Densities, Viscosities, Speeds of Sound, and Relative Permittivities for Methyl Acrylate + 1-Alcohols (C_1−C_6) at T = (308.15 and 318.15) K

John George, Nandhibatla V. Sastry,* Sunil R. Patel, and Mahendra K. Valand[†]

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388120, Gujarat, India

Measurements of densities, viscosities, speeds of sound, and relative permittivities for five binary mixtures of methyl acrylate + 1-alcohols (methanol, 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol) at T = (308.15 and 318.15) K are reported. The experimentally measured viscosities and speeds of sound in binary mixtures have been compared with those calculated using various semiempirical approaches. The isentropic compressibilities, molar electrical susceptibilities, and molar polarizations are calculated from the measured density, speed of sound, relative permittivity, and refractive index data. The excess volumes, excess isentropic compressibilities, excess molar electrical susceptibilities, and deviations in molar polarizations are calculated. These functions are fitted to a Redlich−Kister type equation. The variation of the Kirkwood correlation parameter has also been examined for all the binary mixtures over the whole composition range. Qualitative analysis of the various functions has been performed to elicit information on the nature of bulk molecular interactions in MA + 1-alcohol binary mixtures.

Introduction

The availability of free electrons and the tendency of ester molecules to form hydrogen bonds with 1-alcohols via the participation of the carbonyl group of the COO functionality and hydrogen of the OH functionality have attracted the attention of many experimental investigations on ester + 1-alcohol binary mixtures dealing with the measurements especially of the excess volumes, V^E, and excess enthalpies, H^E.[1−6] These studies show that the lengthening of the carbon chain length of 1-alcohols for given ester + 1-alcohols mixtures results in a quasi-regular increase in V^E and H^E values. Similarly, when the chain length of R or R′ in the esters of H_3CCOOR + or $R'COOCH_3$ types is increased in given alcohol + esters mixtures, the magnitudes of the above-mentioned functions decrease. Interestingly, the binary systems consisting of methyl methacrylate + methanol[7] at T = 298.15 K, methyl, ethyl, propyl, and butyl acetates + methanol[8,9] at T = 293.15 K, ethyl formate + methanol[3] at T = 298.15 K, and butyl formate + methanol[1] at T = 298.15 K showed negative excess volumes. Besides the large amount of experimental data on H^E and V^E, few reports on viscosity and related functions for the alkyl esters + 1-alcohols[9,10] are also reported. As far as we are aware, no literature reference on acoustic and dielectric behavior of alkyl esters + 1-alcohols is presently available in the literature.

Acrylic esters are important industrial chemicals and are widely used as precursors in the production of technically important high polymeric and latex systems. The production of higher homologues of acrylic esters on an industrial scale is done by transesterification reactions in which an acrylic ester is reacted with a 1-alcohol having a longer alkyl chain length. Acrylic esters are also most interesting theoretically because they have unsaturation alongside of a carbonyl group in the same molecule. Despite the above-mentioned industrial and theoretical interests, the theromophysical behavior of binary and ternary liquid mixtures consisting of acrylic esters as one of the components in general and acrylic ester + 1-alcohols in particular is not thoroughly investigated.

Our laboratory is involved in systematic measurements of various thermophysical properties of binary and ternary mixtures consisting of acrylic esters, alcohols, hydrocarbons, and so forth. The volumetric, viscosity, and dielectric behaviors of acrylic esters (methyl, ethyl, and butyl acrylate) + 1-alcohols (C_7−C_{12}) have been discussed previously.[11−13] With an aim to extend our studies to binary mixtures of acrylic ester + lower 1-alcohols, this study reports the densities, viscosities, speeds of sound, and relative permittivities for five binary mixtures of methyl acrylate + methanol, + 1-propanol, + 1-butanol, + 1-pentanol, and + 1-hexanol at T = (308.15 and 318.15) K. From the experimental data, the excess volumes, V^E, excess isentropic compressibilities, κ_s^E, excess molar electrical susceptibilities, χ_m^E, and deviations in molar polarizations, δP_m, have been calculated. The mixture viscosities are correlated by the Grunberg and Nissan, McAllister, and Auslander equations. The speeds of sound in binary mixtures are also calculated by using free length and collision factor theories. The Kirkwood correlation factor, g_K, is also calculated from the relative permittivity and refractive index data over the whole composition range.

Experimental Section

Materials. Methanol, 1-propanol, and 1-butanol were locally acquired analytical reagent grade chemicals. They were further purified by standard procedures.[14] 1-Pentanol and 1-hexanol are of Riedel make products and used as received without any further purification. The GLC measured purities for the 1-alcohols were estimated to be 99.6, 99.5, 99.8, 99.9, and 99.9% on a mole basis. Methyl acrylate (MA) is an Aldrich product with a manufacturer stated purity of greater than 99% on a mole basis and is used as such. MA was stabilized with about 0.002% hydroquinone monomethyl ether.

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* Corresponding author. Fax: 0091-2692-36475. E-mail: nvsastry_ad1@sancharnet.in.

[†] Present address: Department of Chemistry, V. P. Science College, Vallabh Vidyanagar 388120, Gujarat, India.

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Table 1. Densities, ρ, Viscosities, η, Speeds of Sound, u, Relative Permittivities, ϵ_r, and Refractive Indices, n_D, for the Pure Components at T = (308.15 and 318.15) K

