J. Chem. Eng. Data 1993, 38, 31–39

# Densities, Viscosities, Refractive Indices, and Speeds of Sound for Methyl Acetoacetate + Aliphatic Alcohols ($C_1$–$C_8$)[†]

**Tejraj M. Aminabhavi,* Mrityunjaya I. Aralaguppi, Shivaputrappa B. Harogoppad, and Ramachandra H. Balundgi**

Department of Chemistry, Karnatak University, Dharwad 580003, India

Densities, viscosities, refractive indices, and speeds of sound have been measured at 298.15, 303.15, and 308.15 K for the binary mixtures of methyl acetoacetate with methyl alcohol, ethyl alcohol, 1-propanol, 2-propanol, 2-methyl-1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 2-octanol. From these results, excess molar volumes, excess molar refractions, viscosity deviations, and isentropic compressibility deviations have been calculated. These results are further fitted to the polynomial relation to estimate the coefficients and standard errors. The experimental and calculated quantities are used to discuss the mixing behavior of the components.

## Introduction

A study of molecular interactions in binary liquid mixtures has been the subject of active investigation in our laboratories in recent years (*1–7*). Methyl acetoacetate (MAA) is a versatile solvent used in the syntheses of a number of heterocycles and antipyrenes. Moreover, it is known to exhibit a keto–enol tautomerism which, to a great extent, depends on the surrounding medium (*8*). Thus, upon mixing with alcohols of varying chain lengths, these mixtures might generate interesting properties due to specific interactions, hydrogen bond effects, etc. On the other hand, alcohols are the most well known solvents used to study the hydrophobic effects. In view of their simple molecular structure, increasing hydrophobic character with increasing chain length and high solubility in polar solvents, most of their physical properties have been studied extensively (*9*). Thermodynamic properties of MAA + alcohol mixtures are of particular interest because MAA provides both hydroxy (–OH) and ketonic ($\rangle C{=}O$) groups for interactions with alcohols. To the best of our knowledge, the results of excess properties of aliphatic alcohols with an ester such as MAA are not available.

To gain some understanding about the nature of interactions in MAA + alcohol mixtures, properties such as density $\rho$, refractive index $n_D$, viscosity $\eta$, and speed of sound $u$ have been measured in the temperature interval of 298.15–308.15 K. These data are used to calculate the excess quantities which are then fitted to a Redlich–Kister-type polynomial relation (*10*) to estimate the coefficients and standard errors. The present paper is, therefore, concerned about the study of molecular interactions in terms of excess volumes $V^E$, excess molar refractions $R^E$, viscosity deviations $\Delta\eta$, and isentropic compressibility deviations $\Delta k_S$. The temperature dependence of these properties will be discussed.

## Experimental Section

The reagent grade solvents, namely, methyl alcohol, ethyl alcohol, 1-propanol, and 2-methyl-1-propanol, were from S.D. Fine Chemicals, Bombay. 2-Propanol and 1-pentanol were purchased from E. Merck. 1-Butanol, 1-heptanol, and 2-octanol were BDH samples, 1-hexanol was a Fluka chemical, and methyl acetoacetate was purchased from SRL, Bombay. All the solvents were purified according to the well-established procedures (*11, 12*). The gas chromatographic tests of the purified solvents showed a purity of >99 mol %. The purity of solvents was further ascertained by the constancy of their boiling temperatures during final distillations and also by comparing their densities and refractive indices at 298.15 K which agreed reasonably with the corresponding literature values (*12, 13*). See Table I.

Mixtures were prepared by mass in specially designed ground-glass-stoppered bottles. A set of nine compositions was prepared with an increment of 0.1 mole fraction per each system. The possible error in the mole fractions is estimated to be around 0.0001 in all cases.

Densities were measured with a capillary pycnometer of about 20 cm$^3$ capacity. The pycnometers were calibrated with doubly distilled water at the experimental temperatures. The thermostats (Toshniwal, GL-15, and INSREF, 016 AP) were maintained constant to within ±0.1 K at the desired temperatures as checked by means of a calibrated thermometer (Germany).

Viscosities were measured by means of Cannon Fenske viscometers (sizes 75, 100, and 150, ASTM D445, supplied by the Industrial Research Glassware Ltd., New Jersey). The kinetic energy corrections were made according to the recommended method (*14*). The other calibration and experimental details are given in our earlier papers (*1–7*). Standard errors in viscosity measurements were less than ±0.2%.

Refractive indices for the sodium-D line were measured with a thermostated Abbe refractometer (Bellingham and Stanley Ltd., London) with an error of less than 0.0001 unit. The prism assembly was circulated with water maintained at a constant temperature. However, these data were approximated to the fourth place (see Table II). Calibration checks of the refractometer were done routinely with the help of the test glass piece of known refractive index ($n_D$ = 1.5159) provided with the instrument. The reproducibility in the refractive index data was within ±0.2–0.3%.

The speed of sound was determined by using a variable-path single-crystal interferometer (Mittal Enterprises, New Delhi, model M-84). A crystal-controlled high-frequency generator was used to excite the transducer at a frequency of 1 MHz. The frequency was measured with an accuracy of

---

* To whom correspondence to be addressed.

[†] Based on the Ph.D. thesis of M.I.A., submitted to Karnatak University. We dedicate this paper to Professor Petr Munk, University of Texas, on the occasion of his 60th birthday.

0021-9568/93/1738-0031$04.00/0

**Table I. Comparison of Data with Literature Data for Pure Liquids at 298.5 K**

| liquid | $\rho$/(gm·cm$^{-3}$) obsd | $\rho$/(gm·cm$^{-3}$) lit. | $n_D$ obsd | $n_D$ lit. |
|---|---|---|---|---|
| methyl alcohol | 0.7868 | 0.7864 (*40*) | 1.3268 | 1.3264 (*40*) |
| ethyl alcohol | 0.7852 | 0.7850 (*40*) | 1.3595 | 1.3592 (*40*) |
| 1-propanol | 0.8000 | 0.7994 (*41*) | 1.3834 | 1.3834 (*42*) |
| 2-propanol | 0.7812 | 0.7807 (*40*) | 1.3753 | 1.3753 (*40*) |
| 1-butanol | 0.8059 | 0.8056 (*41*) | 1.3971 | 1.3973 (*42*) |
| 2-methyl-1-propanol | 0.7982 | 0.7978 (*12*) | 1.3938 | 1.3939 (*12*) |
| 1-pentanol | 0.8112 | 0.8109 (*30*) | 1.4080 | 1.4079 (*44*) |
| 1-hexanol | 0.8153 | 0.8152 (*43*) | 1.4160 | 1.4158 (*44*) |
| 1-heptanol | 0.8197 | 0.8190 (*41*) | 1.4227 | 1.4226 (*44*) |
| 2-octanol | 0.8168 | 0.8171 (*12*) | 1.4239 | 1.4241 (*12*) |
| methyl acetoacetate | 1.0720 | 1.0724 (*12*) | 1.4167 | 1.4186 (*12*) |

1 in $10^6$ by using a digital frequency meter. The current variations across the transducer were observed on a microammeter. The interferometer cell was filled with the test liquid and was connected to the output terminal of the high-frequency generator through a shielded cable. Water was then circulated around the measuring cell from a thermostat maintained at the desired temperature. The other experimental details were given earlier (*7*). The accuracy of the instrument was checked by measuring the speed of sound of known liquids. Our value of $u$ (1255 m·s$^{-1}$) at 308.15 K for benzene compares well with the data (1255 m·s$^{-1}$) of Nath and Dixit (*15*). Similarly, $u$ at 298.15 K for benzene (1301 m·s$^{-1}$) and toluene (1306 m·s$^{-1}$) agree closely with the literature values of 1301 and 1306 m·s$^{-1}$, respectively, of Nath and Tripathi (*16*). The isentropic compressibilities were calculated as $k_S = 1/(u^2\rho)$. The average uncertainty in $k_S$ is around ±0.01%.

In all the property measurements triplicate experiments were performed at each temperature and composition. The averaged results for various systems are reported in Table II.

## Results and Discussion

The results of excess molar volumes $V^E$, presented in Figure 1, have been calculated as

$$V^E = V_m - V_1x_1 - V_2x_2 \tag{1}$$

where $V_m$ stands for the molar volume of the mixture, $V_1$ and $V_2$ refer to the molar volumes of the two components forming the mixture, and $x_1$ and $x_2$ are the mole fractions of components 1 and 2, respectively.

The observed $V^E$ may be discussed in terms of several effects which may be arbitrarily divided into physical, chemical, and geometrical contributions. The physical interactions involve mainly dispersion forces giving a positive contribution. The chemical or specific interactions result in a volume decrease, and these include charge-transfer-type forces, i.e., forming and/or breaking up of H bonds and other complex-forming interactions. It is well known that alcohols exist as associated structures in the liquid state; this association may be through the H-bonding of their –OH groups. Structural contributions arising from the geometrical fitting of one component into the other, due to differences in the molar volume and free volume between components, lead to negative contributions to $V^E$. With higher alcohols, the latter contribution is negligible, and association decreases with an increase in the chain length of alcohols (*17, 18*). Therefore, mixtures of MAA with higher alcohols give larger $V^E$ as compared to lower alcohols.

