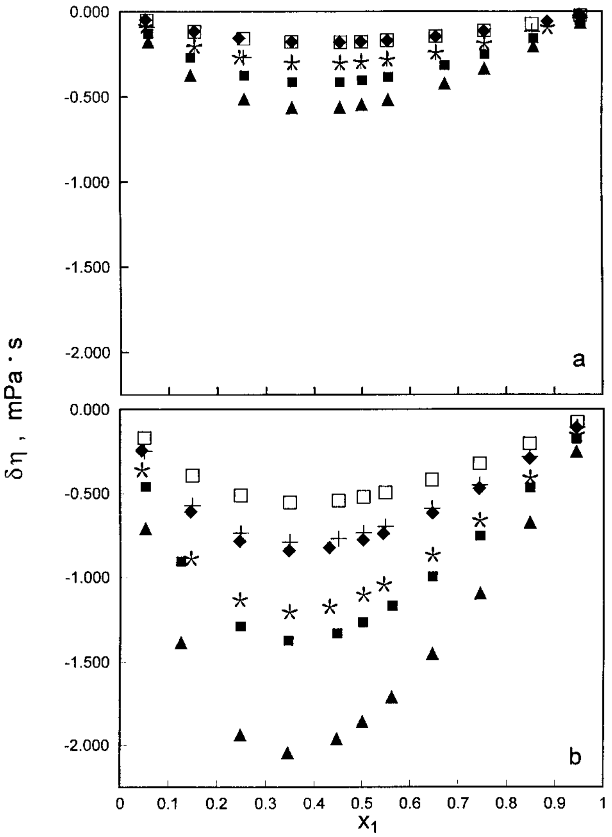

Fig. 3. Excess viscosities as a function of MMA mole fraction: (a) MMA + alkoxyethanols and (b) MMA + 1-alcohols, 298.15 K: + (ME or 1-BuOH), ∗ (EE or 1-PeOH), ▲ (BE or 1-HtOH); 308.15 K: □ (ME or 1-BuOH), ◆ (EE or 1-PeOH), ■ (BE or 1-HtOH).

of MMA, however, may increase the unlike ester–alcohol and like ester–ester interactions and, hence, the decrease in viscosity in the intermediate region is marginal. The skewing of the maxima in $\delta\eta$ values to the ester-dilute region can also be explained by the above considerations. Fort and Moore [20] observed that excess viscosities are negative in mixtures of components having unequal size and in which dispersion forces are present. Large negative excess viscosities have also been observed previously by us in alkyl acrylate + 1-alcohol [9, 10], 1-alcohol + *n*-alkane [21, 22], and 2-butoxyethanol + *n*-alkane [23] mixtures in which structure-breaking dispersion forces are dominant. Liau et al. [6] had also attributed the rupture of hydrogen bonds between 1-butanol molecules by butyl acrylate to be based on negative excess viscosities.

The compositional dependence of excess isentropic compressibilities, K_S^E, for all six binary mixtures at 298.15 and 308.15 K are shown in Figs. 4a and b. The K_S^E values were large and negative over the complete mole fraction range for MMA + ME at both temperatures and for MMA + EE at 298.15 K. While for MMA + BE mixtures (at 298.15 and 308.15 K) and MMA + EE mixtures at 308.15 K, K_s^E vs. x_1 curves showed initial positive values followed by negative values for MMA + BE mixtures and vice versa for MMA + EE mixtures. For all MMA + alkoxyethanol mixtures,