	T = 308.15 K		T = 318.15 K	
	expt	lit.	expt	lit.
	Methyl Acrylate			
$\rho/(g{\cdot}cm^{-3})$	0.935 62		0.925 18	
$\eta/(mPa{\cdot}s)$	0.391		0.333	
$u/(m{\cdot}s^{-1})$	1140		1095	
ϵ_r	6.812		6.719	
n_D	1.3981		1.3952	
	Methanol			
$\rho/(g{\cdot}cm^{-3})$	0.777 35	0.7773[24]	0.768 13	0.7681[24]
$\eta/(mPa{\cdot}s)$	0.477	0.4793[24]	0.422	0.4196[24]
$u/(m{\cdot}s^{-1})$	1080	1073[26]	1048	
ϵ_r	31.173	31.176[23]	29.990	29.996[23]
n_D	1.3220	1.3223[26]	1.3179	
	l-Propanol			
$\rho/(g{\cdot}cm^{-3})$	0.791 41	0.7914[24]	0.783 16	0.7832[24]
$\eta/(mPa{\cdot}s)$	1.536	1.5339[28]	1.230	1.2229[29]
$u/(m{\cdot}s^{-1})$	1180	1182[25]	1156	
ϵ_r	19.045	19.046[23]	17.641	17.641[23]
n_D	1.3790	1.3793[27]	1.3750	
	l-Butanol			
$\rho/(g{\cdot}cm^{-3})$	0.798 17	0.7982[24]	0.790 49	0.7905[24]
$\eta/(mPa{\cdot}s)$	1.968	1.9689[29]	1.558	1.5579[29]
$u/(m{\cdot}s^{-1})$	1210	1208[26]	1194	
ϵ_r	16.060	16.064[23]	14.876	14.875[23]
n_D	1.3926	1.3927[27]	1.3886	
	1-Pentanol			
$\rho/(g{\cdot}cm^{-3})$	0.804 15	0.8041[24]	0.796 78	0.7968[24]
$\eta/(mPa{\cdot}s)$	2.628	2.6299[30]	2.064	2.064[24]
$u/(m{\cdot}s^{-1})$	1246	1246[26]	1220	
ϵ_r	13.590	13.596[23]	12.564	12.560[23]
n_D	1.4033	1.4033[27]	1.3993	
	1-Hexanol			
$\rho/g{\cdot}cm^{-3}$	0.809 04	0.8090[24]	0.801 65	0.8017[24]
$\eta/mPa{\cdot}s$	3.350	3.3510[24]	2.470	2.4710[24]
$u/m{\cdot}s^{-1}$	1273	1273[26]	1250	
ϵ_r	11.480	11.587[23]	10.712	10.712[23]
n_D	1.4111	1.4111[26]	1.4062	

Methods. The binary solutions were prepared by mass in hermetically sealed glass vials. The solutions of each composition were prepared fresh, and all the properties were measured the same day. The mass measurements, accurate to ±0.01 mg, were performed on Dhona single pan analytical balance, Dhona 100 DS (India). The accuracy in the mole fraction was ±0.0001.

Densities of pure liquids and their mixtures were measured with a high precision vibrating tube digital density meter (Anton Paar DMA 5000). The temperature within the oscillating tube was controlled to an uncertainty of ±0.001 K by in-built integrated Pt 100 thermometers. The densities of the standard liquids used for calibration were checked with an uncertainty of 0.000 01 $g{\cdot}cm^{-3}$. The instrument was calibrated with air, double distilled water, and freshly degassed water at (293.15, 313.15, and 333.15) K during every session. The densities of all the mixtures belonging to a given system (including pure components) were measured during one session. The experimental precision (reproducibility of measured densities during a session) was better than three units in the sixth decimal place. The accuracy of the measurements was judged from the values of the density for a given pure compound measured in different sessions. The values varied from session to session, and this variation may be ascribed to the possible effects of hygroscopicity over a long period of time and occasional use of solvents from different manufacturer's lots. However, the variation hardly occurred beyond one unit in the fifth decimal place. The binary mixtures were prepared shortly before the density measurements, and the pure components were remeasured together with the mixtures. We believe that this procedure would cancel any systematic errors in the computation of excess volumes. Viscosities of pure and mixture components were obtained from the measured flow times using two different suspended type Ubbelohde viscometers to cover all the mixtures. The calibration of viscometers was done with triple distilled water and double distilled cyclohexane or toluene. The speeds of sound in pure liquids and in binary mixtures were measured using an ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at a fixed frequency of 2 MHz. The measured values have an uncertainty of ±0.15%. The relative permittivities of the individual pure components and binary mixtures were calculated from the capacitance measurements with a universal dielectrometer type OH-301 of Radelkis, Hungary. The refractive indexes for the sodium D line were measured with an Abbe type research refractometer. The procedure used in the calibration of dielectric cells was the same as that described in detail elsewhere.[15] The temperature during the measurements of all the above properties was maintained accurate to ±0.01 K by using a thermostated INSREF (India) make circulator (model 020A). The measured densities, viscosities, speeds of sound, and relative permittivities are accurate to ±0.000 01 $g{\cdot}cm^{-3}$, ±0.001 $mPa{\cdot}s$, ±1.5 $m{\cdot}s^{-1}$, and ±0.001, respectively. A comparison of our measured properties for all the pure components with other literature reported values is given in Table 1.

Results and Discussion

The experimentally measured densities, viscosities, and relative permittivities of all the five binary mixtures of MA + methanol, + 1-propanol, + 1-butanol, + 1-pentanol, and + 1-hexanol at T = (308.15 and 318.15) K are listed in Table 2. The excess volumes, V^E, and excess isentropic compressibilities, $\kappa_s{}^E$, have been calculated by using the relations

$$V^E/(cm^3{\cdot}mol^{-1}) = \frac{x_1M_1 + x_2M_2}{\rho_{12}} - \left\{\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right\} \quad (1)$$

$$\kappa_s{}^E/(T\ Pa^{-1}) = \kappa_s - \kappa_s{}^{id} \quad (2)$$

where κ_s was calculated using the Laplace equation, that is, $\kappa_s = 1/(u^2\rho)$, and $\kappa_s{}^{id}$ was calculated from the following relations

$$\kappa_s{}^{id} = \sum_{i=1}^{2}\phi_i[\kappa_{s,i} + TV_i(\alpha_i{}^2)/C_{p,i}] - \{T(\sum_{i=1}^{2}x_iV_i)(\sum_{i=1}^{2}\phi_i\alpha_i)^2/\sum_{i=1}^{2}x_iC_{p,i}\} \quad (2a)$$

and the ϕ_i is the ideal state volume fraction and is defined by the relation

$$\phi_i = x_iV_i/(\sum_{i=1}^{2}x_iV_i) \quad (2b)$$

The excess molar electrical susceptibilities, $\chi_m{}^E$, were calculated by using the relation

$$\chi_m{}^E/(cm^{-3}{\cdot}mol) = \chi_{m,12} - (x_1\chi_{m,1} + x_2\chi_{m,2}) \quad (3)$$

