

# Thermophysical Properties of Nonelectrolyte Mixtures. Densities, Viscosities, and Sound Speeds of Binary Mixtures of Methyl Methacrylate + Branched Alcohols (Propan-2-ol, 2-Methylpropan-1-ol, Butan-2-ol, and 2-Methylpropan-2-ol) at $T=298.15$ and $308.15$ K

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Measurements of the densities, viscosities, and sound speeds at  $T=298.15$  and  $308.15$  K for the binary mixtures of methyl methacrylate + propan-2-ol, +2-methylpropan-1-ol, +butan-2-ol, and +2-methylpropan-2-ol are made over the complete composition range. From the measured data, excess isentropic compressibilities have been calculated. The mixture viscosities have been correlated by the Grunberg–Nissan, McAllister, and Auslander equations, while the sound speed in binary mixtures has been analyzed using free length and collision factor theories, and Junjie and Nomoto equations. The excess isentropic compressibilities,  $\kappa_s^E$  are fitted to a third degree polynomial equation. The qualitative analysis of  $\kappa_s^E$  have been made in terms of bulk molecular interactions. The conclusions drawn were supplemented by examining the variation of relative association and solvation numbers over the complete composition range.

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**KEY WORDS:** binary mixtures; butan-2-ol; densities; excess isentropic compressibilities; 2-methylpropan-1-ol; 2-methylpropan-2-ol; methyl methacrylate; propan-2-ol; sound speeds; viscosities.

## 1. INTRODUCTION

Acrylic esters and alcohols are used together in trans-esterification reactions to convert lower alkyl chain esters to their higher homologues. Thus,

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when an acrylic ester of general formula,  $H_2C:CHCOOR'$  or  $H_2C:CRCOOR'$  is reacted with  $R''-OH$  (where  $R''$  = simple alkyl, or branched alkyl or alkoxy moiety, etc), the  $R'$  in the esters is replaced by  $R''$  of alcohol. A knowledge of the thermodynamic, transport, acoustic, and dielectric properties of binary mixtures of acrylic esters with alcohol species is important in understanding the mixing process. The results from such studies could have utility for the efficient design of trans-esterification reactions on an industrial scale. In spite of their fundamental and industrial importance, binary mixtures of acrylic esters + alcohols have been so far studied to a limited extent. This is in stark contrast to the numerous literature reported investigations on various thermophysical properties of alkylalkanoates + alcohols [1-3].

Therefore, we have undertaken a research program, which involves systematic measurements of the thermodynamic, transport, acoustic, and dielectric properties of binary and ternary mixtures consisting of acrylic esters, alcohols, and hydrocarbons. The present paper reports measurements of the density,  $\rho$ , viscosity,  $\eta$ , and sound speeds,  $u$ , for the binary mixtures of methyl methacrylate (MMA) + propan-2-ol, +2-methylpropan-1-ol, +butan-2-ol, and +2-methylpropan-2-ol over the entire composition range at  $T = 298.15$  and  $308.15$  K. This study thus continues our ongoing research work on acrylic esters + alcohols [4-7]. The mixture viscosities were also correlated by semiempirical approaches. The sound speed in the binary mixtures was analyzed using free length and collision factor theories, and Junjie and Nomoto equations. The excess isentropic compressibilities,  $\kappa_s^E$ , were calculated using the experimental results of  $u$  and  $\rho$  at  $T = 298.15$  and  $308.15$  K.

## 2. EXPERIMENTAL

### 2.1. Materials

The methyl methacrylate was a purum grade chemical from Fluka. It was stabilized with a  $2.5 \times 10^{-5}$  mass fraction of hydroquinone monomethyl ether and used as such. Propan-2-ol, 2-methylpropan-1-ol, and 2-methylpropan-2-ol were locally acquired analytical reagent grade chemicals. Propan-2-ol was further purified by drying it with calcium chloride, then with barium oxide, and finally by three careful fractional distillations. 2-Methylpropan-1-ol and 2-methylpropan-2-ol were fractionally distilled repeatedly, and the final fraction at their respective boiling points was collected. Butan-2-ol was obtained from Koch-Light and used as such without further purification. GLC analysis indicated a mole percentage purity of 99.8, 99.6, 99.6, 99.5, and 99.8 for MMA, propan-2-ol,

2-methylpropan-1-ol, butan-2-ol, and 2-methylpropan-2-ol, respectively. Experimental results for the density, viscosity, and sound speed of the pure liquids at  $T=298.15$  and  $308.15$  K are compared with published data, and such a comparison is presented in Table I.