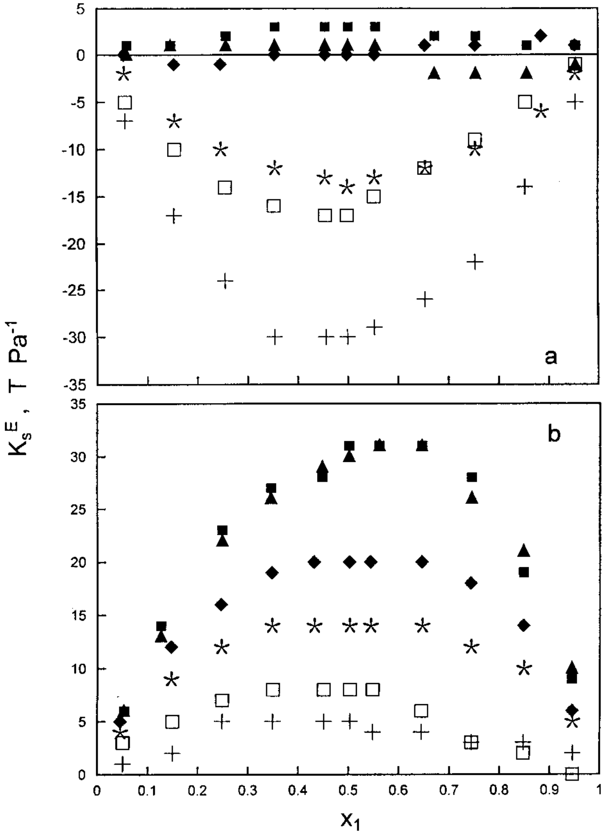

Fig. 4. Excess isentropic compressibilities as a function of MMA mole fraction: (a) MMA + alkoxyethanols and (b) MMA + 1-alcohols; symbols same as in Fig. 3.

the K_s^E values decreased in magnitude from 298.15 to 308.15 K. In contrast to this, Fig. 4b shows that K_s^E values are large and positive in MMA + 1-alcohol mixtures. The $K_{s0.5}^E$ values increase by a factor of three with an increase in carbon chain length from 1-butanol to 1-pentanol and by a factor of more than two from 1-pentanol to 1-heptanol. A large increase in positive K_S^E values is noted in MMA + 1-BuOH and + 1-PeOH mixtures with an increase in temperature from 298.15 to 308.15 K, while the change is small for MMA + 1-HtOH mixtures.

3.4. Discussion

The excess volumes and excess dielectric functions, viz., excess dielectric constants, excess molar and orientation polarization, etc., of these mixtures have been described and discussed elsewhere [24]. The analysis of these functions revealed that alkoxyethanols undergo less self association in contrast to the high tendency of 1-alcohols to undergo self association via intermolecular hydrogen bonding. Nevertheless, the presence of etheric oxygen in alkoxyethanols facilitates the formation of intramolecular hydrogen bonding between the etheric oxygen and hydrogen of –OH group of the same molecule. Infrared, microwave, and calorimetric studies [25–27] have also shown the presence of mostly ten membered dimers and linear intramolecular associates in $R–O–C_2H_5OH$ (where $R = –CH_3$, $–C_2H_5$, $–C_4H_9$, etc.). It is well known that 1-alcohols form a variety of species with different degrees of association in the pure state, however, polymeric linear associates are expected to be predominant in the pure state. Thus, the addition of an acrylic ester to an alkoxyethanol (ME, EE, or BE) and or to a 1-alcohol (1-BuOH, 1-PeOH, or 1-HtOH) may result in the following effects: (i) rupturing or disruption of associate structures in alcohols, (ii) formation of new species because of weak interactions between ester and alcohols, and (iii) free volume changes upon mixing of components of different sizes. The first effect contributes positively to excess volumes and excess isentropic compressibilities and negatively to excess viscosities. However, contributions due to effects (ii) and (iii) are in the opposite direction.

The observed large negative $\delta\eta$ and positive K_S^E values in MMA + 1-alcohols can thus be attributed to the dominance of structure disruptions due to effect (i). The observed almost four-fold decrease in $\delta\eta$ values and large negative K_S^E values (except in MMA + BE mixtures) in MMA + ME, + EE, or + BE in comparison to less negative $\delta\eta$ and positive K_S^E values in MMA + homomorphic linear 1-alcohol mixtures, indicate that structure disruption effects are largely diminished in MMA + alkoxyethanol containing mixtures. The calculations of excess orientation polarizations and excess molar electrical susceptibilities indeed showed that

MMA + alkoxyethanol mixtures are characterized by large positive orientation polarizations and smaller electrical susceptibilities. These results indicate that the preferred partial alignment of dipoles of alkoxyethanols is retained in mixtures in spite of the structure breaking capacity of MMA. As noted in the preceding paragraph, alkoxyethanols in pure state associate predominantly to form ten-membered dimeric rings. These structures can thus resist the structure disruptions in presence of MMA. The $K_{\mathrm{S}}^{\mathrm{E}}$ values of MMA + BE mixtures at 298.15 and 308.15 K are small and either negative or positive. This is rather unexpected because the other excess volumetric and dielectric properties show that structure disruptions in this mixture are very small.

