# Studies on Thermodynamic and Transport Properties of Binary Mixtures of Acetonitrile with Some Cyclic Ethers at Different Temperatures by Volumetric, Viscometric, and Interferometric Techniques

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Densities and viscosities of the binary mixtures of acetronitrile with tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane were measured over the entire range of composition at (298.15, 308.15, and 318.15) K. Ultrasonic speeds of these binary mixtures have also been measured at 298.15 K. From the experimental data, values of excess molar volumes ($V^E$), viscosity deviations ($\Delta\eta$), and deviations in isentropic compressibility ($\Delta K_s$) have been calculated. These results were fitted to Redlich−Kister polynomial equation. The density and viscosity data were analyzed by some semiempirical viscosity models, and the results have been discussed in terms of molecular interactions and structural effects. The excess properties were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures. To explore the nature of the interactions, various thermodynamic parameters (e.g., intermolecular free length, specific acoustic impedance, etc.) have also been derived from the density and ultrasonic speed data.

## Introduction

The mixing of different solvents gives rise to solutions that generally do not behave ideally. This deviation from ideality is expressed by many thermodynamic variables, particularly by excess properties. Excess thermodynamic properties of solvent mixtures correspond to the difference between the actual property and the property if the system behaves ideally and, thus, are useful in the study of molecular interactions and arrangements. In particular, they reflect the interactions that take place between solute−solute, solute−solvent, and solvent−solvent species.[1]

This work is a part of our program to provide data for the characterization of the molecular interactions between solvents in binary systems.[2,3] Acetronitrile is a dipolar aprotic solvent lacking strong specific intermolecular forces, where dipole−dipole forces predominate,[4,5] and tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane are cyclic ethers differing in the number and position of oxygen atom and methylene group.[6,7] Tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane are versatile solvents used in the separation of saturated and unsaturated hydrocarbons, in pharmaceutical synthesis, and serve as solvents for many polymers. Acetonitrile has important technological applications, namely, in battery industry and plating techniques.[8,9]

In the present paper, we report densities, viscosities, and ultrasonic speeds for the binary systems of acetonitrile + tetrahydrofuran, acetronitrile +1,3-dioxolane, and acetronitrile +1,4-dioxane at the temperatures of (298.15, 308.15, and 318.15) K and atmospheric pressure over the entire composition range. The experimental data are used to calculate excess molar volumes ($V^E$), deviations in viscosity ($\Delta\eta$), and deviations in isentropic compressibility ($\Delta K_s$) of the mixtures. Various thermodynamic parameters (e.g., intermolecular free length, specific acoustic impedance, etc.) and their deviations have also been derived from the density and ultrasonic speed data. These results are useful for the interpretation of the nature of interactions that occur between acetonitrile and the cyclic ethers. The work also provides a test of various empirical equations to correlate viscosity and acoustic data of binary mixtures in terms of pure component properties.

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## Experimental Section

***Materials.*** Acetonitrile (Merck, India) was distilled from $P_2O_5$ and then from $CaH_2$ in an all-glass distillation apparatus.[10] The middle fraction was collected. 1,4-Dioxane (Merck, India) was kept several days over potassium hydroxide (KOH), refluxed for 24 h, and distilled over lithium aluminum hydride ($LiAlH_4$) as described earlier.[2] 1,3-Dioxolane (LR) was purified by standard methods. It was refluxed with $PbO_2$ and then fractionally distilled after addition of xylene.[12] Tetrahydrofuran (Merck, India) was kept several days over potassium hydroxide (KOH), refluxed for 24 h, and distilled over $LiAlH_4$ as described earlier.[11] The purity of the solvents was ascertained by GLC and also by comparing experimental values of densities and viscosities with available literature as listed in Table 1.

***Apparatus and Procedure.*** The densities were measured with an Ostwald−Sprengel type pycnometer having a bulb volume of 25 $cm^3$ and an internal diameter of the capillary of about 0.1 cm, calibrated at (298.15, 308.15, and 318.15) K with doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a thermostatic water bath maintained at ± 0.01 K of the desired temperature, removed from the bath, properly dried, and weighed in an electronic balance. The evaporation losses remained insignificant during the time of actual measurements. Averages of triplicate measurements were taken into account.

The mixtures were prepared by mixing known volume of pure liquids in air-tight stoppered bottles. The reproducibility in mole fraction was within ± 0.0002. The mass measurements, accurate to ± 0.01 mg, were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The total uncertainty of density is $\pm 3 \times 10^{-4}$ g·$cm^{-3}$, and that of temperature is ± 0.01 K.