## 2.2. Methods

The binary mixtures were prepared by mixing the pure components in hermetically sealed glass vials. A set of eleven compositions was prepared for each system. The pure components were degassed by double distillation just before mixing. The various physical properties of the prepared mixtures were measured on the same day. The mixtures were prepared gravimetrically with mass measurements to an uncertainty of  $\pm 0.01$  mg using a single pan balance (Dhona 100 DS, India). The reproducibility in mole fractions was within  $\pm 0.0001$  units. Densities of pure liquids and their mixtures were measured with a high precision vibrating-tube digital density meter (Anton Paar DMA 5000). The instrument has a built-in thermostat for maintaining desired temperatures in the range of 0 to  $90^\circ\text{C}$ . The temperature of the measuring cell is displayed with three digits after decimal. The repeatability of the temperature has been found to be  $\pm 0.003$  K and  $\pm 0.002$  K for a given session and two different sessions, respectively. The uncertainty in temperature during the measurements, however, is  $\pm 0.01^\circ\text{C}$  since Pt 100  $\Omega$  sensors were used. The instrument was calibrated with air and freshly degassed double distilled water at  $T=293.15$ ,  $313.15$ , and  $333.15$  K. The measured densities have an estimated uncertainty better than  $\pm 5 \times 10^{-6} \text{ g}\cdot\text{cm}^{-3}$  even though the instrument allows a sixth digit (after decimal point) display. The viscosity,  $\eta$  of pure liquids and liquid mixtures were determined using a Ubbelohde suspended-level viscometer [8]. The viscometer was suspended in a thermostatted water bath maintained to  $\pm 0.01^\circ\text{C}$ . Four sets of readings for the flow times were taken using a Racer stopwatch that can register time to  $\pm 0.1$  s, and the arithmetic mean was taken for the calculation of the viscosity. The estimated uncertainty and precision in viscosity measurements were found to be  $\pm 0.002$  and  $\pm 0.001$  mPa $\cdot$ s, respectively. The sound speeds,  $u$ , at 2 MHz were measured using a multifrequency ultrasonic interferometer (Mittal Enterprises, New Delhi, India, Model M-82). The temperature within the measuring cell was maintained to  $0.01^\circ\text{C}$  by circulating water through the input and output jacket chutes. The reproducibility in the measured sound speeds (as estimated from repeated measurements on the same liquid (or mixture)) was better than  $\pm 0.8 \text{ m}\cdot\text{s}^{-1}$ . However, the uncertainty (as estimated from the mean deviations of our experimental values with the reported literature

**Table I.** Densities ( $\rho$ ), Viscosities ( $\eta$ ), and Sound Speeds ( $u$ ) of Pure Components at  $T = 298.15$  and  $308.15$  K

	$\rho$ ( $\text{g} \cdot \text{cm}^{-3}$ )						$\eta$ ( $\text{mPa} \cdot \text{s}$ )						$u$ ( $\text{m} \cdot \text{s}^{-1}$ )						
	298.15 K		308.15 K		298.15 K		308.15 K		298.15 K		308.15 K		298.15 K		308.15 K				
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.			
Methyl methacrylate	0.93760	0	0.93766	[24]	0.92570	0	----	0.584	----	0.492	----	1182.1	----	1152.1	----	----			
Propan-2-ol	0.78126	0	0.78119	[25]	0.77276	0	----	2.020	2.052	[29]	1.553	1.551	[31]	1147.3	1137.07	[33]	1116.0	1102	[35]
2-Methylpropan-1-ol	0.79780	0	0.79781	[26]	0.79025	0	----	3.332	3.332	[29]	2.426	2.426	[29]	1192.9	1187.95	[34]	1158.2	1154	[35]
Butan-2-ol	0.80262	6	0.80253	[27]	0.79410	7	----	3.083	3.084	[30]	2.582	----	----	1216.1	1212	[34]	1178.8	----	----
2-Methylpropan-2-ol	0.78120	0	0.78163	[28]*	0.77088	0	----	4.439	4.439	[29]	2.550	2.546	[32]	1126.0	----	----	1089.2	1083	[32]

\* Ref. 28 has been rounded up to five digits.

data for the pure components as given in Table I) in the  $u$  values has been found to be  $\pm 0.9\%$ .

### 3. RESULTS AND DISCUSSION

The results of measured densities,  $\rho$ , viscosities,  $\eta$ , and sound speeds,  $u$ , of the four binary mixtures at  $T=298.15$  and  $308.15$  K are given in Table II. The mixture viscosities are also plotted as a function of MMA mole fraction in Parts a and b of Fig. 1. The mixture viscosities were also correlated by the Grunberg–Nissan [9] equation:

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12}, \quad (1)$$

the McAllister [10] equation:

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

and the Auslander [11] equation:

$$x_1(x_1 + B_{12}x_2)(\eta_{12} - \eta_1) + A_{21}x_2(B_{21}x_1 + x_2)(\eta_{12} - \eta_2) = 0 \quad (3)$$

The terms  $\eta_i$ ,  $v_i$ ,  $x_i$ , and  $M_i$  represent the dynamic viscosity, kinematic viscosity, mole fraction, and molar mass of the  $i$ th component ( $i=1$  for MMA and  $i=2$  for branched alcohols), and mixtures are denoted by a subscript 12. The terms  $G_{12}$ ,  $M_{12}$ ,  $M_{21}$ ,  $B_{12}$ ,  $A_{21}$ , and  $B_{21}$  are treated as adjustable parameters, and their values have been determined from the fits of experimental data using a nonlinear regression analysis based on the Marquardt algorithm. These equations are particularly selected because the characteristic constant parameter  $G_{12}$  of Eq. (1) allows for positive and negative deviations from the additivity rule, Eq. (2) is based on the Eyring theory of absolute reaction rates with a three-body model, and Eq. (3) involves three parameters. Table III summarizes the results of analysis. A perusal of the standard deviation  $\sigma$  values from columns 3, 6, and 10 reveals that both the Grunberg–Nissan and McAllister equations can be used to fit mixture viscosities to within  $0.001$  mPa·s while the Auslander equation reproduces viscosity ratios to a maximum uncertainty of  $0.003$  mPa·s. The Grunberg–Nissan correlated dynamic viscosities are also shown along with the experimental values in Fig. 1.