The higher alcohols possess less proton-donating ability than the lower ones ($C_1$ or $C_2$), and effects of this kind of heteroassociation are smaller in their mixtures and not sufficient to outweigh the positive contributions to $V^E$; thus, the $V^E$ vs $x_1$ curves for 1-propanol and 1-butanol can be explained in terms of small differences in their proton-donating abilities, thereby giving the positive values of $V^E$. It is interesting to note that a considerable expansion of volume, i.e., 0.2 cm$^3$·mol$^{-1}$ (for 1-propanol) to 0.95 cm$^3$·mol$^{-1}$ (for 2-octanol) is observed. However, the negative $V^E$ values do not seem to fall below –0.4 cm$^3$·mol$^{-1}$ which suggests that, with methyl and ethyl alcohols, the effects due to heteroassociation (as observed in the cases of $C_3$–$C_8$ alcohol chains) may be canceled by breaking up of the self-associated aggregates of alcohols.

Excess properties of a number of binary mixtures containing alcohols of the type used here have been studied in the literature with a variety of other components. A direct comparison of our data with the literature is not possible in view of the nonavailability of the data for the present mixtures. However, one can, at best, compare the present results with those of some of the mixtures containing alcohols of the type used here.

Excess molar volumes of methylcyclohexane with 1-butanol, 1-pentanol, and 1-hexanol have been studied at 298.15 K by Alonso and Corrales (*19*). In this study, $V^E$ is positive and decreases from 1-hexanol to 1-butanol. On the other hand, Rao and Naidu (*20*) observed higher $V^E$ for 1-pentanol than for 1-butanol or 1-hexanol at 303.15 K in contrast to the results of Alonso and Corrales (*19*). Choudary et al. (*21*) measured $V^E$ for mixtures of 1,1,2,2-tetrachloroethane with 1-alkanols ($C_3$–$C_8$) at 303.15 K and found it to be negative in mixtures rich in alcohols and positive in mixtures containing higher contents of chloroalkane. This effect was attributed to the depolymerization of H-bonded alcohol aggregates, interstitial accommodation of halogenated hydrocarbon in the polymers of alcohols, and weak H bond interactions between unlike molecules. A similar conclusion was arrived by Naorem and Suri (*22*) from a study of excess enthalpies of mixtures of furfural (which also contains a ketonic group) with aliphatic alcohols ($C_1$–$C_4$), wherein the $H^E$ results are positive for all the mixtures and increase systematically with the chain length of alcohols. This effect was attributed to the structure breaking of polymer aggregates of alcohols and furfural molecules. Additional support for the increased $V^E$ in the cases of alcohol-containing mixtures comes from other similar studies (*23–25*).

The effect of temperature on $V^E$ is noteworthy. There is a systematic increase in $V^E$ with a rise in temperature for all the mixtures. However, such changes are very small, and thus these data are not included in Figure 1 to avoid the heavy conjestion of points. This increase in $V^E$ with temperature is also expected from the theoretical considerations and in accordance with the published data (*26–29*).

Though the term excess viscosity has been used in the literature (*30–32*), its use is not acceptable (*33*). Hence, we prefer to calculate the viscosity deviations $\Delta\eta$ from the results of viscosities of binary mixtures as

$$\Delta\eta = \eta_m - \eta_1x_1 - \eta_2x_2 \tag{2}$$

The values of the changes in viscosity calculated from eq 2 are presented in Figure 2. There is a clear trend in $\Delta\eta$ values for all the mixtures. The $\Delta\eta$ values are negative which generally decrease with increasing size of the alcohol molecules. However, discrepancies are observed in some cases. Mixtures of MAA with alcohols show the trend in $\Delta\eta$ values as ethyl alcohol > methyl alcohol > 1-propanol > 2-propanol > 1-butanol > 1-pentanol > 2-methyl-1-propanol > 1-hexanol > 1-heptanol > 2-octanol. The molecular size effect of alcohols from 1-hexanol to 2-octanol is quite considerable on the values of $\Delta\eta$. It changes from –1.3 to –1.8 mPa·s, whereas for other alcohols, namely, $C_1$–$C_4$, the change in $\Delta\eta$ is only from –0.22

**Table II. Densities $\rho$, Viscosities $\eta$, Refractive Indices $n_D$, and Speeds of Sound $u$ for Binary Mixtures**

| $x_1$ | $\rho/(g\cdot cm^{-3})$ | $\eta/(mPa\cdot s)$ | $n_D$ | $u/ms^{-1}$ | $x_1$ | $\rho/(g\cdot cm^{-3})$ | $\eta/(mPa\cdot s)$ | $n_D$ | $u/ms^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| Methyl Acetoacetate (1) + Methyl Alcohol (2) | | | | | | | | | |
| 298.15 K | | | | | | | | | |
| 0.0000 | 0.7868 | 0.542 | 1.3268 | 1102 | 0.6056 | 1.0206 | 1.064 | 1.4006 | 1332 |
| 0.1017 | 0.8565 | 0.599 | 1.3493 | 1169 | 0.7015 | 1.0363 | 1.163 | 1.4055 | 1349 |
| 0.1887 | 0.9008 | 0.662 | 1.3633 | 1208 | 0.8024 | 1.0502 | 1.288 | 1.4095 | 1361 |
| 0.3013 | 0.9450 | 0.757 | 1.3775 | 1253 | 0.8994 | 1.0618 | 1.413 | 1.4135 | 1373 |
| 0.4048 | 0.9765 | 0.858 | 1.3866 | 1283 | 1.0000 | 1.0723 | 1.566 | 1.4164 | 1383 |
| 0.5038 | 1.0004 | 0.954 | 1.3944 | 1310 | | | | | |
| 303.15 K | | | | | | | | | |
| 0.0000 | 0.7822 | 0.506 | 1.3245 | 1086 | 0.6056 | 1.0152 | 0.978 | 1.3989 | 1313 |
| 0.1017 | 0.8517 | 0.563 | 1.3476 | 1149 | 0.7015 | 1.0308 | 1.066 | 1.4035 | 1332 |
| 0.1887 | 0.8959 | 0.618 | 1.3612 | 1189 | 0.8024 | 1.0447 | 1.176 | 1.4077 | 1346 |
| 0.3013 | 0.9399 | 0.704 | 1.3757 | 1235 | 0.8994 | 1.0561 | 1.288 | 1.4114 | 1357 |
| 0.4048 | 0.9715 | 0.793 | 1.3853 | 1267 | 1.0000 | 1.0667 | 1.422 | 1.4141 | 1361 |
| 0.5038 | 0.9951 | 0.879 | 1.3927 | 1291 | | | | | |
| 308.15 K | | | | | | | | | |
| 0.0000 | 0.7772 | 0.474 | 1.3223 | 1073 | 0.6056 | 1.0096 | 0.902 | 1.3967 | 1295 |
| 0.1017 | 0.8465 | 0.525 | 1.3454 | 1135 | 0.7015 | 1.0255 | 0.984 | 1.4014 | 1312 |
| 0.1887 | 0.8908 | 0.578 | 1.3591 | 1173 | 0.8024 | 1.0390 | 1.082 | 1.4056 | 1324 |
| 0.3013 | 0.9358 | 0.657 | 1.3733 | 1215 | 0.8994 | 1.0506 | 1.180 | 1.4093 | 1335 |
| 0.4048 | 0.9659 | 0.737 | 1.3833 | 1248 | 1.0000 | 1.0612 | 1.298 | 1.4116 | 1343 |
| 0.5038 | 0.9895 | 0.815 | 1.3909 | 1274 | | | | | |
| Methyl Acetoacetate (1) + Ethyl Alcohol (2) | | | | | | | | | |
| 298.15 K | | | | | | | | | |
| 0.0000 | 0.7852 | 1.074 | 1.3595 | 1145 | 0.6070 | 0.9988 | 1.121 | 1.4020 | 1330 |
| 0.1051 | 0.8356 | 0.960 | 1.3694 | 1188 | 0.7033 | 1.0194 | 1.202 | 1.4056 | 1340 |
| 0.2040 | 0.8783 | 0.942 | 1.3785 | 1216 | 0.8022 | 1.1385 | 1.300 | 1.4101 | 1364 |
| 0.3085 | 0.9182 | 0.965 | 1.3854 | 1252 | 0.9020 | 1.0565 | 1.422 | 1.4131 | 1368 |
| 0.4046 | 0.9460 | 0.995 | 1.3923 | 1276 | 1.0000 | 1.0725 | 1.564 | 1.4172 | 1383 |
| 0.5070 | 0.9742 | 1.057 | 1.3970 | 1297 | | | | | |
| 303.15 K | | | | | | | | | |
| 0.0000 | 0.7811 | 0.979 | 1.3573 | 1121 | 0.6070 | 0.9935 | 1.027 | 1.4001 | 1308 |
| 0.1051 | 0.8312 | 0.879 | 1.3674 | 1170 | 0.7033 | 1.0141 | 1.099 | 1.4047 | 1321 |
| 0.2040 | 0.8735 | 0.866 | 1.3767 | 1199 | 0.8022 | 1.0334 | 1.187 | 1.4090 | 1341 |
| 0.3085 | 0.9131 | 0.883 | 1.3843 | 1235 | 0.9020 | 1.0509 | 1.294 | 1.4111 | 1354 |
| 0.4046 | 0.9410 | 0.913 | 1.3901 | 1259 | 1.0000 | 1.0671 | 1.421 | 1.4147 | 1361 |
| 0.5070 | 0.9691 | 0.968 | 1.3949 | 1278 | | | | | |
| 308.15 K | | | | | | | | | |
| 0.0000 | 0.7767 | 0.893 | 1.3556 | 1103 | 0.6070 | 0.9880 | 0.946 | 1.3988 | 1293 |
| 0.1051 | 0.8266 | 0.806 | 1.3660 | 1151 | 0.7033 | 1.0087 | 1.011 | 1.4022 | 1305 |
| 0.2040 | 0.8686 | 0.798 | 1.3745 | 1184 | 0.8022 | 1.0278 | 1.092 | 1.4063 | 1322 |
| 0.3085 | 0.9081 | 0.814 | 1.3821 | 1216 | 0.9020 | 1.0456 | 1.186 | 1.4095 | 1334 |
| 0.4046 | 0.9356 | 0.841 | 1.3884 | 1240 | 1.0000 | 1.0616 | 1.298 | 1.4126 | 1343 |
| 0.5070 | 0.9635 | 0.892 | 1.3924 | 1261 | | | | | |
| Methyl Acetoacetate (1) + 1-Propanol (2) | | | | | | | | | |
| 298.15 K | | | | | | | | | |
| 0.0000 | 0.8000 | 1.900 | 1.3834 | 1204 | 0.6090 | 0.9865 | 1.238 | 1.4053 | 1321 |
| 0.1028 | 0.8377 | 1.497 | 1.3875 | 1214 | 0.7057 | 1.0097 | 1.278 | 1.4085 | 1337 |
| 0.2021 | 0.8711 | 1.333 | 1.3916 | 1250 | 0.8054 | 1.0322 | 1.339 | 1.4126 | 1359 |
| 0.3067 | 0.9041 | 1.253 | 1.3956 | 1266 | 0.9036 | 1.0528 | 1.501 | 1.4137 | 1372 |
| 0.4070 | 0.9334 | 1.221 | 1.3987 | 1284 | 1.0000 | 1.0725 | 1.564 | 1.4172 | 1383 |
| 0.5069 | 0.9606 | 1.219 | 1.4027 | 1300 | | | | | |
| 303.15 K | | | | | | | | | |
| 0.0000 | 0.7959 | 1.681 | 1.3814 | 1179 | 0.6090 | 0.9814 | 1.123 | 1.4032 | 1304 |
| 0.1028 | 0.8334 | 1.337 | 1.3856 | 1204 | 0.7057 | 1.0044 | 1.163 | 1.4069 | 1319 |
| 0.2021 | 0.8665 | 1.213 | 1.3898 | 1230 | 0.8054 | 1.0270 | 1.217 | 1.4102 | 1339 |
| 0.3067 | 0.8993 | 1.128 | 1.3934 | 1248 | 0.9036 | 1.0474 | 1.295 | 1.4116 | 1356 |
| 0.4070 | 0.9284 | 1.102 | 1.3975 | 1264 | 1.0000 | 1.0671 | 1.421 | 1.4147 | 1361 |
| 0.5069 | 0.9557 | 1.104 | 1.4003 | 1283 | | | | | |
| 308.15 K | | | | | | | | | |
| 0.0000 | 0.7919 | 1.488 | 1.3799 | 1163 | 0.6090 | 0.9763 | 1.027 | 1.4019 | 1283 |
| 0.1028 | 0.8288 | 1.198 | 1.3831 | 1177 | 0.7057 | 0.9991 | 1.062 | 1.4046 | 1304 |
| 0.2021 | 0.8618 | 1.096 | 1.3876 | 1212 | 0.8054 | 1.0215 | 1.114 | 1.4126 | 1319 |
| 0.3067 | 0.8945 | 1.024 | 1.3916 | 1226 | 0.9036 | 1.0420 | 1.183 | 1.4101 | 1334 |
| 0.4070 | 0.9234 | 1.003 | 1.3957 | 1246 | 1.0000 | 1.0616 | 1.298 | 1.4126 | 1343 |
| 0.5069 | 0.9504 | 1.007 | 1.3978 | 1263 | | | | | |