The viscosity was measured by means of a suspended Ubbelohde type viscometer, which was calibrated at 298.15 K with triple-distilled water and purified methanol using density and viscosity values from the literature. The flow times were accurate to ± 0.1 s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was with-

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**Table 1. Comparison of Density $\rho$, Viscosity $\eta$, and Sound Speeds $u$ with Literature Data at the Experimental Temperatures**

| | $T$ | $\rho \times 10^{-3}$/(kg·m$^{-3}$) | | $\eta$/(mPa·s) | | $u$/(m·s$^{-1}$) | |
|---|---|---|---|---|---|---|---|
| pure solvent | K | expt | lit. | expt | lit. | expt | lit. |
| acetonitrile | 298.15 | 0.7768 | 0.77686[10] | 0.3443 | 0.3446[10] | 1713.2 | |
| | 308.15 | 0.7654 | 0.76564[10] | 0.3124 | 0.3125[10] | | |
| | 318.15 | 0.7547 | 0.75498[10] | 0.2891 | 0.2893[10] | | |
| tetrahydrofuran | 298.15 | 0.8808 | 0.8807[33] | 0.4631 | 0.4630[33] | 1292.2 | 1294[34] |
| | 308.15 | 0.8715 | 0.8712[33] | 0.4276 | 0.4277[33] | | |
| | 318.15 | 0.8608 | 0.8614[33] | 0.3903 | 0.3902[33] | | |
| 1,4-dioxane | 298.15 | 1.0287 | 1.0282[34] | 1.1779 | 1.178[34] | 1344.4 | 1358[34] |
| | 308.15 | 1.0168 | 1.0168[34] | 0.9985 | 0.999[34] | | |
| | 318.15 | 1.0047 | 1.00526[37] | 0.8909 | 0.901[38] | | |
| 1,3 dioxolane | 298.15 | 1.0577 | 1.05862[35] | 0.5878 | 0.5886[35] | 1338.2 | 1338.8[36] |
| | 308.15 | 1.0463 | 1.04620[37] | 0.5128 | | | |
| | 318.15 | 1.0344 | 1.03364[37] | 0.4580 | | | |

**Table 2. Values of Density $\rho$, Viscosity $\eta$, Excess Molar Volume $V^E$, Viscosity Deviation $\Delta\eta$, and Grunberg−Nissan, Tamura−Kurata, and Hind Interaction Parameters $d_{12}$, $T_{12}$, and $H_{12}$ for Binary Mixtures**