Table II. Densities ( $\rho$ ), Viscosities ( $\eta$ ), and Sound Speeds ( $u$ ) for MMA (1)+ Branched Alcohols (2) at  $T = 298.15$  and  $308.15$  K

$x_1$	298.15 K				308.15 K				298.15 K				308.15 K				
	$\rho$ ( $\text{g}\cdot\text{cm}^{-3}$ )	$\eta$ ( $\text{mPa}\cdot\text{s}$ )	$u$ ( $\text{m}\cdot\text{s}^{-1}$ )	$\rho$ ( $\text{g}\cdot\text{cm}^{-3}$ )	$\eta$ ( $\text{mPa}\cdot\text{s}$ )	$u$ ( $\text{m}\cdot\text{s}^{-1}$ )	$x_1$	$\rho$ ( $\text{g}\cdot\text{cm}^{-3}$ )	$\eta$ ( $\text{mPa}\cdot\text{s}$ )	$u$ ( $\text{m}\cdot\text{s}^{-1}$ )	$\rho$ ( $\text{g}\cdot\text{cm}^{-3}$ )	$\eta$ ( $\text{mPa}\cdot\text{s}$ )	$u$ ( $\text{m}\cdot\text{s}^{-1}$ )	$\rho$ ( $\text{g}\cdot\text{cm}^{-3}$ )	$\eta$ ( $\text{mPa}\cdot\text{s}$ )	$u$ ( $\text{m}\cdot\text{s}^{-1}$ )	
	MMA (1)+ Propan-2-ol								MMA (1)+ 2-Methylpropan-1-ol								
0.0556	0.79234	1.716	1150.5	0.78352	4	1.339	1120.3	0.0547	0.80577	6	2.740	1192.6	0.79788	1	2.077	1157.3	
0.1557	0.81159	0	1.314	1155.6	0.80221	6	1.051	1125.4	0.1398	0.81836	6	2.067	1191.9	0.81002	3	1.621	1156.8
0.2605	0.83051	7	1.034	1160.4	0.82063	2	0.845	1129.5	0.2311	0.83173	2	1.576	1191.0	0.82290	9	1.274	1156.5
0.3541	0.84645	0	0.862	1164.1	0.83616	0	0.717	1132.4	0.3300	0.84603	6	1.220	1189.9	0.83670	2	1.012	1156.2
0.4318	0.85903	7	0.760	1166.8	0.84844	7	0.638	1134.4	0.4577	0.86422	0	0.927	1188.6	0.85425	1	0.788	1155.5
0.5041	0.87026	6	0.689	1169.2	0.85942	5	0.583	1136.0	0.5037	0.87068	7	0.852	1188.0	0.86050	0	0.730	1155.0
0.5537	0.87771	8	0.651	1170.6	0.86672	2	0.553	1137.1	0.5427	0.87613	5	0.799	1187.6	0.86576	8	0.687	1154.6
0.6557	0.89245	4	0.596	1173.4	0.88117	4	0.509	1139.2	0.6552	0.89166	0	0.686	1186.4	0.88080	5	0.595	1153.3
0.7561	0.90625	9	0.567	1175.8	0.89474	9	0.484	1141.6	0.7288	0.90165	8	0.638	1185.5	0.89051	5	0.553	1152.3
0.8542	0.91916	5	0.559	1178.1	0.90747	6	0.477	1144.7	0.8409	0.91663	6	0.594	1184.2	0.90510	6	0.512	1151.0
0.9512	0.93144	4	0.571	1180.3	0.91961	9	0.483	1148.6	0.9341	0.92884	7	0.581	1183.0	0.91705	3	0.495	1150.9
	MMA (1)+ Butan-2-ol								MMA (1)+ 2-Methylpropan-2-ol								
0.0597	0.81073	1	2.462	1208.8	0.80204	1	2.057	1173.8	0.0571	0.78998	2	3.463	1128.3	0.77923	4	2.088	1092.3
0.1551	0.82360	7	1.779	1201.8	0.81427	9	1.481	1167.4	0.1587	0.80546	5	2.316	1133.4	0.79421	6	1.510	1098.4
0.2550	0.83714	0	1.320	1196.9	0.82761	8	1.097	1161.9	0.2560	0.82074	8	1.652	1137.9	0.80925	5	1.150	1104.0
0.3562	0.85088	1	1.022	1193.7	0.84114	8	0.848	1157.8	0.3589	0.83693	6	1.217	1142.7	0.82528	4	0.898	1110.0
0.4561	0.86445	7	0.830	1191.7	0.85421	6	0.688	1155.1	0.4561	0.85203	9	0.956	1147.8	0.84023	9	0.738	1116.0
0.5021	0.87070	6	0.766	1191.0	0.86010	6	0.635	1154.3	0.4983	0.85853	2	0.873	1150.2	0.84665	7	0.686	1118.9
0.5571	0.87817	2	0.704	1190.3	0.86705	5	0.584	1153.5	0.5567	0.86748	1	0.782	1153.7	0.85548	9	0.627	1122.6
0.6562	0.89159	9	0.626	1189.2	0.87943	7	0.520	1152.8	0.6571	0.88292	6	0.672	1159.8	0.87072	0	0.555	1129.3
0.7557	0.90502	9	0.581	1187.8	0.89202	0	0.484	1152.6	0.7563	0.89866	3	0.608	1165.8	0.88628	8	0.511	1135.8
0.8552	0.91838	9	0.564	1185.9	0.90534	3	0.472	1152.3	0.8410	0.91296	3	0.580	1170.6	0.90056	9	0.491	1140.7
0.9549	0.93168	4	0.572	1183.2	0.92024	4	0.481	1151.2	0.9335	0.93014	7	0.573	1174.6	0.91799	1	0.486	1145.2