Table 2. Densities, ρ, Viscosities, η, and Relative Permittivities, ϵ_r, for MA (1) + 1-Alcohols (2) at T = (308.15 and 318.15) K

	T = 308.15 K			T = 318.15 K		
x_1	ρ/ (g·cm^{-3})	η/ (mPa·s)	ϵ_r	ρ/ (g·cm^{-3})	η/ (mPa·s)	ϵ_r
MA (1) + Methanol (2)						
0.0546	0.796 41	0.464	28.859	0.786 63	0.419	28.006
0.1570	0.825 98	0.443	25.268	0.815 42	0.412	24.850
0.2569	0.848 95	0.426	22.385	0.837 94	0.404	22.223
0.3537	0.867 12	0.413	19.929	0.855 92	0.397	19.914
0.4530	0.882 62	0.403	17.598	0.871 40	0.388	17.669
0.5010	0.889 19	0.399	16.512	0.878 02	0.384	16.611
0.5588	0.896 44	0.394	15.229	0.885 36	0.379	15.349
0.6550	0.907 14	0.390	13.143	0.896 25	0.369	13.285
0.7566	0.916 91	0.387	11.032	0.906 25	0.359	11.168
0.8561	0.925 29	0.387	9.111	0.914 76	0.349	9.208
0.9556	0.932 61	0.389	7.442	0.922 19	0.338	7.429
MA (1) + 1-Propanol (2)						
0.0501	0.800 69	1.354	18.144	0.791 49	1.107	17.376
0.1464	0.817 42	1.081	16.363	0.807 10	0.916	16.391
0.2331	0.831 48	0.900	14.784	0.820 73	0.782	15.166
0.3469	0.848 81	0.727	12.862	0.838 01	0.648	13.369
0.4436	0.862 81	0.622	11.435	0.852 19	0.561	11.877
0.5011	0.870 89	0.572	10.692	0.860 40	0.519	11.062
0.5436	0.876 77	0.541	10.196	0.866 37	0.492	10.505
0.6429	0.890 23	0.483	9.205	0.879 98	0.439	9.381
0.7442	0.903 61	0.441	8.408	0.893 39	0.397	8.482
0.8449	0.916 55	0.413	7.764	0.906 26	0.365	7.775
0.9424	0.928 68	0.396	7.183	0.918 28	0.343	7.141
MA (1) + 1-Butanol (2)						
0.0466	0.804 63	1.721	15.705	0.796 41	1.393	14.777
0.1448	0.818 18	1.322	14.675	0.809 05	1.115	14.064
0.2429	0.831 64	1.042	13.430	0.821 88	0.908	12.942
0.3387	0.844 71	0.847	12.162	0.834 58	0.755	11.709
0.4481	0.859 61	0.688	10.796	0.849 25	0.625	10.371
0.5003	0.866 71	0.630	10.207	0.856 31	0.575	9.809
0.5436	0.872 60	0.589	9.758	0.862 19	0.539	9.393
0.6469	0.886 67	0.512	8.841	0.876 30	0.468	8.589
0.7461	0.900 25	0.459	8.155	0.889 94	0.416	8.040
0.8469	0.914 16	0.422	7.603	0.903 88	0.375	7.600
0.9456	0.927 94	0.399	7.110	0.917 60	0.346	7.106
MA (1) + 1-Pentanol (2)						
0.0469	0.808 94	2.288	13.070	0.801 38	1.820	12.190
0.1480	0.819 80	1.725	12.038	0.811 89	1.406	11.431
0.2501	0.831 46	1.327	11.102	0.823 24	1.104	10.726
0.3489	0.843 34	1.053	10.282	0.834 83	0.890	10.093
0.4436	0.855 25	0.860	9.568	0.846 44	0.735	9.526
0.5084	0.863 68	0.758	9.117	0.854 65	0.651	9.157
0.5450	0.868 55	0.708	8.875	0.859 38	0.610	8.954
0.6489	0.882 75	0.594	8.243	0.873 19	0.514	8.402
0.7484	0.896 92	0.513	7.717	0.886 99	0.445	7.900
0.8456	0.911 34	0.454	7.288	0.901 10	0.392	7.430
0.9477	0.927 19	0.409	6.941	0.916 75	0.350	6.955
MA (1) + 1-Hexanol (2)						
0.0466	0.812 80	2.892	10.909	0.805 28	2.186	10.280
0.1490	0.821 86	2.128	9.888	0.814 08	1.687	9.483
0.2479	0.831 54	1.616	9.146	0.823 53	1.331	8.873
0.3487	0.842 29	1.247	8.572	0.834 03	1.059	8.376
0.4466	0.853 54	0.989	8.142	0.845 00	0.859	7.982
0.4989	0.859 87	0.881	7.949	0.851 17	0.772	7.799
0.5479	0.866 01	0.795	7.787	0.857 15	0.701	7.643
0.6418	0.878 39	0.662	7.513	0.869 18	0.588	7.376
0.7501	0.893 79	0.549	7.246	0.884 14	0.486	7.116
0.8501	0.909 30	0.472	7.038	0.899 26	0.414	6.920
0.9438	0.925 24	0.417	6.882	0.914 91	0.360	6.779

where the molar electrical susceptibility, $\chi_{m,i}$, is defined as

$$\chi_{m,i} = (\epsilon_r - 1)/V_i \tag{3a}$$

The deviation in the molar polarization, δP_m, was calculated using the following expression

$$\delta P_m/(\mathrm{cm^3 \cdot mol^{-1}}) = P_{12} - \sum x_i P_i \tag{4}$$

The molar polarization of the mixture was calculated using the relation

$$P_{12} = \left\{\frac{(\epsilon_{r,12} - 1)((2\epsilon_{r,12}) + 1)}{9\epsilon_{r,12}}\right\}\left\{\frac{x_1 M_1 + x_2 M_2}{\rho_{12}}\right\} \tag{5}$$

and similarly, the molar polarizations of the pure components are calculated from

$$P_i = \left\{\frac{(\epsilon_{r,i} - 1)((2\epsilon_{r,i}) + 1)}{9\epsilon_{r,i}}\right\}\left\{\frac{M_i}{\rho_i}\right\} \tag{6}$$