**Table II. (Continued)**

| $x_1$ | $\rho/(\mathrm{g\cdot cm^{-3}})$ | $\eta/(\mathrm{mPa\cdot s})$ | $n_D$ | $u/\mathrm{ms^{-1}}$ | $x_1$ | $\rho/(\mathrm{g\cdot cm^{-3}})$ | $\eta/(\mathrm{mPa\cdot s})$ | $n_D$ | $u/\mathrm{ms^{-1}}$ |
|---|---|---|---|---|---|---|---|---|---|
| Methyl Acetoacetate (1) + 2-Propanol (2) | | | | | | | | | |
| 298.15 K | | | | | | | | | |
| 0.0000 | 0.7812 | 2.012 | 1.3753 | 1141 | 0.6057 | 0.9783 | 1.189 | 1.4027 | 1296 |
| 0.1028 | 0.8203 | 1.457 | 1.3806 | 1170 | 0.7079 | 1.0046 | 1.243 | 1.4062 | 1317 |
| 0.2052 | 0.8569 | 1.267 | 1.3855 | 1199 | 0.8053 | 1.0281 | 1.315 | 1.4102 | 1344 |
| 0.3051 | 0.8903 | 1.195 | 1.3900 | 1221 | 0.9038 | 1.0510 | 1.419 | 1.4129 | 1363 |
| 0.4085 | 0.9225 | 1.168 | 1.3944 | 1260 | 1.0000 | 1.0725 | 1.564 | 1.4172 | 1383 |
| 0.5084 | 0.9513 | 1.160 | 1.3986 | 1270 | | | | | |
| 303.15 K | | | | | | | | | |
| 0.0000 | 0.7769 | 1.724 | 1.3737 | 1122 | 0.6057 | 0.9728 | 1.080 | 1.4004 | 1278 |
| 0.1028 | 0.8157 | 1.279 | 1.3784 | 1149 | 0.7079 | 0.9992 | 1.127 | 1.4046 | 1302 |
| 0.2052 | 0.8519 | 1.124 | 1.3830 | 1182 | 0.8053 | 1.0228 | 1.197 | 1.4081 | 1324 |
| 0.3051 | 0.8853 | 1.068 | 1.3877 | 1202 | 0.9038 | 1.0457 | 1.287 | 1.4105 | 1342 |
| 0.4085 | 0.9173 | 1.051 | 1.3926 | 1241 | 1.0000 | 1.0671 | 1.421 | 1.4147 | 1361 |
| 0.5084 | 0.9461 | 1.049 | 1.3974 | 1252 | | | | | |
| 308.15 K | | | | | | | | | |
| 0.0000 | 0.7726 | 1.485 | 1.3710 | 1097 | 0.6057 | 0.9675 | 1.985 | 1.3980 | 1261 |
| 0.1028 | 0.8101 | 1.023 | 1.3759 | 1132 | 0.7079 | 0.9938 | 1.032 | 1.4026 | 1285 |
| 0.2052 | 0.8469 | 1.006 | 1.3810 | 1154 | 0.8053 | 1.0174 | 1.094 | 1.4057 | 1315 |
| 0.3051 | 0.8802 | 1.963 | 1.3853 | 1190 | 0.9038 | 1.0401 | 1.133 | 1.4085 | 1325 |
| 0.4085 | 0.9121 | 1.952 | 1.3901 | 1222 | 1.0000 | 1.0616 | 1.298 | 1.4126 | 1343 |
| 0.5084 | 0.9409 | 1.956 | 1.3952 | 1227 | | | | | |
| Methyl Acetoacetate (1) + 1-Butanol (2) | | | | | | | | | |
| 298.15 K | | | | | | | | | |
| 0.0000 | 0.8059 | 2.484 | 1.3971 | 1240 | 0.6074 | 0.9743 | 1.311 | 1.4087 | 1316 |
| 0.1022 | 0.8361 | 1.886 | 1.3984 | 1250 | 0.7044 | 0.9997 | 1.321 | 1.4111 | 1330 |
| 0.2039 | 0.8652 | 1.628 | 1.4005 | 1259 | 0.8051 | 1.0249 | 1.368 | 1.4127 | 1352 |
| 0.3060 | 0.8940 | 1.465 | 1.4031 | 1272 | 0.9038 | 1.0492 | 1.436 | 1.4148 | 1365 |
| 0.4081 | 0.9220 | 1.378 | 1.4053 | 1286 | 1.0000 | 1.0725 | 1.564 | 1.4172 | 1383 |
| 0.5110 | 0.9497 | 1.328 | 1.4065 | 1301 | | | | | |
| 303.15 K | | | | | | | | | |
| 0.0000 | 0.8020 | 2.174 | 1.3954 | 1223 | 0.6074 | 0.9692 | 1.183 | 1.4071 | 1300 |
| 0.1022 | 0.8318 | 1.669 | 1.3968 | 1230 | 0.7044 | 0.9945 | 1.197 | 1.4107 | 1315 |
| 0.2039 | 0.8607 | 1.447 | 1.3987 | 1240 | 0.8051 | 1.0196 | 1.211 | 1.4105 | 1332 |
| 0.3060 | 0.8893 | 1.308 | 1.4016 | 1255 | 0.9038 | 1.0439 | 1.302 | 1.4127 | 1346 |
| 0.4081 | 0.9172 | 1.235 | 1.4031 | 1267 | 1.0000 | 1.0671 | 1.421 | 1.4147 | 1361 |
| 0.5110 | 0.9447 | 1.197 | 1.4046 | 1279 | | | | | |
| 308.15 K | | | | | | | | | |
| 0.0000 | 0.7981 | 1.913 | 1.3929 | 1208 | 0.6074 | 0.9642 | 1.080 | 1.4068 | 1281 |
| 0.1022 | 0.8276 | 1.487 | 1.3952 | 1216 | 0.7044 | 0.9893 | 1.093 | 1.4075 | 1296 |
| 0.2039 | 0.8564 | 1.301 | 1.3968 | 1222 | 0.8051 | 1.0143 | 1.131 | 1.4086 | 1315 |
| 0.3060 | 0.8848 | 1.195 | 1.3991 | 1236 | 0.9038 | 1.0384 | 1.190 | 1.4106 | 1332 |
| 0.4081 | 0.9124 | 1.118 | 1.4008 | 1251 | 1.0000 | 1.0616 | 1.298 | 1.4126 | 1343 |
| 0.5110 | 0.9397 | 1.090 | 1.4028 | 1262 | | | | | |
| Methyl Acetoacetate (1) + 2-Methyl-1-propanol (2) | | | | | | | | | |
| 298.15 K | | | | | | | | | |
| 0.0000 | 0.7982 | 3.247 | 1.3938 | 1191 | 0.6057 | 0.9711 | 1.352 | 1.4076 | 1298 |
| 0.1046 | 0.8295 | 2.240 | 1.3962 | 1205 | 0.7026 | 0.9969 | 1.350 | 1.4099 | 1323 |
| 0.2052 | 0.8591 | 1.810 | 1.3985 | 1224 | 0.8059 | 1.0236 | 1.380 | 1.4121 | 1344 |
| 0.3095 | 0.8883 | 1.598 | 1.4004 | 1240 | 0.9020 | 1.0477 | 1.449 | 1.4143 | 1364 |
| 0.4094 | 0.9176 | 1.463 | 1.4029 | 1261 | 1.0000 | 1.0725 | 1.564 | 1.4172 | 1383 |
| 0.5075 | 0.9449 | 1.385 | 1.4054 | 1279 | | | | | |
| 303.15 K | | | | | | | | | |
| 0.0000 | 0.7943 | 2.745 | 1.3914 | 1172 | 0.6057 | 0.9661 | 1.221 | 1.4053 | 1281 |
| 0.1046 | 0.8252 | 1.944 | 1.3939 | 1191 | 0.7026 | 0.9916 | 1.223 | 1.4077 | 1302 |
| 0.2052 | 0.8548 | 1.591 | 1.3962 | 1202 | 0.8059 | 1.0181 | 1.251 | 1.4100 | 1324 |
| 0.3095 | 0.8830 | 1.412 | 1.3985 | 1223 | 0.9020 | 1.0427 | 1.312 | 1.4120 | 1346 |
| 0.4094 | 0.9127 | 1.303 | 1.4001 | 1241 | 1.0000 | 1.0671 | 1.421 | 1.4147 | 1361 |
| 0.5075 | 0.9396 | 1.241 | 1.4035 | 1264 | | | | | |
| 308.15 K | | | | | | | | | |
| 0.0000 | 0.7903 | 2.316 | 1.3892 | 1154 | 0.6057 | 0.9607 | 1.108 | 1.4034 | 1262 |
| 0.1046 | 0.8210 | 1.696 | 1.3915 | 1173 | 0.7026 | 0.9863 | 1.114 | 1.4054 | 1283 |
| 0.2052 | 0.8502 | 1.407 | 1.3939 | 1186 | 0.8059 | 1.0128 | 1.143 | 1.4079 | 1309 |
| 0.3095 | 0.8782 | 1.257 | 1.3963 | 1203 | 0.9020 | 1.0371 | 1.198 | 1.4101 | 1324 |
| 0.4094 | 0.9077 | 1.170 | 1.3987 | 1221 | 1.0000 | 1.0616 | 1.298 | 1.4126 | 1343 |
| 0.5075 | 0.9346 | 1.124 | 1.4012 | 1244 | | | | | |