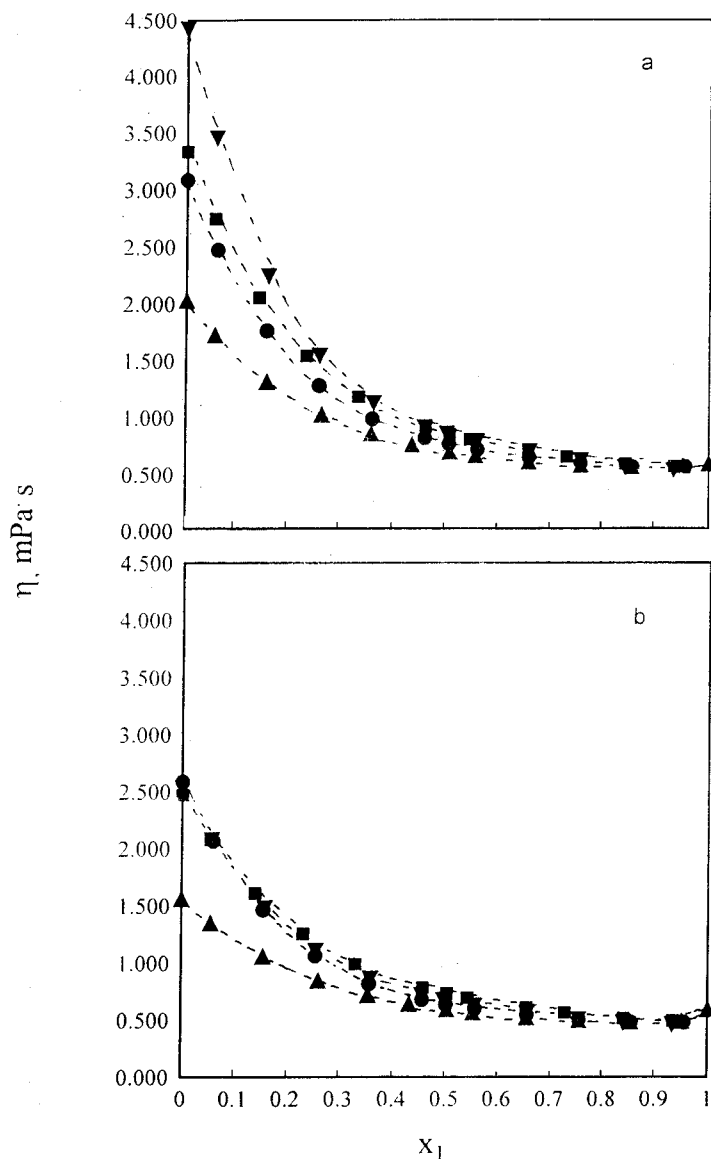


Fig. 1. Variation of experimental viscosities with ester mole fraction for MMA + branched alcohols at (a)  $T = 298.15$  K and (b)  $T = 308.15$  K, MMA (▲) + propan-2-ol; (■) + 2-methylpropan-1-ol, (●) + butan-2-ol, and (▼) + 2-methylpropan-2-ol, (·····), Grunberg-Nissan equation correlated values.

**Table III.** Adjustable Parameters and Standard Deviations ( $\sigma$ ) for the Correlation of Mixture Viscosities of MMA (1)+ Branched Alcohols (2) at  $T=298.15$  and  $308.15$  K

	$G_{12}$	$\sigma$	$M_{12}$	$M_{21}$	$\sigma$	$A_{21}$	$B_{21}$	$B_{12}$	$\sigma$
298.15 K									
MMA+									
Propan-2-ol	-1.801	0.001	0.545	0.878	0.001	0.360	-0.440	1.540	0.003
2-Methylpropan-1-ol	-1.945	0.001	0.613	1.155	0.001	0.211	0.004	0.948	0.003
Butan-2-ol	-2.229	0.001	0.543	0.998	0.001	0.244	-0.303	1.182	0.002
2-Methylpropan-2-ol	-2.462	0.001	0.571	1.201	0.001	0.164	-0.112	0.853	0.002
308.15 K									
MMA+									
Propan-2-ol	-1.603	0.001	0.482	0.751	0.001	0.401	-0.386	1.623	0.003
2-Methylpropan-1-ol	-1.624	0.001	0.558	1.004	0.001	0.261	0.097	1.059	0.002
Butan-2-ol	-2.281	0.001	0.456	0.830	0.001	0.243	-0.345	1.195	0.002
2-Methylpropan-2-ol	-1.971	0.001	0.507	0.936	0.001	0.243	-0.126	1.090	0.002