The various terms (viz. x, ρ, u, ϵ_r, κ_s, and M) that appear in eqs 1−6 are the mole fraction, density, speed of sound, relative permittivity, isentropic compressibility, and molecular weight of the respective components. α_i are the isobaric thermal expansion coefficients and were estimated from the accurate densities measured at intervals of 2 °C from 20 °C to high temperatures within 5 °C of their respective boiling points. The literature molar heat capacities, $C_{p,i}$ (in J K^{-1} mol^{-1}), of 163.3,[16] 78.1,[17] 149.7,[17] 184.5,[17] 216.4,[17] and 250.3[17] at T = 308.15 K and 165.1,[16] 79.9,[17] 156.0,[17] 192.5,[17] 225.4,[17] and 260.8[17] at T = 318.15 K were used for MA, methanol, 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol, respectively.

The correlation of the mixture viscosities (dynamic as well as kinematic) was also made by using the below-given one-parameter Grunberg−Nissan,[18] two-parameter McAllister,[19] and three-parameter Auslander[20] equations:

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \tag{7}$$

$$\ln \nu_{12} = {x_1}^3 \ln \nu_1 + 3{x_1}^2 x_2 \ln M_{12} + 3x_1{x_2}^2 \ln M_{21} + {x_2}^3 \ln \nu_2 - \ln\left(x_1 + \frac{x_2 M_2}{M_1}\right) + 3{x_1}^2 x_2 \ln\left(\frac{2}{3} + \frac{M_2}{3M_1}\right) + 3x_1{x_2}^2 \ln\left(\frac{1}{3} + \frac{2M_2}{3M_1}\right) + {x_2}^3 \ln\left(\frac{M_2}{M_1}\right) \tag{8}$$

$$x_1(x_1 + B_{12}x_2)(\eta_{12} - \eta_1) + A_{21}x_2(B_{21}x_1 + x_2)(\eta_{12} - \eta_2) = 0 \tag{9}$$

The terms G_{12}, M_{12}, M_{21}, B_{12}, A_{21}, and B_{21} in the above equations have been considered as adjustable parameters and were estimated by a nonlinear regression analysis based on a least-squares method. These equations are particularly selected because the characteristic constant parameter G_{12} of eq 7 allows for the positive and negative deviations from the additivity rule, eq 8 is based on the Eyring theory on absolute reaction rates with a three-body model, and eq 9 involves three parameters. The summary of the analysis is given in Table 3. A perusal of the root-mean-square standard deviation, σ, values given in Table 3 shows that all three equations adequately correlate the mixture viscosities. However, the GN and McAllister equations that have one and two adjustable parameters can be considered superior over the Auslander equation (which has three adjustable parameters) in correlating mixture viscosities. A graphical presentation of the mole fraction dependence of experimental and GN equation correlated viscosities is shown in Figure 1.

The speeds of sound of MA + 1-alcohol mixtures are also predicted by using the free length and collision factors.[21−22] The basic properties of the pure components that are needed for the calculations are molar volume, V_m, molar volume at absolute zero, V_0, available volume, V_a, actual volume, B_i, surface area factor, Y, free length, L_f, collision

Table 3. Adjustable Parameters of Eqs 7−9 for the Correlation of Mixture Viscosities at T = (308.15 and 318.15) K

MA +	G_{12}	σ	M_{12}	M_{21}	σ	A_{21}	B_{21}	B_{12}	σ
				T = 308.15 K					
methanol	−0.320	0.001	0.420	0.489	0.001	0.866	−0.602	2.521	0.005
1-propanol	−1.207	0.001	0.463	0.770	0.001	0.320	0.242	1.110	0.003
1-butanol	−1.321	0.001	0.486	0.874	0.001	0.248	0.376	0.910	0.002
1-pentanol	−1.101	0.001	0.588	1.151	0.001	0.204	0.718	0.720	0.001
1-hexanol	−1.055	0.001	0.644	1.378	0.001	0.188	0.768	0.682	0.001
				T = 318.15 K					
methanol	0.097	0.001	0.421	0.499	0.001				
1-propanol	−0.830	0.001	0.443	0.724	0.001	0.396	0.443	1.168	0.001
1-butanol	−0.898	0.001	0.470	0.829	0.001	0.286	0.629	0.890	0.001
1-pentanol	−0.904	0.001	0.526	1.001	0.001	0.224	0.803	0.729	0.005
1-hexanol	−0.652	0.001	0.604	1.231	0.001	0.221	0.955	0.675	0.005

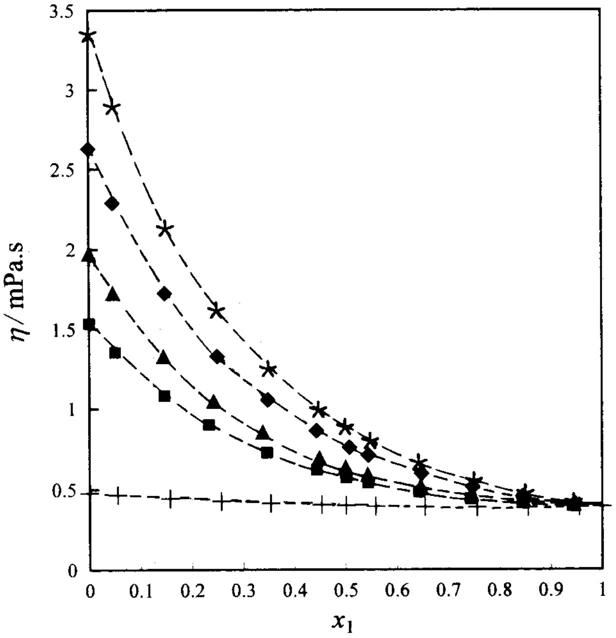

Figure 1. Variation of experimental viscosities with MA mole fraction for MA + 1-alcohols at 308.15 K: +, methanol; ■, 1-propanol; ▲, 1-butanol; ◆, 1-pentanol; *, 1-hexanol; - - -, Grunberg−Nissan equation correlated values.

factor, S_i, and molar heat capacity, $C_{p,i}$. The values of these various parameters were calculated using the relations mentioned in the above references. The calculated speeds of sound for all binary mixtures along with the σ % deviations between experimental and predicted values are given in Table 4. A perusal of σ % values reveals that collision factor theory predicts speeds of sound more adequately than free length theory.