**Table II. (Continued)**

| $x_1$ | $\rho/(\mathrm{g{\cdot}cm^{-3}})$ | $\eta/(\mathrm{mPa{\cdot}s})$ | $n_D$ | $u/\mathrm{ms^{-1}}$ | $x_1$ | $\rho/(\mathrm{g{\cdot}cm^{-3}})$ | $\eta/(\mathrm{mPa{\cdot}s})$ | $n_D$ | $u/\mathrm{ms^{-1}}$ |
|---|---|---|---|---|---|---|---|---|---|
| Methyl Acetoacetate (1) + 1-Pentanol (2) | | | | | | | | | |
| 298.15 K | | | | | | | | | |
| 0.0000 | 0.8112 | 3.286 | 1.4080 | 1277 | 0.6099 | 0.9658 | 1.439 | 1.4117 | 1322 |
| 0.1031 | 0.8361 | 2.467 | 1.4086 | 1279 | 0.7075 | 0.9920 | 1.408 | 1.4133 | 1332 |
| 0.2056 | 0.8618 | 2.053 | 1.4087 | 1281 | 0.8063 | 1.0187 | 1.408 | 1.4140 | 1351 |
| 0.3072 | 0.8877 | 1.796 | 1.4092 | 1287 | 0.9019 | 1.0477 | 1.449 | 1.4154 | 1367 |
| 0.4083 | 0.9134 | 1.637 | 1.4099 | 1296 | 1.0000 | 1.0725 | 1.564 | 1.4172 | 1383 |
| 0.5091 | 0.9395 | 1.520 | 1.4112 | 1308 | | | | | |
| 303.15 K | | | | | | | | | |
| 0.0000 | 0.8074 | 2.833 | 1.4062 | 1263 | 0.6099 | 0.9608 | 1.294 | 1.4095 | 1303 |
| 0.1031 | 0.8322 | 2.156 | 1.4063 | 1261 | 0.7075 | 0.9869 | 1.268 | 1.4110 | 1317 |
| 0.2056 | 0.8574 | 1.809 | 1.4064 | 1266 | 0.8063 | 1.0134 | 1.275 | 1.4116 | 1332 |
| 0.3072 | 0.8834 | 1.588 | 1.4068 | 1270 | 0.9019 | 1.0391 | 1.313 | 1.4134 | 1347 |
| 0.4083 | 0.9086 | 1.453 | 1.4079 | 1276 | 1.0000 | 1.0671 | 1.421 | 1.4147 | 1361 |
| 0.5091 | 0.9347 | 1.356 | 1.4089 | 1288 | | | | | |
| 308.15 K | | | | | | | | | |
| 0.0000 | 0.8038 | 2.441 | 1.4036 | 1246 | 0.6099 | 0.9560 | 1.175 | 1.4077 | 1284 |
| 0.1031 | 0.8281 | 1.903 | 1.4043 | 1245 | 0.7075 | 0.9816 | 1.156 | 1.4086 | 1295 |
| 0.2056 | 0.8532 | 1.606 | 1.4042 | 1247 | 0.8063 | 1.0081 | 1.164 | 1.4093 | 1314 |
| 0.3072 | 0.8789 | 1.419 | 1.4047 | 1251 | 0.9019 | 1.0339 | 1.201 | 1.4111 | 1328 |
| 0.4083 | 0.9041 | 1.300 | 1.4060 | 1263 | 1.0000 | 1.0616 | 1.298 | 1.4126 | 1343 |
| 0.5091 | 0.9298 | 1.223 | 1.4068 | 1272 | | | | | |
| Methyl Acetoacetate (1) + 1-Hexanol (2) | | | | | | | | | |
| 298.15 K | | | | | | | | | |
| 0.0000 | 0.8153 | 4.317 | 1.4160 | 1306 | 0.6081 | 0.9574 | 1.609 | 1.4147 | 1319 |
| 0.1036 | 0.8367 | 3.185 | 1.4158 | 1303 | 0.7063 | 0.9845 | 1.521 | 1.4148 | 1334 |
| 0.2040 | 0.8586 | 2.588 | 1.4151 | 1301 | 0.8060 | 1.0126 | 1.473 | 1.4154 | 1349 |
| 0.3064 | 0.8822 | 2.204 | 1.4148 | 1304 | 0.9023 | 1.0413 | 1.478 | 1.4162 | 1361 |
| 0.4075 | 0.9063 | 1.947 | 1.4145 | 1307 | 1.0000 | 1.0725 | 1.564 | 1.4172 | 1383 |
| 0.5096 | 0.9319 | 1.749 | 1.4145 | 1312 | | | | | |
| 303.15 K | | | | | | | | | |
| 0.0000 | 0.8118 | 3.670 | 1.4139 | 1289 | 0.6081 | 0.9526 | 1.442 | 1.4128 | 1306 |
| 0.1036 | 0.8331 | 2.760 | 1.4138 | 1287 | 0.7063 | 0.9791 | 1.364 | 1.4130 | 1315 |
| 0.2040 | 0.8547 | 2.257 | 1.4131 | 1283 | 0.8060 | 1.0074 | 1.330 | 1.4134 | 1330 |
| 0.3064 | 0.8777 | 1.932 | 1.4128 | 1285 | 0.9023 | 1.0361 | 1.340 | 1.4137 | 1346 |
| 0.4075 | 0.9022 | 1.720 | 1.4125 | 1290 | 1.0000 | 1.0671 | 1.421 | 1.4147 | 1361 |
| 0.5096 | 0.9272 | 1.547 | 1.4125 | 1296 | | | | | |
| 308.15 K | | | | | | | | | |
| 0.0000 | 0.8081 | 3.130 | 1.4111 | 1273 | 0.6081 | 0.9478 | 1.302 | 1.4104 | 1286 |
| 0.1036 | 0.8290 | 2.409 | 1.4114 | 1268 | 0.7063 | 0.9741 | 1.238 | 1.4106 | 1299 |
| 0.2040 | 0.8505 | 1.989 | 1.4110 | 1267 | 0.8060 | 1.0023 | 1.211 | 1.4111 | 1310 |
| 0.3064 | 0.8736 | 1.711 | 1.4106 | 1268 | 0.9023 | 1.0307 | 1.222 | 1.4116 | 1327 |
| 0.4075 | 0.8975 | 1.527 | 1.4105 | 1272 | 1.0000 | 1.0616 | 1.298 | 1.4126 | 1343 |
| 0.5096 | 0.9225 | 1.387 | 1.4104 | 1275 | | | | | |
| Methyl Acetoacetate (1) + 1-Heptanol (2) | | | | | | | | | |
| 298.15 K | | | | | | | | | |
| 0.0000 | 0.8197 | 5.690 | 1.4227 | 1330 | 0.6072 | 0.9508 | 1.842 | 1.4175 | 1326 |
| 0.1016 | 0.8377 | 4.066 | 1.4218 | 1321 | 0.7071 | 0.9781 | 1.663 | 1.4168 | 1337 |
| 0.2071 | 0.8582 | 3.167 | 1.4205 | 1318 | 0.8059 | 1.0073 | 1.546 | 1.4167 | 1350 |
| 0.3081 | 0.8793 | 2.651 | 1.4195 | 1315 | 0.9033 | 1.0386 | 1.512 | 1.4163 | 1361 |
| 0.4096 | 0.9020 | 2.278 | 1.4189 | 1317 | 1.0000 | 1.0723 | 1.566 | 1.4164 | 1383 |
| 0.5099 | 0.9262 | 2.012 | 1.4185 | 1321 | | | | | |
| 303.15 K | | | | | | | | | |
| 0.0000 | 0.8160 | 4.771 | 1.4210 | 1313 | 0.6072 | 0.9406 | 1.624 | 1.4154 | 1309 |
| 0.1016 | 0.8342 | 3.465 | 1.4195 | 1304 | 0.7071 | 0.9732 | 1.485 | 1.4146 | 1314 |
| 0.2071 | 0.8542 | 2.734 | 1.4187 | 1302 | 0.8059 | 1.0022 | 1.393 | 1.4143 | 1330 |
| 0.3081 | 0.8752 | 2.298 | 1.4177 | 1301 | 0.9033 | 1.0331 | 1.366 | 1.4141 | 1347 |
| 0.4096 | 0.8976 | 1.981 | 1.4166 | 1300 | 1.0000 | 1.0667 | 1.422 | 1.4141 | 1361 |
| 0.5099 | 0.9214 | 1.754 | 1.4161 | 1304 | | | | | |
| 308.15 K | | | | | | | | | |
| 0.0000 | 0.8125 | 4.002 | 1.4185 | 1295 | 0.6072 | 0.9411 | 1.452 | 1.4135 | 1289 |
| 0.1016 | 0.8302 | 2.970 | 1.4179 | 1287 | 0.7071 | 0.9681 | 1.337 | 1.4130 | 1300 |
| 0.2071 | 0.8502 | 2.357 | 1.4165 | 1284 | 0.8059 | 0.9970 | 1.264 | 1.4123 | 1315 |
| 0.3081 | 0.8709 | 1.998 | 1.4154 | 1280 | 0.9033 | 1.0277 | 1.245 | 1.4120 | 1324 |
| 0.4096 | 0.8933 | 1.733 | 1.4145 | 1282 | 1.0000 | 1.0612 | 1.298 | 1.4116 | 1343 |
| 0.5099 | 0.9167 | 1.545 | 1.4138 | 1285 | | | | | |