The sound speeds in the binary liquid mixtures were calculated from free length theory (FLT) [12], collision factor theory (CFT) [13], as well as using the Junjie [14] and Nomoto [15] equations. The basic parameters needed for the prediction of the sound speed, viz., the molar volume,  $V_T$ ; the molar volume at absolute zero,  $V_0$ ; the available volume,  $V_a$ ; the free length,  $L_f$ ; the surface factor,  $Y$ ; the collision factor,  $S$ ; the actual volume,  $B_i$ ; and the molecular radius,  $r_j$ , etc., were calculated by using the relations described in the above references. The free length,  $L_f$ , was calculated from the relation,  $L_f = 2V_a/Y$ , where  $V_a$  is the available volume, i.e.,  $V_a = V_T - V_0$  and  $Y$  is the internal surface area of all the molecules per mole.  $Y$  was evaluated from the relation,  $Y = (36\pi N V_0^2)^{1/3}$ . The collision factor,  $S_i$  was calculated as  $S_i = u V_T / (B_i u_\alpha)$ , where  $u$  is the experimental sound speed of the respective pure components and  $u_\alpha = 1600 \text{ m} \cdot \text{s}^{-1}$ . The molecular radius,  $r_j$ , was calculated from the expression due to Schaaffs [16];  $r_j = \alpha [1 - \beta \{ (1 + 1/3\beta)^{1/2} - 1 \}]^{1/3}$  where  $\alpha = (3V_T / (16\pi N))^{1/3}$  and  $\beta = (\gamma RT / (M u^2))$ ; and  $\gamma$ ,  $R$ , and  $M$  stand for the heat capacity ratio,  $C_p/C_v$ , the gas constant, and the molar mass of a pure component, respectively. The actual volume for a mole of a pure compound,  $B_i$ , was calculated as  $B_i = 4\pi / (3r_j^3 N_A)$  [17], where  $N_A$  is Avogadro's number. These parameters for the pure components at  $T=298.15$  and  $308.15$  K are given in Table IV. A representative plot to show comparisons between experimental and calculated sound speeds as a function of MMA mole fraction for MMA + propan-2-ol mixtures is displayed in Parts a ( $T=298.15$  K) and b ( $T=308.15$  K) of Fig. 2. It can be seen from the figure that the trend in the variation of the sound speed as predicted by CFT and the Nomoto



**Table IV.** Molar Volumes ( $V_T$ ), Molar Volumes at Absolute Zero ( $V_0$ ), Available Volumes ( $V_a$ ), Free Lengths ( $L_f$ ), Surface Area Factors ( $Y$ ), Collision Factors ( $S$ ), Actual Volumes ( $B$ ), Molecular Radii ( $r_j$ ), and Molar Heat Capacities ( $C_p$ ) for Pure Components at  $T = 298.15$  and  $308.15$  K

	$V_T$ ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )	$V_0$ ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )	$V_a$ ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )	$L_f$ ( $\text{\AA}$ )	$Y$ ( $\text{\AA}^2$ )	$S$	$B$ ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )	$r_j$ ( $\text{\AA}$ )	$C_p$ ( $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )
	298.15 K								
MMA	106.78328	84.40800	22.37528	0.5696	78.56	2.9674	26.5841	2.193	191.1
Propan-2-ol	76.92189	58.50147	18.42042	0.5987	61.53	2.8826	19.1296	1.965	154.6
2-Methylpropan-1-ol	92.90800	73.22487	19.68313	0.5509	71.46	2.9963	23.1203	2.093	181.0
Butan-2-ol	92.34936	72.17566	20.17370	0.5701	70.77	3.0549	22.9748	2.089	196.9
2-Methylpropan-2-ol	94.88223	72.46116	22.42107	0.6319	70.96	2.8289	23.6041	2.108	220.3
	308.15 K								
MMA	108.15599		23.74799	0.6046		2.8926	26.9202	2.202	198.2
Propan-2-ol	77.76800		19.26653	0.6262		2.8042	19.3436	1.972	162.7
2-Methylpropan-1-ol	93.79563		20.57076	0.5757		2.9073	23.3496	2.099	189.2
Butan-2-ol	93.34007		21.16441	0.5981		2.9609	23.2298	2.096	207.4
2-Methylpropan-2-ol	96.15245		23.69129	0.6677		2.7354	23.9248	2.117	228.2