The excess and deviation functions (viz. V^E, κ_s^E, χ_m^E, and δP_m) for all binary mixtures are fitted to an equation of Redlich−Kister type:

$$A^E = x_1(1 - x_1)\sum_{j=0}^{j=n} a_j(2x_1 - 1)^j \tag{10}$$

where $A^E = V^E/(\mathrm{cm^3{\cdot}mol^{-1}})$, $\kappa_s^E/(\mathrm{T\ Pa^{-1}})$, $\chi_m^E/(\mathrm{cm^{-3}{\cdot}mol})$, and $\delta P_m/(\mathrm{cm^3{\cdot}mol^{-1}})$. x_1 is the MA mole fraction, and a_j are the coefficients needed for smoothing of the data. The values of a_j were estimated by a least-squares method. The values of the coefficients along with the standard deviations, σ, between the experimental and fitted values are summarized in Table 5.

The V^E values as a function of MA mole fraction are also graphically presented in Figure 2. It can be seen from the figure that V^E values for MA + methanol are negative over the whole mole fraction range at both the temperatures and that the curves for MA + 1-propanol or + 1-butanol at T = 308.15 K are sigmoidal with initial negative lobes followed by positive points. Otherwise, the V^E curves are positive over the whole ester mole fraction range. A systematic increase in V^E is noted with the rise in the carbon chain length of 1-alcohols from methanol to 1-hexanol at both the temperatures. The rise in temperature from T = 308.15 to 318.15 K is found to increase the V^E values in all the mixtures. As far as we are aware, there are no literature data on any of the properties for the binary mixtures of MA + 1-alcohol with which we can compare our results. However, a few excess volume data points have been published in the literature for the binary mixtures of methyl propanoate + 1-propanol to 1-hexanol at T = 298.15 K. Methyl propanoate and methyl acrylate have analogous molecular structures, the only difference being the presence of unsaturation in the latter. Our $V^E_{(x=0.5)}$ values of −0.0309, −0.0093, 0.1835, and 0.3032 $\mathrm{cm^3{\cdot}mol^{-1}}$ for MA + 1-propanol, + 1-butanol, + 1-pentanol, and + 1-hexanol at T = 308.15 K are far smaller than the $V^E_{(x=0.5)}$ values of 0.1926, 0.2538, 0.3128, and 0.3828 $\mathrm{cm^3{\cdot}mol^{-1}}$ for methyl propanoate + the same 1-alcohols.[5,6] On a qualitative basis, the positive excess volumes have been attributed in general to structure disrupting interactions and negative excess volumes have been analyzed in terms of structure making interactions. The positive V^E values in MA + 1-butanol to 1-hexanol mixtures hint at the predominance of structure disruptive interactions. However, specific interactions (viz. formation of new structures due to the interaction between the ester carbonyl group and the hydroxyl group of the 1-alcohol, packing effects in the form of n···π complex formation between the 1-alcohol and the unsaturated ester species, and the interstitial accommodation of 1-alcohols into ester structures) are also possible. The later effects are highly dependent on the sizes of the respective pure components. Methanol is the lowest member of the 1-alcohol group, and in MA + methanol mixtures, the possible incorporation of methanol molecules into MA structures may predominate besides other specific interactions. This is reflected in the observed negative V^E values for MA + methanol systems. The formation of n···π complexes in MA + methanol mixtures is not totally ruled out. As the carbon chain length of the 1-alcohol increases, the steric factors prevent geometrical fitting and thus the negative contributions to V^E from this effect are expected to vanish in MA + 1-butanol or + 1-pentanol or + 1-hexanol mixtures.

A graphical representation of the variation of excess isentropic compressibilites with the ester mole fraction for all the binary mixtures at T = (308.15 and 318.15) K is given in Figure 3. The κ_s^E values for MA + methanol at both the temperatures showed a sigmoidal trend with

Table 4. Experimental and Calculated Speeds of Sound (in m·s^{-1}) for MA (1) + 1-Alcohols (2) at T = (308.15 and 318.15) K[a]