Further insight into the nature of molecular interactions was gained by calculating the acoustic parameters, viz., relative association (R.A.) and solvation number (S_{n}). The R.A. and S_{n} values were calculated using the relations [39, 40]:

$$\mathrm{R.A.} = (L_{\mathrm{f}}'/L_{\mathrm{f}})^3 \tag{14}$$

and

$$S_{\mathrm{n}} = \frac{n_1}{n_2}\left(1 - \frac{K_{\mathrm{s.12}}}{K_{\mathrm{s.1}}}\right) \tag{15}$$

where L_{f}' is the free length for a given composition of binary mixtures calculated by using the Eq. (6). The L_{f} values are as usual obtained from the available volume and molecular surface area factors using Eq. (6a). Though experimentally measured isentropic compressibilities and molar volumes of the binary mixtures are employed in Eqs. (6) and (6a), the free length values calculated by Eq. (6) represent the ideal state in which association effects are neglected because the constants $\log k$ and p that appear in it were evaluated from a linear relation between the isentropic compressibilities and free lengths for 54 non-associating liquids [14]. Thus, the ratio as defined by Eq. (14) fairly represents the measure of association degree in binary mixtures. n_1 and n_2 are the number of moles of MMA and alcohol components, respectively.

The variation of R.A. as a function of the MMA mole fraction is shown in Figs. 5a and b. The comparison of parts a and b revealed interesting observations. The relative association measures the ability of molecules to build associates or supramolecular structures by intermolecular interactions. 1-alcohols in a pure state form linear associates through intermolecular hydrogen bonding and, hence, the R.A. values of 1-butanol and 1-pentanol are greater than for corresponding alkoxyethanols, namely,

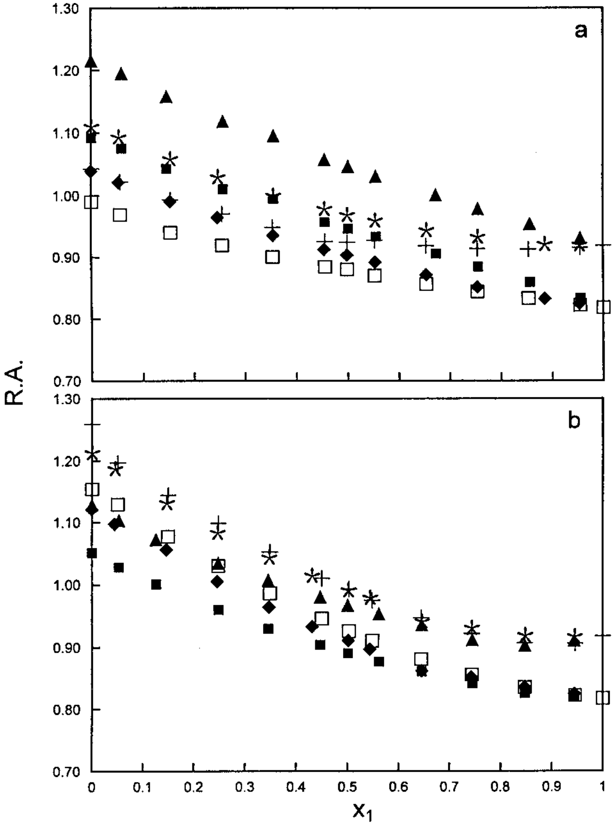

Fig. 5. Relative association as a function of MMA mole fraction (a) MMA + alkoxyethanols and (b) MMA + 1-alcohols; symbols same as in Fig. 3.