| $x_1$ | $\rho \times 10^{-3}$ kg·m$^{-3}$ | $\eta$ mPa·s | $V^E \times 10^6$ m$^3$·mol$^{-1}$ | $\Delta\eta$ mPa·s | $d_{12}$ | $T_{12}$ | $H_{12}$ | $x_1$ | $\rho \times 10^{-3}$ kg·m$^{-3}$ | $\eta$ mPa·s | $V^E \times 10^6$ m$^3$·mol$^{-1}$ | $\Delta\eta$ mPa·s | $d_{12}$ | $T_{12}$ | $H_{12}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Acetonitrile + Tetrahydrofuran | | | | | | | | | | | | | | | |
| 298.15 K | | | | | | | | | | | | | | | |
| 0 | 0.8808 | 0.4631 | 0 | 0 | 0 | 0 | 0 | 0.7249 | 0.8162 | 0.3701 | −0.062 | −0.007 | −0.047 | 0.384 | 0.387 |
| 0.1633 | 0.8703 | 0.4419 | −0.104 | −0.002 | 0.011 | 0.393 | 0.397 | 0.8039 | 0.8058 | 0.3611 | −0.037 | −0.007 | −0.067 | 0.382 | 0.383 |
| 0.3052 | 0.8595 | 0.4236 | −0.142 | −0.003 | 0.006 | 0.392 | 0.396 | 0.8754 | 0.7959 | 0.3539 | −0.020 | −0.005 | −0.087 | 0.380 | 0.380 |
| 0.4295 | 0.8486 | 0.4075 | −0.145 | −0.005 | −0.002 | 0.390 | 0.394 | 0.9405 | 0.7862 | 0.3481 | −0.007 | −0.003 | −0.119 | 0.376 | 0.375 |
| 0.5394 | 0.8376 | 0.3932 | −0.124 | −0.006 | −0.015 | 0.389 | 0.392 | 1 | 0.7768 | 0.3443 | 0 | 0 | 0 | 0 | 0 |
| 0.6372 | 0.8268 | 0.3808 | −0.093 | −0.007 | −0.029 | 0.387 | 0.389 | | | | | | | | |
| 308.15 K | | | | | | | | | | | | | | | |
| 0 | 0.8715 | 0.4276 | 0 | 0 | 0 | 0 | 0 | 0.7249 | 0.8057 | 0.3321 | −0.082 | −0.012 | −0.126 | 0.338 | 0.339 |
| 0.1633 | 0.8604 | 0.4066 | −0.070 | −0.002 | 0.006 | 0.357 | 0.361 | 0.8039 | 0.7953 | 0.3242 | −0.066 | −0.011 | −0.155 | 0.336 | 0.336 |
| 0.3052 | 0.8492 | 0.3875 | −0.099 | −0.005 | −0.013 | 0.353 | 0.358 | 0.8754 | 0.7852 | 0.3184 | −0.049 | −0.008 | −0.184 | 0.333 | 0.332 |
| 0.4295 | 0.8380 | 0.3701 | −0.110 | −0.008 | −0.039 | 0.349 | 0.354 | 0.9405 | 0.7752 | 0.3145 | −0.028 | −0.005 | −0.214 | 0.331 | 0.328 |
| 0.5394 | 0.8270 | 0.3550 | −0.106 | −0.012 | −0.067 | 0.345 | 0.349 | 1 | 0.7654 | 0.3124 | 0 | 0 | 0 | 0 | 0 |
| 0.6372 | 0.8162 | 0.3425 | −0.096 | −0.012 | −0.095 | 0.342 | 0.345 | | | | | | | | |
| 318.15 K | | | | | | | | | | | | | | | |
| 0 | 0.8608 | 0.3903 | 0 | 0 | 0 | 0 | 0 | 0.7249 | 0.7963 | 0.3001 | −0.196 | −0.017 | −0.349 | 0.298 | 0.298 |
| 0.1633 | 0.8510 | 0.3683 | −0.201 | −0.005 | −0.106 | 0.313 | 0.319 | 0.8039 | 0.7855 | 0.2938 | −0.141 | −0.015 | −0.443 | 0.294 | 0.292 |
| 0.3052 | 0.8405 | 0.3497 | −0.290 | −0.010 | −0.135 | 0.311 | 0.317 | 0.8754 | 0.7750 | 0.2901 | −0.094 | −0.012 | −0.581 | 0.291 | 0.287 |
| 0.4295 | 0.8296 | 0.3340 | −0.311 | −0.013 | −0.169 | 0.309 | 0.313 | 0.9405 | 0.7647 | 0.2879 | −0.045 | −0.007 | −0.960 | 0.284 | 0.276 |
| 0.5394 | 0.8184 | 0.3202 | −0.288 | −0.016 | −0.218 | 0.305 | 0.308 | 1 | 0.7547 | 0.2890 | 0 | 0 | 0 | 0 | 0 |
| 0.6372 | 0.8073 | 0.3089 | −0.245 | −0.017 | −0.277 | 0.301 | 0.303 | | | | | | | | |
| Acetonitrile + 1,3-Dioxolane | | | | | | | | | | | | | | | |
| 298.15 K | | | | | | | | | | | | | | | |
| 0 | 1.0577 | 0.5878 | 0 | 0 | 0 | 0 | 0 | 0.7302 | 0.8721 | 0.3591 | −0.197 | −0.051 | −0.519 | 0.330 | 0.337 |
| 0.1670 | 1.0227 | 0.5233 | −0.124 | −0.024 | −0.193 | 0.355 | 0.380 | 0.8081 | 0.8465 | 0.3444 | −0.160 | −0.047 | −0.660 | 0.314 | 0.315 |
| 0.3109 | 0.9899 | 0.4737 | −0.233 | −0.038 | −0.231 | 0.355 | 0.376 | 0.8783 | 0.8221 | 0.3380 | −0.111 | −0.036 | −0.782 | 0.301 | 0.298 |
| 0.4361 | 0.9585 | 0.4360 | −0.277 | −0.046 | −0.266 | 0.355 | 0.373 | 0.9420 | 0.7989 | 0.3366 | −0.062 | −0.022 | −0.982 | 0.277 | 0.266 |
| 0.5461 | 0.9282 | 0.4046 | −0.268 | −0.0502 | −0.328 | 0.350 | 0.364 | 1 | 0.7768 | 0.3443 | 0 | 0 | 0 | 0 | 0 |
| 0.6435 | 0.8994 | 0.3783 | −0.239 | −0.053 | −0.421 | 0.340 | 0.351 | | | | | | | | |
| 308.15 K | | | | | | | | | | | | | | | |
| 0 | 1.0463 | 0.5128 | 0 | 0 | 0 | 0 | 0 | 0.7302 | 0.8619 | 0.3251 | −0.297 | −0.041 | −0.477 | 0.302 | 0.307 |