**Table II. (Continued)**

| $x_1$ | $\rho$/(g·cm$^{-3}$) | $\eta$/(mPa·s) | $n_D$ | $u$/ms$^{-1}$ | $x_1$ | $\rho$/(g·cm$^{-3}$) | $\eta$/(mPa·s) | $n_D$ | $u$/ms$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Methyl Acetoacetate (1) + 2-Octanol (2) | | | | | |
| | | | | 298.15 K | | | | | |
| 0.0000 | 0.8168 | 5.929 | 1.4239 | 1309 | 0.6079 | 0.9415 | 1.900 | 1.4178 | 1318 |
| 0.1041 | 0.8337 | 4.231 | 1.4227 | 1306 | 0.7081 | 0.9695 | 1.699 | 1.4171 | 1328 |
| 0.2072 | 0.8516 | 3.315 | 1.4214 | 1304 | 0.8070 | 1.0003 | 1.574 | 1.4167 | 1344 |
| 0.3091 | 0.8713 | 2.753 | 1.4205 | 1302 | 0.9036 | 1.0342 | 1.520 | 1.4166 | 1358 |
| 0.4101 | 0.8928 | 2.358 | 1.4192 | 1308 | 1.0000 | 1.0723 | 1.566 | 1.4164 | 1383 |
| 0.5107 | 0.9164 | 2.075 | 1.4187 | 1309 | | | | | |
| | | | | 303.15 K | | | | | |
| 0.0000 | 0.8131 | 4.794 | 1.4214 | 1293 | 0.6079 | 0.9363 | 1.661 | 1.4155 | 1298 |
| 0.1041 | 0.8295 | 3.511 | 1.4205 | 1288 | 0.7081 | 0.9645 | 1.506 | 1.4150 | 1309 |
| 0.2072 | 0.8475 | 2.796 | 1.4191 | 1285 | 0.8070 | 0.9952 | 1.413 | 1.4143 | 1324 |
| 0.3091 | 0.8669 | 2.344 | 1.4180 | 1284 | 0.9036 | 1.0287 | 1.374 | 1.4142 | 1341 |
| 0.4101 | 0.8882 | 2.026 | 1.4168 | 1286 | 1.0000 | 1.0667 | 1.422 | 1.4141 | 1361 |
| 0.5107 | 0.9118 | 1.796 | 1.4162 | 1289 | | | | | |
| | | | | 308.15 K | | | | | |
| 0.0000 | 0.8092 | 3.909 | 1.4193 | 1273 | 0.6079 | 0.9314 | 1.476 | 1.4135 | 1279 |
| 0.1041 | 0.8253 | 2.939 | 1.4184 | 1272 | 0.7081 | 0.9595 | 1.352 | 1.4129 | 1291 |
| 0.2072 | 0.8432 | 2.377 | 1.4169 | 1270 | 0.8070 | 0.9902 | 1.279 | 1.4121 | 1307 |
| 0.3091 | 0.8626 | 2.015 | 1.4161 | 1269 | 0.9036 | 1.0235 | 1.251 | 1.4119 | 1323 |
| 0.4101 | 0.8839 | 1.756 | 1.4147 | 1269 | 1.0000 | 1.0612 | 1.298 | 1.4116 | 1343 |
| 0.5107 | 0.9070 | 1.567 | 1.4140 | 1274 | | | | | |

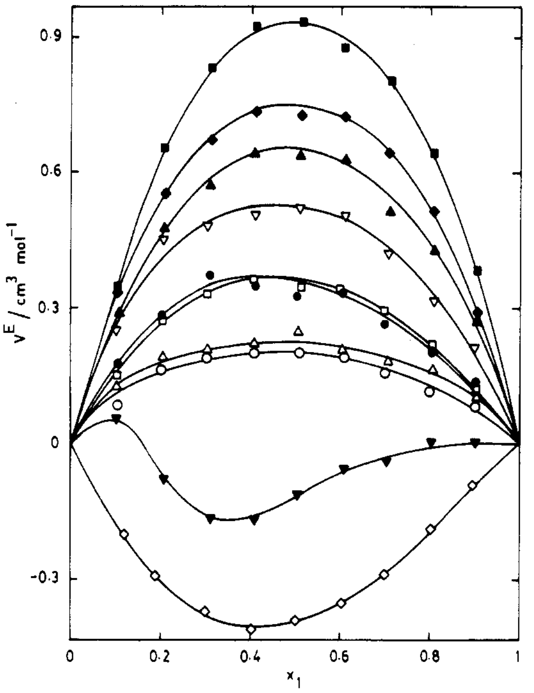

**Figure 1.** Variation of the excess molar volume with mole fraction at 298.15 K. Symbols: MAA with (◇) methyl alcohol; (▼) ethyl alcohol; (○) 1-propanol; (△) 2-propanol; (□) 1-butanol; (●) 2-methyl-1-propanol; (▽) 1-pentanol; (▲) 1-hexanol; (◆) 1-heptanol; (■) 2-octanol.

to −1.1 mPa·s. The minima of the $\Delta\eta$ versus $x_1$ curves occur in the low mole fraction region of MAA. In this region, the endothermic enthalpy of mixing may cause this effect due to the breaking of H bonds between alcohol molecules as they disperse throughout the mixtures. This endothermic effect outweighs the exothermic formation of the MAA–lower alcohol interactions. This should result in more negative $\Delta\eta$ values for higher alcohols than for the lower ones. The effect of a temperature increase is, in all cases, to break interactions and permit an easier flow of the liquid. The result is a net higher $\Delta\eta$ at higher temperatures. This is indeed the case with the present systems.