	T = 308.15 K			T = 318.15 K				T = 308.15 K			T = 318.15 K		
x_1	u_{exp}	u_{CFT}	u_{FLT}	u_{exp}	u_{CFT}	u_{FLT}	x_1	u_{exp}	u_{CFT}	u_{FLT}	u_{exp}	u_{CFT}	u_{FLT}
		MA (1) + Methanol (2)							MA (1) + Propanol (2)				
0.0546	1083	1085	1266	1051	1052	1266	0.0501	1175	1179	1250	1150	1153	1244
0.1570	1091	1093	1223	1056	1057	1219	0.1464	1165	1176	1225	1139	1146	1213
0.2569	1099	1099	1188	1061	1062	1182	0.2331	1159	1172	1204	1130	1141	1188
0.3537	1105	1105	1158	1065	1067	1151	0.3469	1151	1167	1170	1121	1134	1157
0.4530	1112	1111	1131	1070	1072	1124	0.4436	1147	1163	1143	1113	1128	1134
0.5010	1114	1114	1119	1072	1074	1112	0.5011	1145	1160	1128	1109	1124	1121
0.5588	1117	1117	1106	1074	1076	1099	0.5436	1144	1158	1118	1107	1122	1111
0.6550	1122	1122	1086	1078	1081	1080	0.6429	1141	1154	1095	1102	1116	1090
0.7566	1127	1127	1067	1083	1085	1062	0.7442	1140	1150	1075	1098	1110	1071
0.8561	1132	1132	1050	1088	1089	1046	0.8449	1139	1146	1056	1095	1104	1052
0.9556	1138	1138	1035	1093	1093	1032	0.9424	1140	1142	1039	1095	1098	1035
σ %		0.1	8.4		0.2	9.7	σ %		1.1	5.2		1.1	4.5
		MA (1) + 1-Butanol (2)							MA (1) + 1-Pentanol (2)				
0.0466	1202	1207	1255	1185	1189	1252	0.0469	1237	1240	1284	1210	1213	1284
0.1448	1188	1200	1229	1167	1178	1222	0.1480	1219	1229	1251	1188	1200	1250
0.2429	1174	1193	1204	1152	1168	1194	0.2501	1202	1217	1221	1168	1188	1219
0.3387	1163	1187	1179	1138	1159	1169	0.3489	1187	1207	1193	1151	1174	1191
0.4489	1153	1179	1152	1123	1148	1142	0.4436	1174	1197	1168	1136	1162	1165
0.5003	1149	1175	1139	1117	1143	1130	0.5084	1166	1191	1151	1127	1154	1147
0.5436	1146	1172	1129	1112	1138	1120	0.5450	1162	1186	1141	1123	1149	1138
0.6469	1141	1165	1104	1103	1129	1097	0.6489	1151	1175	1115	1111	1137	1110
0.7461	1138	1157	1082	1096	1119	1076	0.7484	1143	1165	1090	1102	1125	1085
0.8469	1137	1150	1060	1092	1109	1055	0.8456	1139	1155	1066	1097	1113	1061
0.9456	1139	1144	1040	1093	1100	1036	0.9477	1138	1145	1041	1094	1101	1037
σ %		1.8	4.5		1.9	3.5	σ %		1.7	4.2		1.9	3.8
		MA (1) + 1-Hexanol (2)											
0.0466	1260	1266	1290	1237	1242	1288							
0.1490	1237	1251	1257	1212	1225	1254							
0.2479	1218	1237	1228	1191	1209	1224							
0.3487	1200	1223	1199	1171	1193	1196							
0.4466	1185	1210	1173	1154	1177	1169							
0.4989	1177	1203	1159	1146	1169	1155							
0.5479	1171	1197	1146	1139	1162	1142							
0.6418	1159	1185	1120	1124	1147	1116							
0.7501	1148	1171	1091	1111	1131	1087							
0.8501	1141	1158	1065	1101	1116	1061							
0.9438	1139	1146	1042	1096	1103	1038							
σ%		1.8	4.1		1.7	3.0							

[a] exp, experimental; CFT, collision factor theory; FLT, free length theory.

Table 5. Parameters of Eq 10 for the Mathematical Representation of Deviation and Excess Functions for MA (1) + 1-Alcohols (2) at T = (308.15 and 318.15) K

		T = 308.15 K				T = 318.15 K			
MA +		a_0	a_1	a_2	σ	a_0	a_1	a_2	σ
methanol	V^{E}/(cm^3·mol^{-1})	−0.7209	0.3139	−0.0681	0.0002	−0.4049	0.0796	−0.1963	0.0002
	$\kappa_{\mathrm{s}}{}^{\mathrm{E}}$/(T Pa^{-1})	−17.0	24.4	−3.8	0.1	4.3	32.3	−15.4	0.1
	$\chi_{\mathrm{m}}{}^{\mathrm{E}}$/(cm^{-3}·mol)	−0.653	0.361	−0.230	0.003	−0.581	0.308	−0.193	0.002
	δP_{m}/(cm^3·mol^{-1})	128.6	−5.3	−67.8	0.5	162.7	−3.6	−53.1	0.3
1-propanol	V^{E}/(cm^3·mol^{-1})	−0.1237	0.7006	−0.6004	0.0003	0.2961	−0.1506	−0.0055	0.0002
	$\kappa_{\mathrm{s}}{}^{\mathrm{E}}$/(T Pa^{-1})	21.3	−1.2	0.0	0.1	26.3	17.4	15.7	0.1
	$\chi_{\mathrm{m}}{}^{\mathrm{E}}$/(cm^{-3}·mol)	−0.141	0.009	0.050	0.001	−0.083	−0.066	0.083	0.001
	δP_{m}/(cm^3·mol^{-1})	−122.1	−9.8	63.7	0.2	−42.4	−103.0	120.1	0.3
1-butanol	V^{E}/(cm^3·mol^{-1})	−0.0373	0.3101	0.0347	0.0004	0.5714	−0.2357	0.0462	0.0003
	$\kappa_{\mathrm{s}}{}^{\mathrm{E}}$/(T Pa^{-1})	76.7	6.9	−6.6	0.1	94.6	48.2	21.6	0.1
	$\chi_{\mathrm{m}}{}^{\mathrm{E}}$/(cm^{-3}·mol)	−0.053	−0.035	0.054	0.001	−0.041	−0.045	0.082	0.001
	δP_{m}/(cm^3·mol^{-1})	−102.2	−63.4	95.0	0.1	−81.5	−84.4	168.1	0.1
1-pentanol	V^{E}/(cm^3·mol^{-1})	0.7338	−0.3470	0.2817	0.0002	0.8906	−0.2531	0.5195	0.0004
	$\kappa_{\mathrm{s}}{}^{\mathrm{E}}$/(T Pa^{-1})	100.6	38.5	29.7	0.1	129.7	34.7	20.9	0.1
	$\chi_{\mathrm{m}}{}^{\mathrm{E}}$/(cm^{-3}·mol)	−0.032	−0.001	−0.012	0.001	−0.012	0.008	0.000	0.001
	δP_{m}/(cm^3·mol^{-1})	−117.3	6.7	−10.1	0.1	−60.7	13.2	−1.8	0.1
1-hexanol	V^{E}/(cm^3·mol^{-1})	1.2127	−0.2548	0.7290	0.0004	1.2841	−0.1715	0.9315	0.0005
	$\kappa_{\mathrm{s}}{}^{\mathrm{E}}$/(T Pa^{-1})	131.7	18.9	26.6	0.1	156.1	27.7	58.9	0.1
	$\chi_{\mathrm{m}}{}^{\mathrm{E}}$/(cm^{-3}·mol)	−0.038	0.016	−0.016	0.001	−0.028	0.006	−0.015	0.001
	δP_{m}/(cm^3·mol^{-1})	−150.7	77.8	−36.6	0.1	−119.0	47.9	−23.0	0.1

initial small negative values followed by small positive values in ester-rich regions. With the increase in the carbon chain length of 1-alcohols from methanol to 1-hexanol, a systematic increase in the $\kappa_{\mathrm{s}}{}^{\mathrm{E}}$ values has been noted. Interestingly, except for MA + methanol, $\kappa_{\mathrm{s}}{}^{\mathrm{E}}$ versus x_1 curves are characterized by all positive values. The $\kappa_{\mathrm{s}}{}^{\mathrm{E}}{}_{(x=0.5)}$ values increased with the rise in temperature from T = 308.15 to 318.15 K. The observed positive $\kappa_{\mathrm{s}}{}^{\mathrm{E}}$ values, in