| 0.1670 | 1.0116 | 0.4618 | −0.160 | −0.018 | −0.158 | 0.330 | 0.349 | 0.8081 | 0.8361 | 0.3134 | −0.248 | −0.038 | −0.593 | 0.290 | 0.292 |
| 0.3109 | 0.9792 | 0.4235 | −0.295 | −0.027 | −0.174 | 0.333 | 0.349 | 0.8783 | 0.8116 | 0.3077 | −0.190 | −0.029 | −0.706 | 0.279 | 0.277 |
| 0.4361 | 0.9478 | 0.3913 | −0.352 | −0.034 | −0.221 | 0.329 | 0.343 | 0.9420 | 0.7882 | 0.3070 | −0.114 | −0.017 | −0.845 | 0.264 | 0.257 |
| 0.5461 | 0.9177 | 0.3646 | −0.357 | −0.034 | −0.284 | 0.323 | 0.334 | 1 | 0.7654 | 0.3124 | 0 | 0 | 0 | 0 | 0 |
| 0.6435 | 0.8890 | 0.3419 | −0.334 | −0.042 | −0.377 | 0.312 | 0.321 | | | | | | | | |
| 318.15 K | | | | | | | | | | | | | | | |
| 0 | 1.0344 | 0.4580 | 0 | 0 | 0 | 0 | 0 | 0.7302 | 0.8511 | 0.2910 | −0.342 | −0.044 | −0.597 | 0.260 | 0.262 |
| 0.1670 | 1.0003 | 0.4132 | −0.202 | −0.017 | −0.188 | 0.297 | 0.313 | 0.8081 | 0.8255 | 0.2817 | −0.290 | −0.040 | −0.737 | 0.246 | 0.245 |
| 0.3109 | 0.9679 | 0.3791 | −0.336 | −0.026 | −0.215 | 0.298 | 0.311 | 0.8783 | 0.8009 | 0.2780 | −0.219 | −0.032 | −0.890 | 0.231 | 0.225 |
| 0.4361 | 0.9366 | 0.3502 | −0.390 | −0.034 | −0.275 | 0.292 | 0.304 | 0.9420 | 0.7775 | 0.2797 | −0.128 | −0.019 | −1.093 | 0.210 | 0.198 |
| 0.5461 | 0.9065 | 0.3263 | −0.392 | −0.039 | −0.354 | 0.284 | 0.293 | 1 | 0.7547 | 0.2891 | 0 | 0 | 0 | 0 | 0 |
| 0.6435 | 0.8780 | 0.3065 | −0.369 | −0.043 | −0.460 | 0.274 | 0.280 | | | | | | | | |
| Acetonitrile + 1,4-Dioxane | | | | | | | | | | | | | | | |
| 298.15 K | | | | | | | | | | | | | | | |
| 0 | 1.0287 | 1.1780 | 0 | 0 | 0 | 0 | 0 | 0.7630 | 0.8645 | 0.4099 | −0.237 | −0.132 | −0.648 | 0.396 | 0.353 |
| 0.1926 | 0.9976 | 0.9468 | −0.100 | −0.071 | 0.119 | 0.534 | 0.414 | 0.8336 | 0.8412 | 0.3679 | −0.191 | −0.115 | −0.998 | 0.346 | 0.322 |
| 0.3492 | 0.9686 | 0.7720 | −0.193 | −0.115 | 0.031 | 0.509 | 0.403 | 0.8957 | 0.8185 | 0.3482 | −0.115 | −0.083 | −1.253 | 0.316 | 0.310 |
| 0.4791 | 0.9410 | 0.6349 | −0.258 | −0.144 | −0.115 | 0.473 | 0.383 | 0.9508 | 0.7972 | 0.3389 | −0.057 | −0.046 | −1.632 | 0.265 | 0.280 |
| 0.5886 | 0.9146 | 0.5315 | −0.289 | −0.156 | −0.297 | 0.440 | 0.365 | 1 | 0.7768 | 0.3443 | 0 | 0 | 0 | 0 | 0 |
| 0.6822 | 0.8891 | 0.4573 | −0.275 | −0.152 | −0.494 | 0.411 | 0.352 | | | | | | | | |
| 308.15 K | | | | | | | | | | | | | | | |
| 0 | 1.0168 | 0.9985 | 0 | 0 | 0 | 0 | 0 | 0.7630 | 0.8430 | 0.4079 | −0.301 | −0.067 | −0.048 | 0.424 | 0.469 |
| 0.1926 | 0.9812 | 0.8244 | −0.194 | −0.042 | 0.207 | 0.432 | 0.520 | 0.8336 | 0.8212 | 0.3775 | −0.229 | −0.049 | −0.029 | 0.438 | 0.478 |
| 0.3492 | 0.9484 | 0.6862 | −0.288 | −0.073 | 0.135 | 0.415 | 0.495 | 0.8957 | 0.8014 | 0.3531 | −0.168 | −0.031 | 0.014 | 0.453 | 0.490 |
| 0.4791 | 0.9187 | 0.5802 | −0.342 | −0.090 | 0.055 | 0.405 | 0.475 | 0.9508 | 0.7828 | 0.3340 | −0.090 | −0.012 | 0.207 | 0.486 | 0.525 |
| 0.5886 | 0.8914 | 0.5030 | −0.357 | −0.092 | −0.007 | 0.405 | 0.466 | 1 | 0.7654 | 0.3124 | 0 | 0 | 0 | 0 | 0 |
| 0.6822 | 0.8661 | 0.4477 | −0.331 | −0.083 | −0.044 | 0.412 | 0.464 | | | | | | | | |
| 318.15 K | | | | | | | | | | | | | | | |
| 0 | 1.0047 | 0.8909 | 0 | 0 | | 0 | 0 | 0.7630 | 0.8430 | 0.3542 | −0.364 | −0.078 | −0.352 | 0.341 | 0.375 |
| 0.1926 | 0.9755 | 0.7189 | −0.254 | −0.056 | 0.015 | 0.322 | 0.409 | 0.8336 | 0.8193 | 0.3354 | −0.276 | −0.054 | −0.279 | 0.366 | 0.395 |
| 0.3492 | 0.9468 | 0.5994 | −0.364 | −0.081 | −0.014 | 0.337 | 0.411 | 0.8957 | 0.7968 | 0.3194 | −0.188 | −0.033 | −0.190 | 0.389 | 0.416 |
| 0.4791 | 0.9194 | 0.5014 | −0.430 | −0.101 | −0.143 | 0.324 | 0.387 | 0.9508 | 0.7752 | 0.3076 | −0.093 | −0.011 | 0.142 | 0.438 | 0.471 |
| 0.5886 | 0.8930 | 0.4305 | −0.450 | −0.106 | −0.268 | 0.318 | 0.370 | 1 | 0.7547 | 0.2891 | 0 | 0 | | 0 | 0 |
| 0.6822 | 0.8675 | 0.3854 | −0.421 | −0.095 | −0.324 | 0.328 | 0.371 | | | | | | | | |