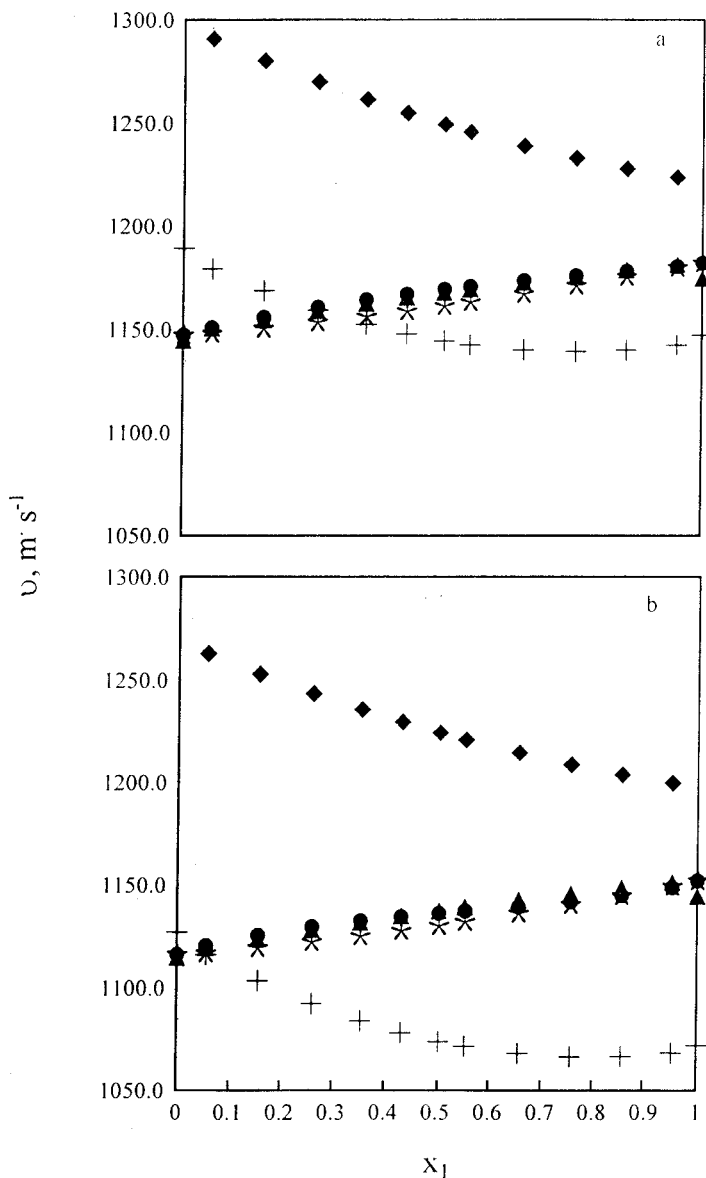


Fig. 2. Variation of sound speed with ester mole fraction for binary mixtures of MMA + propan-2-ol at (a)  $T=298.15\text{ K}$  and (b)  $T=308.15\text{ K}$ , (●) experimental, (+) FLT, (\*) CFT, (▲) Junjie, and (◆) Nomoto.

equation is consistent with the experimental results. In general, for all four mixtures, the standard deviations,  $\sigma$  (in %) between experimental values and CFT and the Nomoto equation calculated sound speeds are found to lie in the 0.1 to 0.7% range. The FLT and Junjie equation fail to predict not only the trend in  $u$  versus  $x_1$  variations, but also the calculated values deviate from the experimental results by 2.5 to 7.9% (FLT) and by 8.1 to 9.5% (Junjie equation).

The excess isentropic compressibility,  $\kappa_s^E$  in binary mixtures has been calculated using the relation,

$$\kappa_s^E = \kappa_{s,12} - \kappa_s^{\text{id}} \quad (4)$$

where  $\kappa_{s,12}$  is the isentropic compressibility of the mixture.  $\kappa_s^{\text{id}}$  was calculated from the relation [18],

$$\kappa_s^{\text{id}} = \sum_{i=1}^2 \phi_i [\kappa_{s,i} + TV_i(\alpha_i^2)/C_{p,i}] - \left\{ T \left( \sum_{i=1}^2 x_i V_i \right) \left( \sum_{i=1}^2 \phi_i \alpha_i \right)^2 / \sum_{i=1}^2 x_i C_{p,i} \right\} \quad (5)$$

$\phi_i$  is the ideal state volume fraction and is defined by the relation,

$$\phi_i = x_i V_i / \left( \sum_{i=1}^2 x_i V_i \right) \quad (5a)$$

$\alpha_i$  and  $V_i$  are the isobaric thermal expansion coefficients and molar volumes of the pure components. The  $\alpha_i$  for each of the pure components was calculated from the densities measured over a wide temperature range. The molar heat capacities,  $C_{p,i}$ , for the pure components were taken from the literature [19–21].

The compositional dependence of  $\kappa_s^E$  was mathematically represented by an equation of the type,

$$\kappa_s^E / (\text{TPa})^{-1} = x_1 (1 - x_1) \sum_{j=0}^{j=2} a_j (2x_1 - 1)^{j-1} \quad (6)$$

where  $x_1$  is the MMA mole fraction and  $a_j$ 's are the coefficients. The values of the coefficients,  $a_j$ , were estimated by multiple regression analysis based on a least-squares method. The standard deviation,  $\sigma$ , between the fitted values and the values determined from experimental results were calculated as

$$\sigma = \left[ \frac{\sum (\kappa_s^{\text{Exp}} - \kappa_s^{\text{Fitt}})^2}{n - p} \right]^{1/2} \quad (7)$$

**Table V.** Values of Coefficients of Eq. (6) and the Standard Deviations ( $\sigma$ ) for Mathematical Representation of Excess Isentropic Compressibilities ( $\kappa_s^E$ ) (in  $\text{TPa}^{-1}$ ) of the Binary Mixtures of MMA (1) + Branched Alcohols (2) at  $T=298.15$  and  $308.15$  K

		$a_0$	$a_1$	$a_2$	$\sigma$	$a_0$	$a_1$	$a_2$	$\sigma$
		298.15 K				308.15 K			
MMA +									
Propan-2-ol	$K_s^E$	-49.9	31.2	-1.6	0.1	-33.0	63.2	-5.6	0.1
2-Methylpropan-1-ol	$K_s^E$	-31.1	3.5	-3.4	0.1	-27.0	11.6	23.8	0.1
Butan-2-ol	$K_s^E$	17.1	-55.2	9.6	0.1	43.0	-26.5	4.4	0.1
2-Methylpropan-2-ol	$K_s^E$	-7.9	1.0	-12.7	0.1	-21.1	1.5	2.5	0.1

where  $n$  is the number of experimental points and  $p$  is the number of coefficients. The values of the parameters along with the standard deviations are presented in Table V.