2-methoxy- and 2-ethoxyethanols. The increase in carbon chain length is expected to weaken the self association and, hence, 1-heptanol has lower R.A. values than 1-BuOH or 1-PeOH. 2-butoxyethanol has a R.A. value larger than for lower homologues, i.e., ME and EE. It was concluded earlier from the analysis of excess dielectric functions that BE molecules retain higher preferential dipole order, and hence, it may be stated that BE molecules have better organized structures in the form of cyclic ten-membered rings. The higher R.A. value for BE over ME and EE is consistent with this observation. MMA, as expected, has an R.A. value much lower than for pure alcohols. The R.A. values decreased nonlinearly as the alcohols are diluted with MMA. The fall in R.A. up to $x_1 \approx 0.65 - 0.75$ is sharp, and the R.A. value changes smoothly in ester-rich regions. The decreased R.A. values support our earlier conclusion that structure disruptions are more predominant in these mixtures.

The solvation number (calculated assuming MMA as solvent) is plotted as a function of ester mole fraction in Figs. 6a and b. S_n values showed a gradual increase with increasing proportion of MMA in MMA + alkoxyethanol mixtures. The solvation number values are negative in MMA + 1-BuOH and + 1-PeOH mixtures at both temperatures. S_n values are positive and showed a gradual initial increase followed by a decrease (become negative) in the ester-rich regions of MMA + 1-heptanol mixtures. The observed positive solvation numbers in MMA + alkoxyethanols are rather unexpected since the qualitative analysis of various excess functions

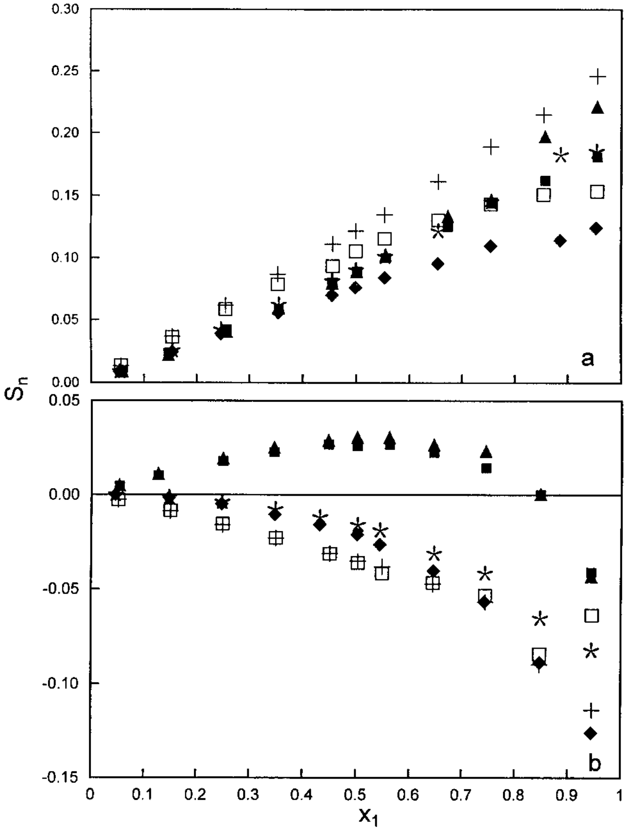

Fig. 6. Solvation number as a function of MMA mole fraction (a) MMA + alkoxyethanols and (b) MMA + 1-alcohols; symbols same as in Fig. 3.

indicated that structure disruptions are predominant in these mixtures. But the possible accommodation of MMA molecules into interstices caused by the dimeric ten-membered ring structures in alkoxyethanols, cannot be ruled out. The fact that the excess volumes are less positive and excess viscosities are less negative in these mixtures than in MMA + 1-alcohols, possibly supports the positive solvation interactions. The negative solvation in MMA + 1-BuOH or + 1-PeOH mixtures and much diminished positive S_n in MMA + 1-HtOH mixtures confirm the dominance of structure-breaking interactions in these mixtures.

4. CONCLUDING REMARKS

The qualitative analysis of excess viscosities and excess isentropic compressibilities revealed that structure-disruption interactions are predominant in MMA + alkoxyethanol or + 1-alcohol binary liquid mixtures. However, alkoxyethanols differ from 1-alcohols in their self-association ability. The presence of dimeric ten-membered cyclic structures in alkoxyethanols may cause solvation of MMA molecules in terms of interstitial accommodation of MMA in to alkoxyethanol structures. The mixture viscosities are best correlated by Grunberg Nissan and McAllister (two body-interaction) equations. The sound speeds were predicted by FLT, CFT, Junjie, and Nomoto equations.

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