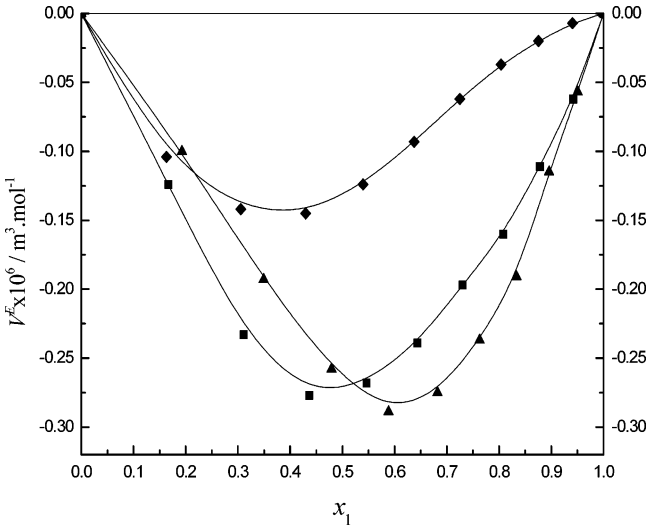


**Figure 1.** Excess molar volumes ($V^E$) for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

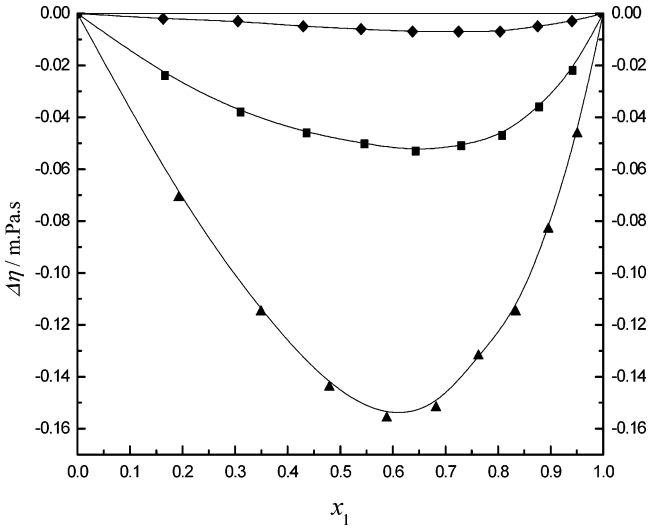


**Figure 2.** Viscosity deviations ($\Delta\eta$) for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

in ± 0.03 % of the reported value. Details of the methods and techniques of density and viscosity measurements have been described earlier.[11,13,14]

Speeds of sound were determined by a multifrequency ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 5 MHz, calibrated with water, methanol, and benzene at 298.15 K. The details of the methods and techniques have been described earlier.[11,13] The uncertainty of ultrasonic speed measurements is ± 0.2 m s$^{-1}$.