The variation of excess isentropic compressibilities as a function of MMA mole fraction is shown in Fig. 3. The  $\kappa_s^E$  values are negative over the entire composition range for MMA + 2-methylpropan-1-ol and MMA + 2-methylpropan-2-ol mixtures at  $T=298.15$  and  $308.15$  K. The curves for MMA + propan-2-ol are characterized mostly by large negative values except for a few positive points in ester-rich regions at  $308.15$  K. In contrast, the trend in the curves for MMA + butan-2-ol show large positive  $\kappa_s^E$  values at  $T=308.15$  K and positive regions followed by a negative dip (in the ester rich region) at  $T=298.15$  K. The observed positive and less negative  $\kappa_s^E$  values for MMA + butan-2-ol and MMA + 2-methylpropan-2-ol mixtures indicate the predominance of structure disruption upon mixing. However, the observed negative  $\kappa_s^E$  values in MMA + propan-2-ol and +2-methylpropan-1-ol indicate that structure-making interactions are also present in addition to structure disruptions in these mixtures.

To gain further insight into the nature of the interactions, the acoustic parameters, namely, the relative association, R.A. [22], and solvation number,  $S_n$  [23], were calculated by using the relations,

$$R.A. = (L'_f/L_f)^3 \quad (10)$$

and

$$S_n = \frac{n_1}{n_2} \left( 1 - \frac{\kappa_{S,12}}{\kappa_{S,1}} \right) \quad (11)$$

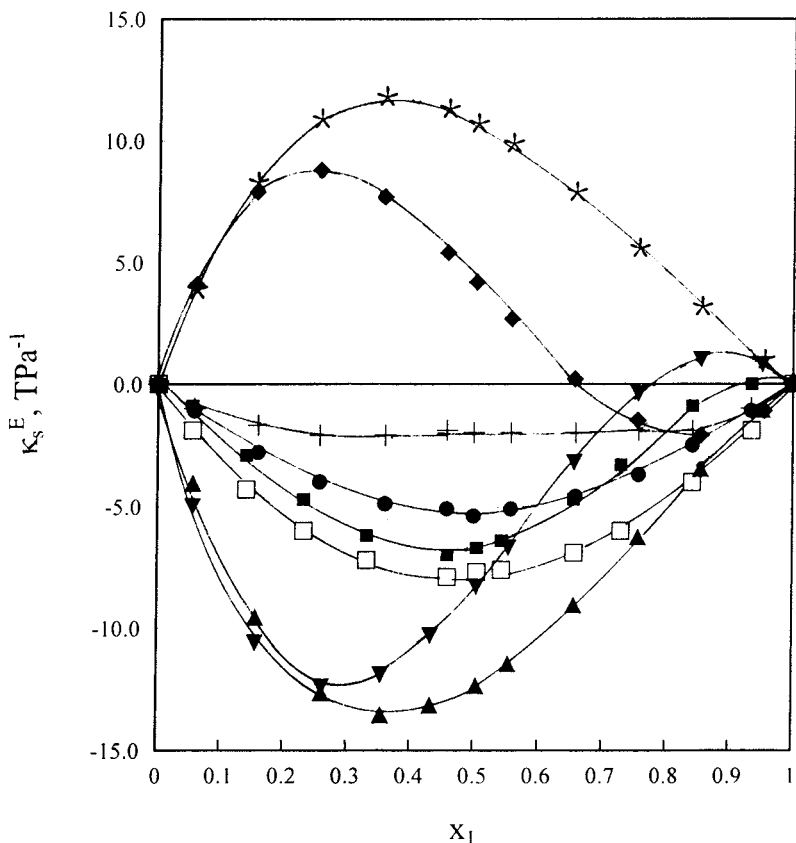
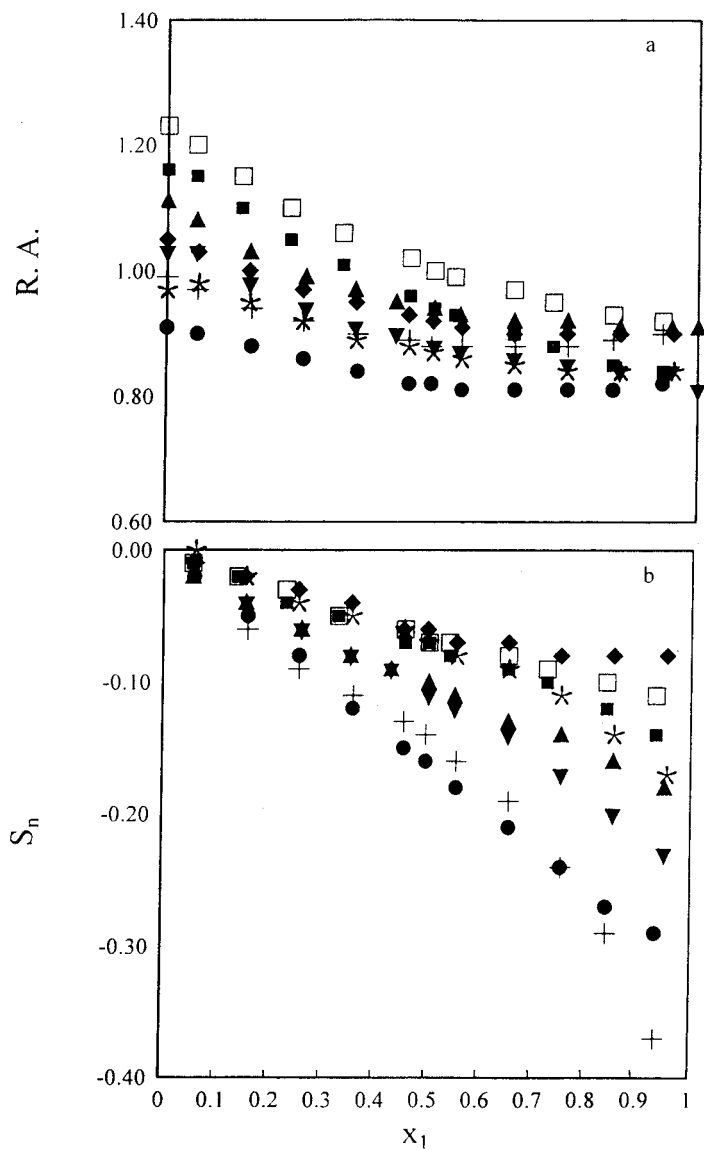