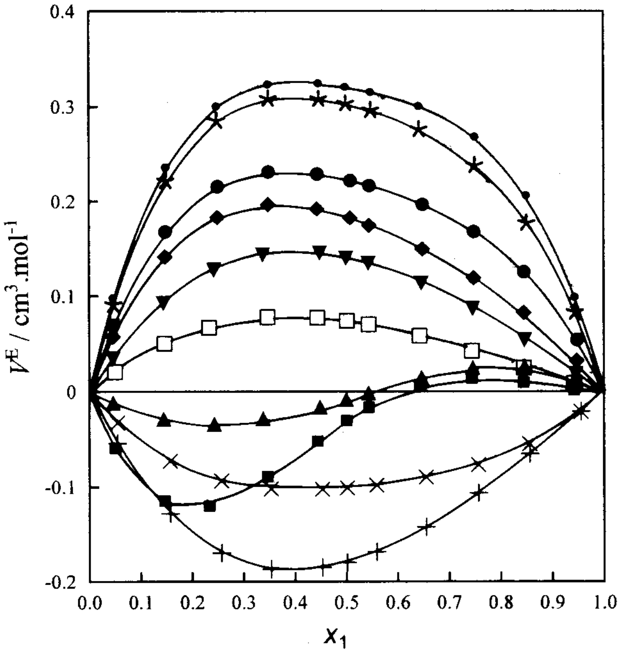

Figure 2. Variation of excess volumes with MA mole fraction for binary mixtures of MA + 1-alcohols at 308.15 K: +, methanol; ■, 1-propanol; ▲, 1-butanol; ◆, 1-pentanol; *, 1-hexanol; and at 318.15 K: ×, methanol; □, 1-propanol; ▼, 1-butanol; ●, 1-pentanol; •, 1-hexanol.

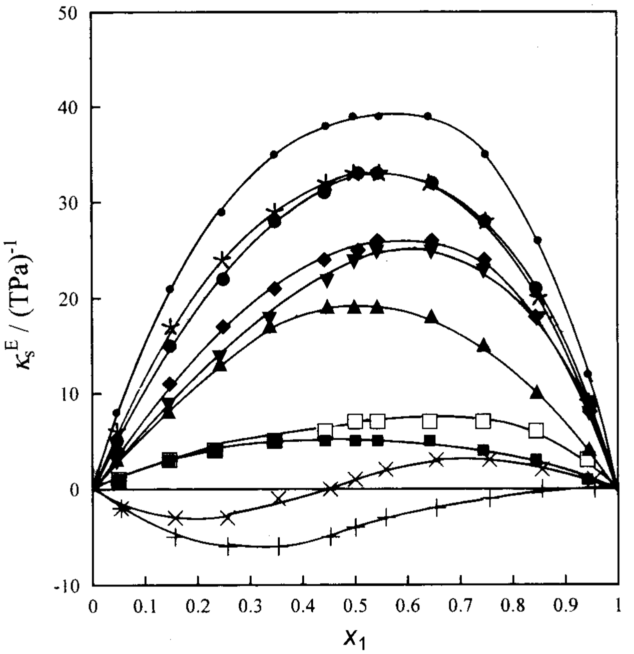

Figure 3. Variation of excess isentropic compressibilities with MA mole fractions for binary mixtures of MA + 1-alcohols at 308.15 and 318.15 K (The symbols are the same as those in Figure 2).

general, indicate the increased compressions in MA + 1-propanol to MA + 1-hexanol mixtures. The observed small negative initial κ_s^E values in MA + methanol on the other hand hint at the decreased compression in this mixture. The increase in carbon chain length may thus be expected to exert a steric influence for the close approach of the two components.

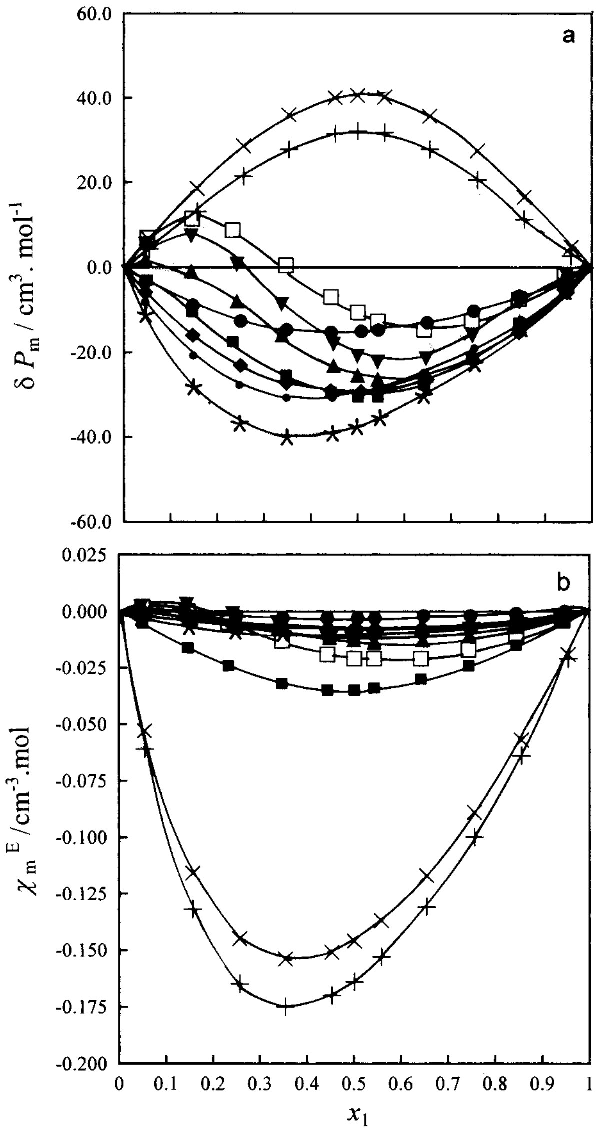

Figure 4. Variation of (a) deviation in molar polarization and (b) excess molar electrical susceptibilities for binary mixtures of MA + 1-alcohols at 308.15 and 318.15 K (The symbols are the same as those in Figure 2).