## Results and Discussion

The physical properties of the pure liquids along with their literature values are recorded in Table 1. However no literature data for viscosity of 1,3-dioxolane at (308.15 and 318.15) K and sound speed of acetonitrile at 298.15 K were available to us. Table 2 lists the experimental values of densities ($\rho_i$) and viscosities ($\eta_i$) of the binary mixtures along with the corresponding mole fractions of acetronitrile ($x_1$), excess molar volumes ($V^E$), viscosity deviations ($\Delta\eta$), and interaction parameters ($d_{12}$, $T_{12}$, and $H_{12}$) at all the experimental temperatures. The plots of $V^E$ and $\Delta\eta$ against $x_1$ at 298.15 K are represented in Figures 1 and 2, respectively. Because of similarity in nature, the plots at the other two temperatures are not presented here.

The excess molar volumes ($V^E$) were calculated using eq 1:[15,16]

$$V^E = \sum_{i=1}^{j} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right) \quad (1)$$

where $\rho$ is the density of the mixture; $M_i$, $x_i$, and $\rho_i$ are the molecular weight, mole fraction, and density of $i$th component, respectively. The estimated uncertainty for $V^E$ is from (0.001 to 0.014) cm$^3$·mol$^{-1}$.

$\Delta n$ can be computed using eq 2:[16,17]

$$\Delta\eta = \eta - \sum_{i=1}^{j} (x_i \eta_i) \quad (2)$$

where $\eta$ is the absolute viscosity of the mixture; $x_i$ and $\eta_i$ are the mole fraction and viscosity of $i$th component in the mixture, respectively. The estimated uncertainty for $\Delta\eta$ is from (0.001 to 0.003) mPa·s.

It is seen that, the values of $V^E$ and $\Delta\eta$ (see Table 2) for all the experimental binary mixtures are negative over the entire range of composition and temperature. The negative values of

**Table 3. Values of Ultrasonic Speeds $u$, Isentropic Compressibility $K_s$, Deviations in Isentropic Compressibility $\Delta K_s$, Deviations in Intermolecular Free Length ($\Delta L_f$), and Deviations in Specific Acoustic Impedance ($\Delta Z$) for Binary Mixtures at 298.15 K**

| $x_1$ | $u$ / m·s$^{-1}$ | $K_s \times 10^{12}$ / Pa$^{-1}$ | $\Delta K_s \times 10^{12}$ / Pa$^{-1}$ | $\Delta L_f$ / Å | $\Delta Z$ / kg·m$^2$·s$^{-1}$ |
|---|---|---|---|---|---|
| | | Acetonitrile + Tetrahydrofuran | | | |
| 0 | 1292.2 | 679.94 | 0 | 0 | 0 |
| 0.1633 | 1344.3 | 635.81 | −4.72 | −0.0004 | 0.3119 |
| 0.3052 | 1395.2 | 597.70 | −8.16 | −0.0013 | 2.2063 |
| 0.4295 | 1443.9 | 565.25 | −10.64 | −0.0020 | 4.3811 |
| 0.5394 | 1490.4 | 537.47 | −12.11 | −0.0025 | 6.2800 |
| 0.6372 | 1533.8 | 514.14 | −11.73 | −0.0027 | 7.2298 |
| 0.7249 | 1573.6 | 494.81 | −9.96 | −0.0023 | 6.5553 |
| 0.8039 | 1610.3 | 478.56 | −7.36 | −0.0015 | 4.5467 |
| 0.8754 | 1645.5 | 464.04 | −4.62 | −0.0008 | 2.8429 |
| 0.9405 | 1679.0 | 451.20 | −1.75 | −0.0001 | 0.6821 |
| 1 | 1713.2 | 438.59 | 0 | 0 | 0 |
| | | Acetonitrile + 1,3-Dioxolane | | | |
| 0 | 1338.2 | 527.95 | 0 | 0 | 0 |
| 0.1670 | 1388.9 | 506.89 | −6.14 | −0.0006 | 2.7010 |
| 0.3109 | 1436.2 | 489.75 | −10.42 | −0.0013 | 8.2001 |
| 0.4361 | 1481.5 | 475.34 | −13.65 | −0.0024 | 15.5741 |
| 0.5461 | 1524.4 | 463.62 | −15.54 | −0.0039 | 25.0101 |
| 0.6435 | 1563.5 | 454.83 | −15.63 | −0.0048 | 29.1401 |
| 0.7302 | 1597.8 | 449.15 | −13.56 | −0.0045 | 27.6649 |
| 0.8081 | 1628.8 | 445.28 | −10.47 | −0.0037 | 23.1053 |
| 0.8783 | 1658.2 | 442.39 | −7.09 | −0.0026 | 16.1342 |
| 0.9420 | 1686.4 | 440.14 | −3.65 | −0.0015 | 8.6832 |
| 1 | 1713.2 | 438.61 | 0 | 0 | 0 |
| | | Acetonitrile + 1,4-Dioxane | | | |
| 0 | 1344.4 | 537.84 | 0 | 0 | 0 |
| 0.1926 | 1399.3 | 511.94 | −6.79 | −0.0007 | 3.7000 |
| 0.3492 | 1451.0 | 490.37 | −12.82 | −0.0015 | 9.1001 |
| 0.4791 | 1498.4 | 473.32 | −16.98 | −0.0025 | 15.5741 |
| 0.5886 | 1540.2 | 460.91 | −18.52 | −0.0036 | 25.0101 |
| 0.6822 | 1575.7 | 453.00 | −17.15 | −0.0045 | 29.1401 |
| 0.7630 | 1606.5 | 448.20 | −13.93 | −0.0042 | 27.6649 |
| 0.8336 | 1633.5 | 445.52 | −9.60 | −0.0034 | 23.1053 |
| 0.8957 | 1660.1 | 443.32 | −5.64 | −0.0023 | 16.1342 |
| 0.9508 | 1686.3 | 441.13 | −2.36 | −0.0012 | 8.6832 |
| 1 | 1713.2 | 438.61 | 0 | 0 | 0 |