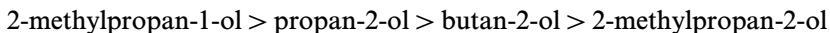
Fig. 3. Variation of excess isentropic compressibilities with ester mole fraction for ester + branched alcohols at  $T = 298.15 \text{ K}$ , MMA ( $\blacktriangle$ ) + propan-2-ol, ( $\square$ ) + 2-methylpropan-1-ol, ( $\blacklozenge$ ) + butan-2-ol, and ( $+$ ) + 2-methylpropan-2-ol; at  $T = 308.15 \text{ K}$ , ( $\blacktriangledown$ ) + propan-2-ol, ( $\blacksquare$ ) + 2-methylpropan-1-ol, ( $\blackstar$ ) + butan-2-ol, and ( $\bullet$ ) + 2-methylpropan-2-ol.

where  $L'_f$  is the free length calculated from the relation,  $\log L'_f = (\log \kappa_s - \log k)/p$ ,  $\log k$  and  $p$  are temperature dependent constants [12], and their values in cgs units are 7.274, 2.106 and 7.629, 2.148 at  $T = 298.15$  and 308.15 K, respectively.  $n_1$  and  $n_2$  are the number of moles of the respective components. Parts a and b of Fig. 4 present a graphical representation of the variation of R.A. and  $S_n$  as a function of the MMA mole fraction for all four binary mixtures. It can be seen from Part a of Fig. 4 that R.A. values for pure alcohols are larger than those for pure MMA. An R.A. value of close to 1.00 is expected for a simple nonassociating liquid,



**Fig. 4.** Variation of (a) relative association and (b) solvation number with ester mole fraction for MMA + branched alcohols at  $T = 298.15$  and  $308.15$  K, legends same as Fig. 3.

i.e., MMA in the present case. The R.A. values over the composition range of this study for all four binary mixtures and at both temperatures of 298.15 and 308.15 K showed the following order,



Furthermore, the trend in R.A. values with ester composition has been found to be complex and rectilinear. The values for propan-2-ol and 2-methylpropan-2-ol containing mixtures, show a continuous decrease with an increase in the ester mole fraction over the whole composition range and at both temperatures. But, in MMA + butan-2-ol mixtures, the R.A. values show a decreasing trend up to  $x_1 = 0.55$  and, thereafter, remained constant at both temperatures. The same trend was also observed in MMA + 2-methylpropan-2-ol mixtures at  $T = 308.15$  K. The R.A. values for the MMA + 2-methylpropan-2-ol system at  $T = 298.15$  K, however, show a decreasing trend up to  $x_1 = 0.55$ , then remained constant up to  $x_1 = 0.75$ , and increased again in the ester-rich region. The initial rapid decrease in R.A. values for MMA + propan-2-ol and +2-methylpropan-1-ol mixtures at both temperatures confirms that disruptions in the associate structures of branched alcohols are predominant at MMA-deficient compositions. The larger R.A. values in MMA + 2-methylpropan-1-ol and MMA + propan-2-ol relative to the other two mixtures suggest that structure disruptions are relatively weak in the former. This is consistent with the fact that  $\kappa_s^E$  values are negative in these mixtures.

The  $S_n$  values as shown in part b of Fig. 4 are all negative over the complete composition range for all mixtures. The  $S_n$  values show a steep decrease up to  $x_1 \approx 0.25$  to 0.30 for all mixtures at both temperatures. The values further decrease steeply for 2-methylpropan-2-ol and propan-2-ol containing mixtures at  $T = 298.15$  and 308.15 K. The values become less steep for MMA + butan-2-ol and +2-methylpropan-1-ol mixtures at  $T = 308.15$  K and for MMA + 2-methylpropan-1-ol mixtures at  $T = 298.15$  K. However, for the system MMA + butan-2-ol,  $S_n$  values remain almost constant beyond  $x_1 = 0.75$ .

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