The variations in δP_m and χ_m^E as a function of ester mole fraction are shown in parts a and b of Figure 4. It is worth mentioning that the dielectric functions such as molar electrical susceptibility and molar polarizations are not thermodynamic properties in the true sense and in fact they are mixed thermodynamic–dielectric properties. Moreover, the significance of molar polarizations and hence their deviations is tied to a particular theoretical model. Hence, the interpretation of χ_m^E is more straightforward than that of δP_m. The magnitude and sign of χ_m^E values for MA + methanol mixtures strikingly differ from those for the same function in the rest of the mixtures. The χ_m^E values for MA + methanol mixtures are large and negative at both the temperatures and in contrast to highly diminished negative (or even slight positive) points noted for MA + 1-propanol to + 1-hexanol mixtures. The $\chi_m^E{}_{(x=0.5)}$ value has been found to become less negative by 4.7–6.9 times from MA + methanol to MA + 1-propanol and by 2.0–2.7 times from MA + 1-propanol to MA + 1-butanol mixtures. In the MA + higher alcohols the variation in the same function is found to be too small.

The δP_m values for MA + methanol at both the temperatures are large and positive over the whole ester mole fraction. The δP_m versus x_1 curves for MA + 1-propanol at T = 318.15 K and + 1- butanol at T = (308.15 and 318.15)

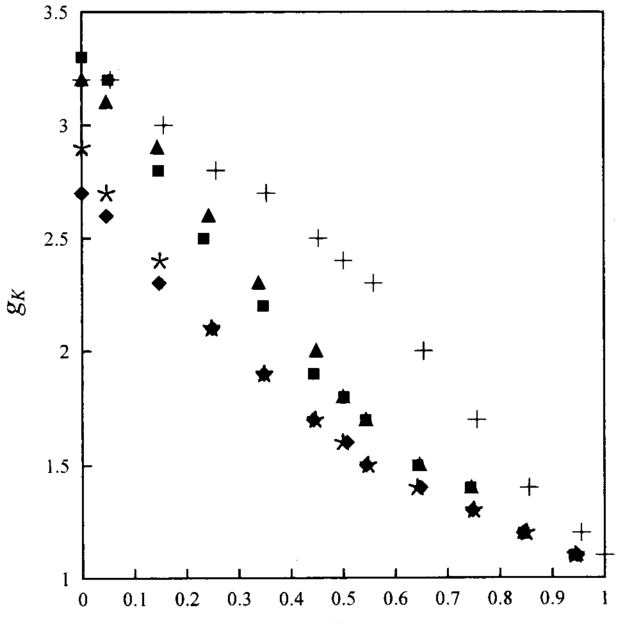

Figure 5. Variation of the Kirkwood correlation factor with MA mole fraction for binary mixtures of MA + 1-alcohols at 308.15 K (The symbols are the same as those in Figure 1).

K have been characterized by a sigmoidal trend with initial small positive humps followed by steep negative lobes at the ester-rich region. At the same time, δP_m versus x_1 curves for MA + 1- pentanol and + 1-hexanol were all negative in the whole mole fraction range at both the temperatures.

The rationalization of dielectric functions in terms of structural changes in a given binary mixture is often made by calculating the Kirkwood correlation parameter, g_K. The following relation is used to calculate the g_K:

$$g_K = \left\{\frac{(\epsilon_r - \epsilon_\alpha)(2\epsilon_r + \epsilon_\alpha)}{\epsilon_r(\epsilon_\alpha + 2)^2}\right\}\left\{\frac{9kT}{4\pi N(x_1\mu_1 + x_2\mu_2)^2}\right\}V_{12} \qquad (11)$$

where ϵ_r is the relative permittivity of the mixture, ϵ_α is the relative permittivity at high frequency and is equated to $1.1n_D^2$ of the mixture, k is the Boltzmann constant, T is the temperature, N is Avogadro's number, and μ_1 and μ_2 are the dipole moments of MA (1) and 1-alcohol (2), respectively. The mixture refractive indices were found to be best correlated in terms of mole fraction additives of the n_D values of the respective pure components.

The calculated g_K values for MA + 1-alcohol mixtures at T = 308.15 K are plotted as a function of ester mole fraction in Figure 5. Pure MA and 1-alcohols are characterized by g_K values close to unity and more than unity, respectively. The addition of MA to methanol resulted in a characteristic g_K versus x_1 variation with three regions: the first one ($x_1 \equiv 0-0.1$), in which only small changes are noted, the second region, in which g_K falls gradually between $x_1 \equiv 0.1$ and 0.40, followed by the ester-rich region, which exhibits a sharp fall of the g_K values. In contrast to this, the g_K versus x_1 profiles for MA + 1-propanol to 1-hexanol mixtures have been characterized by an initial sharp fall (up to $x_1 \approx 0.5-0.6$) followed by a gradual decrease. The g_K values in the ester-rich region for all the mixtures have been found to be too close irrespective of carbon chain length of 1-alcohols. The small changes in g_K values of MA + methanol in the initial MA mole fraction ranges indicate that the species in the mixed state still retain the same degree of parallel alignment of dipoles as that in the pure state. This could also be due to a direct consequence of possible structure making effects in MA + methanol mixtures in this mole fraction range. The further sharp fall of g_K in MA + 1-alcohol mixtures in general indicates the changed alignment in dipoles of 1-alcohol species from favorable parallel to unfavorable antiparallel orientations in the presence of MA.

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