$V^E$ for the three systems are in the following order:

acetronitrile + 1,4-dioxane > acetronitrile + 1,3-dioxolane > acetronitrile + tetrahydrofuran

Negative values of $V^E$ [18] indicate a specific interaction between the mixing components. The chemical or specific interaction between the mixing molecules results in a volume decrease. The negative values of $V^E$ for the binary mixtures of acetonitrile with the ethers may be attributed to the dipole-induced dipole interactions between the mixing components.[19]

The molar volumes of acetonitrile are (52.84, 53.63, and 54) cm$^3$·mol$^{-1}$, and those of tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane are (81.87, 82.74, and 83.77) cm$^3$·mol$^{-1}$; (70.03, 70.80,

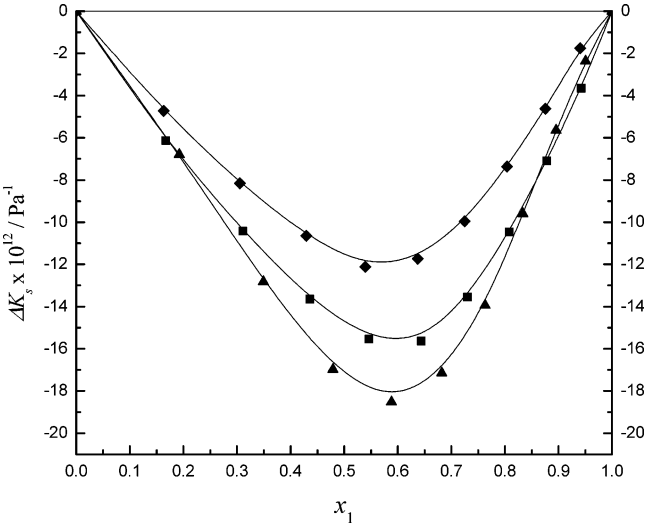


**Figure 3.** Deviations in isentropic compressibility ($\Delta K_s$) for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

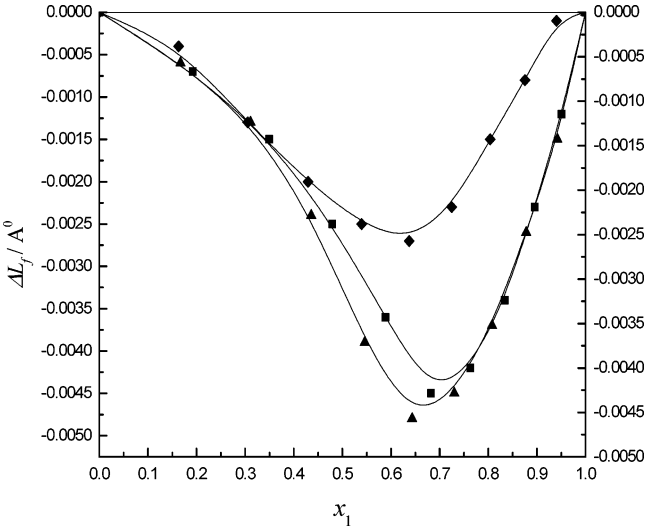


**Figure 4.** Deviations in intermolecular free length ($\Delta L_f$) for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

and 71.62) cm$^3$·mol$^{-1}$; and (85.65, 86.66, and 87.70) cm$^3$·mol$^{-1}$ at (298.15, 308.15, and 318.15) K, respectively. It is clear that the molar volume values of acetonitrile and the other components differ considerably; hence, nonassociated acetonitrile molecules are interstitially accommodated into clusters of ethers yielding a negative contribution to observed $V^E$ values. This implies that the complex-forming interactions are almost absent in the experimental binary systems; therefore, observed $\Delta\eta$ values are also negative.[20]