The changes in isentropic compressibilities, $\Delta k_S$, have been calculated from the isentropic compressibility data on mixtures and the pure components by using

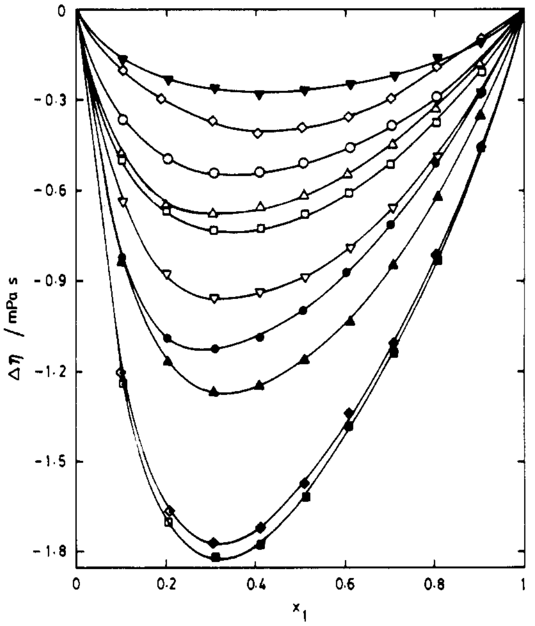

**Figure 2.** Dependence of the molar viscosity deviation on mole fraction at 298.15 K. Symbols have the same meaning as in Figure 1.

$$\Delta k_S = k_S^{\text{mix}} - k_{S,1}\phi_1 - k_{S,2}\phi_2 \qquad (3)$$

where $\phi_1$ is the volume fraction of the $i$th component of the mixture and is defined as

$$\phi_i = x_i V_i / \sum_{i=1}^{2} x_i V_i \qquad (4)$$

The plots of $\Delta k_S$ versus $\phi_1$ are shown in Figure 3. It is observed that the $\Delta k_S$ results vary systematically with the chain length of alcohols. For some mixtures, namely, MAA with $C_1$–$C_4$, the $\Delta k_S$ values are negative, whereas with others, i.e., $C_5$–$C_8$, the $\Delta k_S$ values are positive. However, for 1-heptanol, the positive values of $\Delta k_S$ are higher than those of 2-octanol-containing mixtures. These values show the trend methyl alcohol < ethyl alcohol < 2-propanol < 1-propanol < 2-methyl-1-propanol < 1-butanol < 1-pentanol < 1-hexanol < 2-octanol < 1-heptanol. It is to be noted here that $\Delta k_S$

**Table III. Coefficients of Derived Quantities**

| $Y^{\mathrm{E}}$/unit | t/K | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ | $Y^{\mathrm{E}}$/unit | t/K | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Methyl Acetoacetate (1) + Methyl Alcohol (2) | | | | | | | | | | | | | |
| $V^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | −1.583 | −0.453 | −0.399 | −0.008 | 0.006 | $10^{11}\Delta k_s/\mathrm{Pa^{-1}}$ | 298.15 | −29.921 | −2.592 | −12.870 | −18.347 | 0.135 |
| | 303.15 | −1.626 | −0.495 | −0.506 | −0.179 | 0.012 | | 303.15 | −31.296 | −1.611 | −7.111 | −18.683 | 0.086 |
| | 308.15 | −1.692 | −0.879 | 0.157 | 0.123 | 0.027 | | 308.15 | −31.218 | −0.083 | −16.083 | −22.771 | 0.115 |
| $\Delta\eta/(\mathrm{mPa\cdot s})$ | 298.15 | −0.413 | 0.017 | −0.197 | −0.003 | 0.003 | $R^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 1.506 | 0.330 | −0.299 | −0.031 | 0.013 |
| | 303.15 | −0.350 | 0.012 | −0.149 | 0.034 | 0.003 | | | | | | | |
| | 308.15 | −0.295 | 0.015 | −0.118 | −0.002 | 0.001 | | | | | | | |
| Methyl Acetoacetate (1) + Ethyl Alcohol (2) | | | | | | | | | | | | | |
| $V^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | −0.468 | −1.234 | 2.399 | 1.918 | 0.064 | $10^{11}\Delta k_s/\mathrm{Pa^{-1}}$ | 298.15 | −19.925 | −3.041 | 2.430 | −15.702 | 0.973 |
| | 303.15 | −0.404 | −1.072 | 2.062 | 2.089 | 0.059 | | 303.15 | −25.967 | −4.517 | −2.821 | −16.751 | 0.359 |
| | 308.15 | −0.298 | −1.179 | 2.330 | 1.701 | 0.066 | | 308.15 | −27.631 | −5.160 | 0.422 | −12.620 | 0.370 |
| $\Delta\eta/(\mathrm{mPa\cdot s})$ | 298.15 | −1.071 | −0.197 | −0.513 | −0.370 | 0.004 | $R^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 2.027 | 0.136 | 1.030 | 0.029 | 0.035 |
| | 303.15 | −0.944 | −0.190 | −0.443 | −0.288 | 0.003 | | | | | | | |
| | 308.15 | −0.830 | −0.171 | −0.367 | −0.266 | 0.004 | | | | | | | |
| Methyl Acetoacetate (1) + 1-Propanol (2) | | | | | | | | | | | | | |
| $V^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 0.813 | 0.226 | −0.259 | 0.342 | 0.010 | $10^{11}\Delta k_s/\mathrm{Pa^{-1}}$ | 298.15 | −11.115 | −8.763 | 34.316 | 17.707 | 0.345 |
| | 303.15 | 0.880 | 0.352 | −0.612 | 0.406 | 0.018 | | 303.15 | −13.998 | −5.833 | 9.559 | −11.818 | 0.229 |
| | 308.15 | 0.985 | 0.353 | −0.279 | 0.685 | 0.009 | | 308.15 | −13.353 | −6.392 | 25.578 | 9.383 | 0.450 |
| $\Delta\eta/(\mathrm{mPa\cdot s})$ | 298.15 | −2.065 | −0.591 | −0.984 | −1.684 | 0.016 | $R^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 1.727 | 0.358 | −0.180 | −0.063 | 0.033 |
| | 303.15 | −1.772 | −0.668 | −1.094 | −0.568 | 0.012 | | | | | | | |
| | 308.15 | −1.529 | −0.551 | −0.928 | −0.464 | 0.010 | | | | | | | |
| Methyl Acetoacetate (1) + 2-Propanol (2) | | | | | | | | | | | | | |
| $V^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 0.926 | 0.122 | 0.093 | 0.989 | 0.013 | $10^{11}\Delta k_s/\mathrm{Pa^{-1}}$ | 298.15 | −18.348 | −5.437 | 5.789 | 1.346 | 0.571 |
| | 303.15 | 1.075 | 0.110 | 0.325 | 0.792 | 0.011 | | 303.15 | −20.319 | −5.460 | 8.783 | 4.547 | 0.562 |
| | 308.15 | 1.156 | 0.249 | 0.252 | 1.159 | 0.010 | | 308.15 | −23.154 | −6.589 | 9.182 | −10.884 | 0.904 |
| $\Delta\eta/(\mathrm{mPa\cdot s})$ | 298.15 | −2.457 | −1.026 | −1.949 | −1.680 | 0.014 | $R^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 1.629 | 0.254 | 0.495 | −0.068 | 0.018 |
| | 303.15 | −2.049 | −0.835 | −1.595 | −1.278 | 0.012 | | | | | | | |
| | 308.15 | −1.643 | −0.509 | −2.041 | −1.762 | 0.043 | | | | | | | |
| Methyl Acetoacetate (1) + 1-Butanol (2) | | | | | | | | | | | | | |
| $V^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 1.480 | 0.081 | 0.256 | 0.130 | 0.023 | $10^{11}\Delta k_s/\mathrm{Pa^{-1}}$ | 298.15 | −3.315 | 1.989 | −2.011 | −3.067 | 0.142 |
| | 303.15 | 1.609 | 0.080 | 0.512 | 0.160 | 0.024 | | 303.15 | −2.911 | 1.970 | 2.569 | 2.705 | 0.217 |
| | 308.15 | 1.704 | 0.106 | 0.421 | 0.277 | 0.018 | | 308.15 | −2.655 | 3.860 | 2.686 | −5.133 | 0.186 |
| $\Delta\eta/(\mathrm{mPa\cdot s})$ | 298.15 | −2.738 | −1.074 | −1.720 | −1.217 | 0.014 | $R^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 1.082 | 0.291 | −0.441 | −0.723 | 0.017 |
| | 303.15 | −2.366 | −0.880 | −1.570 | −0.898 | 0.013 | | | | | | | |
| | 308.15 | −2.030 | −0.706 | −1.229 | −0.873 | 0.012 | | | | | | | |
| Methyl Acetoacetate (1) + 2-Methyl-1-propanol (2) | | | | | | | | | | | | | |
| $V^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 1.456 | 0.882 | −1.090 | 0.633 | 0.045 | $10^{11}\Delta k_s/\mathrm{Pa^{-1}}$ | 298.15 | −8.287 | 0.981 | 4.118 | −0.806 | 0.174 |
| | 303.15 | 1.684 | 1.122 | −1.289 | 0.340 | 0.066 | | 303.15 | −8.874 | 4.590 | −5.540 | −7.253 | 0.233 |
| | 308.15 | 1.833 | 1.254 | −1.548 | 0.291 | 0.065 | | 308.15 | −9.077 | 5.225 | −8.908 | −11.627 | 0.185 |
| $\Delta\eta/(\mathrm{mPa\cdot s})$ | 298.15 | −4.000 | −2.085 | −2.986 | −2.377 | 0.017 | $R^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 1.018 | 0.215 | 0.316 | −0.164 | 0.007 |
| | 303.15 | −3.300 | −1.699 | −2.344 | −1.680 | 0.013 | | | | | | | |
| | 308.15 | −2.505 | −0.740 | −2.150 | −2.317 | 0.088 | | | | | | | |
| Methyl Acetoacetate (1) + 1-Pentanol (2) | | | | | | | | | | | | | |
| $V^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 2.116 | 0.299 | 0.196 | 1.326 | 0.027 | $10^{11}\Delta k_s/\mathrm{Pa^{-1}}$ | 298.15 | 1.487 | 3.812 | −0.488 | 2.600 | 0.131 |
| | 303.15 | 2.244 | 0.253 | −0.293 | 1.278 | 0.014 | | 303.15 | 2.212 | 5.501 | −0.398 | −0.191 | 0.148 |
| | 308.15 | 2.402 | 0.185 | 0.145 | 1.279 | 0.008 | | 308.15 | 2.516 | 4.494 | 2.037 | 0.436 | 0.183 |
| $\Delta\eta/(\mathrm{mPa\cdot s})$ | 298.15 | −3.557 | −1.439 | −2.201 | −1.417 | 0.012 | $R^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 0.092 | −0.131 | 0.686 | 0.121 | 0.014 |
| | 303.15 | −3.030 | −1.199 | −1.773 | −1.038 | 0.010 | | | | | | | |
| | 308.15 | −2.548 | −0.987 | −1.316 | −0.608 | 0.006 | | | | | | | |
| Methyl Acetoacetate (1) + 1-Hexanol (2) | | | | | | | | | | | | | |
| $V^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 2.595 | 0.256 | −0.254 | 1.291 | 0.014 | $10^{11}\Delta k_s/\mathrm{Pa^{-1}}$ | 298.15 | 5.002 | 3.334 | −2.363 | 1.067 | 0.164 |
| | 303.15 | 2.781 | 0.037 | 0.057 | 0.980 | 0.026 | | 303.15 | 4.776 | 4.445 | −0.245 | −1.003 | 0.111 |
| | 308.15 | 2.897 | 0.072 | 0.175 | 1.211 | 0.012 | | 308.15 | 5.722 | 4.241 | 0.682 | −0.620 | 0.167 |
| $\Delta\eta/(\mathrm{mPa\cdot s})$ | 298.15 | −4.664 | −2.096 | −2.820 | −1.755 | 0.012 | $R^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | −1.033 | 0.012 | 0.072 | 0.578 | 0.006 |
| | 303.15 | −3.895 | −1.700 | −2.184 | −1.196 | 0.009 | | | | | | | |
| | 308.15 | −3.235 | −1.379 | −1.607 | −0.642 | 0.006 | | | | | | | |
| Methyl Acetoacetate (1) + 1-Heptanol (2) | | | | | | | | | | | | | |
| $V^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 3.031 | −0.025 | 0.376 | 1.403 | 0.022 | $10^{11}\Delta k_s/\mathrm{Pa^{-1}}$ | 298.15 | 6.990 | 4.803 | −1.921 | 6.510 | 0.091 |
| | 303.15 | 3.161 | 0.137 | −0.351 | 0.914 | 0.018 | | 303.15 | 7.271 | 1.245 | 8.409 | −1.567 | 0.135 |
| | 308.15 | 3.333 | −0.033 | 0.489 | 1.320 | 0.015 | | 308.15 | 7.648 | 5.434 | −0.427 | 2.422 | 0.174 |
| $\Delta\eta/(\mathrm{mPa\cdot s})$ | 298.15 | −6.278 | −3.489 | −4.324 | −2.277 | 0.022 | $R^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | −2.095 | −0.260 | 0.270 | 0.277 | 0.013 |
| | 303.15 | −5.196 | −2.787 | −3.286 | −1.641 | 0.021 | | | | | | | |
| | 308.15 | −4.266 | −2.309 | −2.466 | −0.923 | 0.017 | | | | | | | |
| Methyl Acetoacetate (1) + 2-Octanol (2) | | | | | | | | | | | | | |
| $V^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | 3.798 | 0.324 | −1.240 | 0.823 | 0.022 | $10^{11}\Delta k_s/\mathrm{Pa^{-1}}$ | 298.15 | 5.649 | 4.626 | −3.424 | 2.922 | 0.160 |
| | 303.15 | 4.021 | 0.245 | −0.482 | 1.251 | 0.018 | | 303.15 | 6.661 | 5.829 | −0.343 | 0.523 | 0.041 |
| | 308.15 | 4.093 | 0.022 | 0.275 | 1.181 | 0.014 | | 308.15 | 6.041 | 4.952 | −3.246 | −5.278 | 0.117 |
| $\Delta\eta/(\mathrm{mPa\cdot s})$ | 298.15 | −6.485 | −3.709 | −4.283 | −1.973 | 0.023 | $R^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}})$ | 298.15 | −3.393 | −0.320 | −0.167 | 0.367 | 0.008 |
| | 303.15 | −5.083 | −2.765 | −3.052 | −1.235 | 0.018 | | | | | | | |
| | 308.15 | −3.990 | −2.122 | −2.157 | −0.601 | 0.017 | | | | | | | |

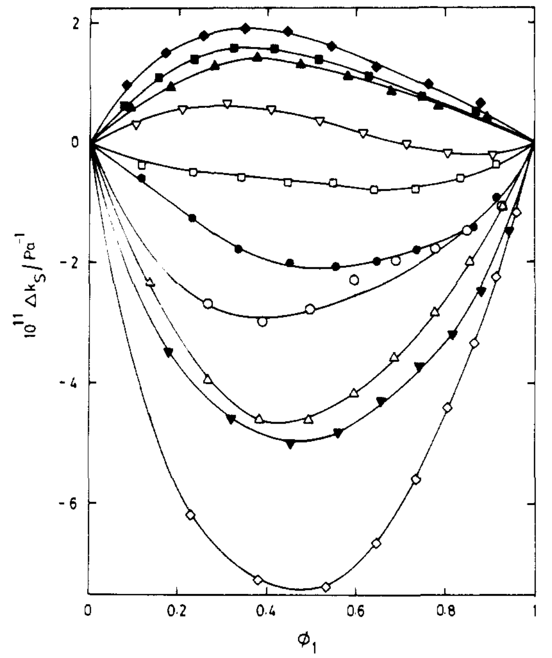

**Figure 3.** Variation of the deviation in isentropic compressibility with volume fraction at 298.15 K. Symbols have the same meaning as in Figure 1.

values of the branched-chain alcohols are smaller than those of their straight-chain homologues. Such effects have also been observed earlier by Karunakar et al. (*34*) for mixtures of benzonitrile with aliphatic alcohols and also by others (*35*). It has been reported that $\Delta k_S$ becomes increasingly negative as the strength of the interaction increases (*36*). The maximum negative $\Delta k_S$ as obtained in the case of the MAA + methyl alcohol mixture supports this conjecture. With higher alcohols, however, $\Delta k_S$ becomes less negative. This suggests somewhat less of an interaction of MAA with such alcohols.

Isentropic compressibilities of mixtures of 1-chlorobutane with normal and branched alcohols have also been reported by Chandramouli et al. (*37, 38*). The positive $\Delta k_S$ has been explained in terms of (i) dissociation of self-associated alcohols and chlorobutane and (ii) interstitial accommodation of chloroalkane molecules in the aggregates of alcohols and weak hydrogen bond interactions between unlike molecules. The former effect contributes to the positive deviations in $\Delta k_S$, while the latter effect contributes to the negative deviation in $\Delta k_S$. However, the actual value of the deviation depends upon the relative strengths of the two opposing effects. The positive $\Delta k_S$ suggests that the first effect is stronger than the second. On the whole, the strength of bonding is expected to decrease with an increase in the chain length of alcohols, and the present results of $V^E$, $\Delta\eta$, and $\Delta k_S$ corroborate this fact.

Systematic variations of excess quantities with the chain length of alcohols prompted us to develop empirical relations for $V^E$, $\Delta\eta$, and $\Delta k_S$ data at equimolar compositions to give the following relation:

$$V^E(x_1 \simeq 0.5) = 1.625 - \frac{9.283}{C_n + 2} + \frac{11.143}{(C_n + 2)^2} - \frac{4.408}{(C_n + 2)^3} \qquad (5)$$

with $\sigma = 0.019\ \mathrm{cm^3 \cdot mol^{-1}}$. Here, $C_n$ represents the number of carbon atoms of straight-chain alcohols. The branched alcohols are not considered here. For 1-heptanol with $C_n = 7$, eq 5 gives $V^E = 0.7254\ \mathrm{cm^3 \cdot mol^{-1}}$ at $x_1 \simeq 0.5$, while the observed $V^E$ is $0.7238\ \mathrm{cm^3 \cdot mol^{-1}}$. Similarly, for $\Delta\eta$ and $\Delta k_S$, we get

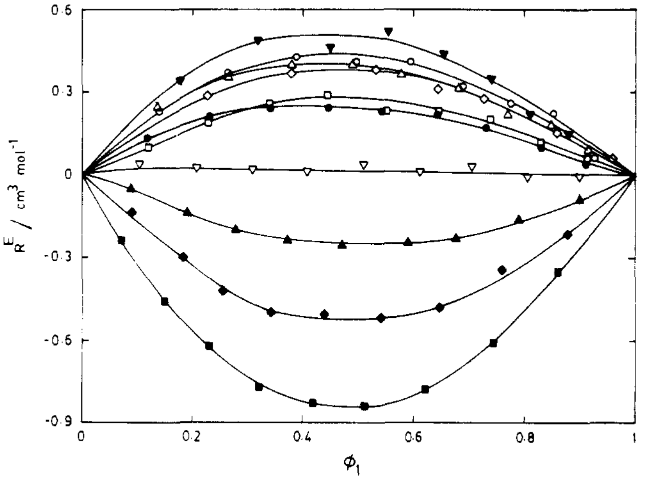

**Figure 4.** Dependence of the deviation in molar refraction $R^E$ on volume fraction at 298.15 K. Symbols have the same meaning as in Figure 1.

$$\Delta\eta(x_1 \simeq 0.5) = -6.036 - \frac{63.074}{C_n + 2} - \frac{238.165}{(C_n + 2)^2} + \frac{303.543}{(C_n + 2)^3} \qquad (6)$$

$$10^{11}\Delta k_S(\phi_1 \simeq 0.5) = 2.175 - \frac{41.345}{C_n + 2} - \frac{498.802}{(C_n + 2)^2} + \frac{848.285}{(C_n + 2)^3} \qquad (7)$$

These relations are applicable only at 298.15 K. The average standard errors in the calculations of $\Delta\eta$ and $\Delta k_S$ from eqs 6 and 7 are, respectively, 0.08 mPa·s and $0.267 \times 10^{-11}\ \mathrm{Pa^{-1}}$.

Increased interest in the optical properties of liquids and liquid mixtures prompted us to calculate the excess molar refractions $R^E$ from the Lorentz–Lorenz mixing rule (*39*) as

$$R^E = R_m - R_1\phi_1 - R_2\phi_2 \qquad (8)$$

where $R_m$ is the molar refraction of the binary mixture calculated from the Lorentz–Lorenz relation. The quantities $R_1$ and $R_2$ refer to molar refractions of pure components. The results of $R^E$ are shown in Figure 4. The $R^E$ values for MAA + 1-pentanol system are very close to zero, while for mixtures of MAA with 1-hexanol, 1-heptanol, and 2-octanol these increase in the negative direction. However, for the remaining mixtures, $R^E$ values are positive and show a very systematic behavior throughout the composition of the mixture.

Each set of derived quantities $Y^E$ (= $V^E$, $\Delta\eta$, $\Delta k_S$, and $R^E$) have been fitted to the Redlich–Kister (*10*) polynomial relation

$$Y^E = c_1 c_2 \sum_{i=0}^{3} a_i (c_2 - c_1)^i \qquad (9)$$

to estimate the regression coefficients $a_i$ and standard errors $\sigma$. The $\Delta k_S$ and $R^E$ results are fitted by using the volume fraction differences while those of $V^E$ and $\Delta\eta$ are fitted by mole fraction differences as given in eq 9. These values are summarized in Table III. A third-order fit in almost all cases reproduced insignificant differences between the calculated and observed excess quantities. The back-calculated values of $V^E$, $\Delta\eta$, $\Delta k_S$, and $R^E$ are used as guidelines to draw the smooth curves given in Figures 1–4. Different symbols in all these figures represent the observed points.

## Literature Cited

(1) Joshi, S. S.; Aminabhavi, T. M.; Shukla, S. S. *Can. J. Chem.* **1990**, *68*, 251.
(2) Joshi, S. S.; Aminabhavi, T. M.; Shukla, S. S. *J. Chem. Eng. Data* **1990**, *35*, 247.

(3) Joshi, S. S.; Aminabhavi, T. M.; Shukla, S. S. *J. Chem. Eng. Data* **1990**, *35*, 187.
(4) Joshi, S. S.; Aminabhavi, T. M. *Fluid Phase Equilib.* **1990**, *60*, 319.
(5) Aminabhavi, V. A.; Aminabhavi, T. M.; Balundgi, R. H. *Ind. Eng. Chem. Res.* **1990**, *29*, 2106.
(6) Aminabhavi, T. M.; Joshi, S. S.; Balundgi, R. H.; Shukla, S. S. *Can. J. Chem.* **1991**, *69*, 1028.
(7) Aralaguppi, M. I.; Aminabhavi, T. M.; Balundgi, R. H.; Joshi, S. S. *J. Phys. Chem.* **1991**, *95*, 5299.
(8) Chatwal, G. R. *Reaction Mechanism and Reagents in Organic Chemistry*; Himalaya Publishing House: Bombay, 1987.
(9) Franks, F.; Desnoyers, J. E. In *Water Sciences Reviews*; Franks, F., Ed.; Cambridge University Press: Cambridge 1985; Vol. 1, p 171.
(10) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 435.
(11) Vogel, A. I. In *Text Book of Practical Organic Chemistry*, 5th ed.; Furniss, B. S., Hannaford, A. J., Smith, P. W. G., Tatchel, A. R., Eds.; John Wiley and Sons: New York, 1989 (revised).
(12) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. Organic Solvents. *Techniques of Chemistry*; Wiley: New York, 1986; Vol. II.
(13) *C.R.C. Handbook of Chemistry and Physics*; Weast, R. C., Ed.; CRC Press: Cleveland 1974.
(14) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 97.
(15) Nath, J.; Dixit, A. P. *J. Chem. Eng. Data* **1984**, *29*, 320.
(16) Nath, J.; Tripathi, A. D. *J. Chem. Eng. Data* **1983**, *28*, 263.
(17) Wilson, J. N. *Chem. Rev.* **1939**, *25*, 377.
(18) Mecke, R. *Discuss. Faraday Soc.* **1950**, *9*, 161.
(19) Alonso, R.; Corrales, J. A. *J. Chem. Thermodyn.* **1989**, *21*, 515.
(20) Rao, M. V. P.; Naidu, P. R. *Can. J. Chem.* **1974**, *52*, 788.
(21) Choudary, N. V.; Krishnaiah, A.; Naidu, P. R. *J. Chem. Eng. Data* **1982**, *27*, 412.
(22) Naorem, H.; Suri, S. K. *J. Chem. Eng. Data* **1989**, *34*, 395.
(23) Karunakar, J.; Reddy, K. D.; Rao, M. V. P. *J. Chem. Eng. Data* **1982**, *27*, 346.
(24) Mouli, J. C.; Naidu, P. R.; Choudary, N. V. *J. Chem. Eng. Data* **1986**, *31*, 493.
(25) Vijayalakshmi, T. S.; Naidu, P. R. *J. Chem. Eng. Data* **1989**, *34*, 413.
(26) Ramkumar, D. H. S.; Kudchadkar, A. P. *J. Chem. Eng. Data* **1989**, *34*, 459.
(27) Paez, S.; Contreras, M. *J. Chem. Eng. Data* **1989**, *34*, 455.
(28) Heintz, A. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 172.
(29) Grunberg, L.; Nissan, A. H. *Trans. Faraday Soc.* **1949**, *45*, 125.
(30) Garcia, B.; Herrera, C.; Leal, J. M. *J. Chem. Eng. Data* **1991**, *36*, 269.
(31) Pikkarainen, L. *J. Chem. Eng. Data* **1983**, *28*, 344.
(32) Kumar, A.; Prakash, O.; Prakash, S. *J. Chem. Eng. Data* **1981**, *26*, 64.
(33) Oswal, S. *Can. J. Chem.* **1988**, *66*, 111.
(34) Karunakar, J.; Reddy, K. D.; Rao, M. V. P. *J. Chem. Eng. Data* **1982**, *27*, 348.
(35) Kumar, A.; Prakash, O.; Prakash, S. *J. Chem. Eng. Data* **1981**, *26*, 64.
(36) Fort, R. J.; Moore, W. R. *Trans. Faraday Soc.* **1965**, *61*, 2102.
(37) Chandramouli, J.; Choudary, N. V.; Krishnaiah, A.; Naidu, P. R. *Fluid Phase Equilib.* **1982**, *8*, 72.
(38) Chandramouli, J.; Choudary, N. V.; Naidu, P. R. *Indian J. Pure Appl. Phys.* **1982**, *20*, 755.
(39) Lorentz, H. A. *Theory of Electrons*; Teubner: Leipzig, 1909.
(40) Eduljee, G. H.; Boyes, A. P. *J. Chem. Eng. Data* **1980**, *25*, 249.
(41) Rauf, M. A.; Stewart, G. H.; Farhataziz. *J. Chem. Eng. Data* **1983**, *28*, 324.
(42) Uosaki, Y.; Hamaguchi, T.; Moriyoshi, T. *J. Chem. Thermodyn.* **1992**, *24*, 549.
(43) Dewan, R. K.; Mehta, S. K.; Parashar, R.; Bala, K. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1561.
(44) Sarmiento, F.; Paz Andrade, M. I.; Fernandez, J.; Bravo, R.; Pintos, M. *J. Chem. Eng. Data* **1985**, *30*, 321.

Received for review January 15, 1992. Revised August 11, 1992. Accepted September 11, 1992. The authors are thankful to the University Grants Commission, New Delhi, for financial support (F.12-55/88-SR-III) of this study.