From close observation of Table 2, it is seen that the negative $V^E$ values are much higher than those of $\Delta\eta$ for all the binary systems under consideration. This clearly supports mere addition of acetonitrile molecules into aggregates of the other components.[20]

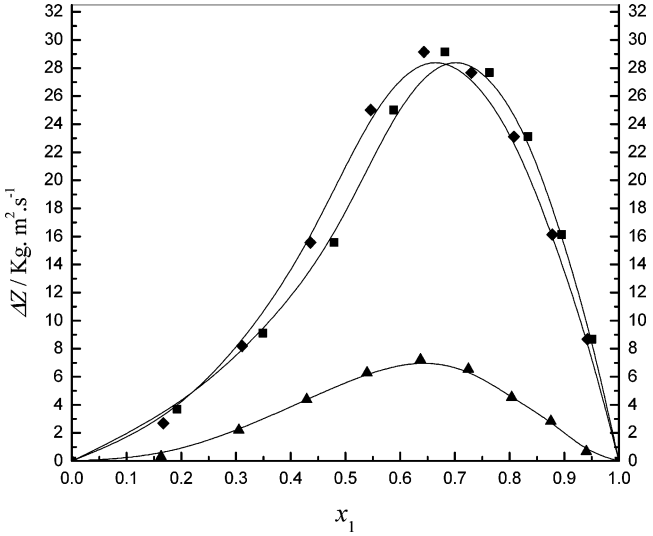


**Figure 5.** Deviations in specific acoustic impedance ($\Delta Z$) for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

Isentropic compressibility ($K_s$) values were calculated from experimental densities $\rho$ and speeds of sound $u$, using

$$K_s = (u^2\rho)^{-1} \tag{3}$$

where $K_s$ gives the isentropic compressibility for the $i$th component of the mixture. We also derived the deviations in isentropic compressibility ($\Delta K_s$), deviations in intermolecular free length ($\Delta L_f$), and deviations in specific acoustic impedance ($\Delta Z$) for the binary mixtures using

$$\Delta K_s = K_s - \sum_{i=1}^{2} x_i K_{s,i} \tag{4}$$

$$\Delta L_f = L_f - \sum_{i=1}^{2} x_i L_{fi} \tag{5}$$

$$\Delta Z = Z - \sum_{i=1}^{2} x_i Z_i \tag{6}$$

where $K_s$, $L_f$, and $Z$ are the isentropic compressibility, intermolecular free length, and specific acoustic impedance of the mixture and $x_i$, $K_{si}$, $L_{fi}$, and $Z_i$ are the mole fraction, isentropic compressibility, intermolecular free length, and specific acoustic impedance of $i$th component in the mixture, respectively. Experimental values of $u$, $K_s$, $\Delta K_s$, $\Delta L_f$, and $\Delta Z$ are listed in Table 3, and the plots of $\Delta K_s$, $\Delta L_f$, and $\Delta Z$ against $x_1$ are shown in Figures 3 to 5.

For the investigated binary mixtures, the deviations in isentropic compressibility are negative. The composition dependence of $\Delta K_s$ for the investigated binary mixtures is shown in Figure 3; it shows that $\Delta K_s$ decrease in the following order:

acetronitrile + 1,4-dioxane > acetonitrile + 1,3-dioxolane > acetonitrile + tetrahydrofuran

These results can be explained in terms of molecular interactions

**Table 4. van der Waals Constant *b*, Molecular Radius *r*, Geometrical Volume *B*, Collision Factor *S*, Molar Speed of Sound *R*, Available Volume $V_a$, Intermolecular Free Length $L_f$, Molar Volume at Absolute Zero $V_0$, Molar Surface Area *Y*, and Specific Acoustic Impedance *Z* of the Pure Components at 298.15 K**

| pure solvent | $b \times 10^5$ / m$^3$ | $r$ / nm | $B \times 10^5$ / m$^3$·mol$^{-1}$ | $S$ | $R \times 10^6$ / m$^3$·mol$^{-1}$·(m·s$^{-1}$)$^{1/3}$ | $V_a \times 10^5$ / m$^3$ | $L_f$ / Å | $V_0 \times 10^5$ / m$^3$ | $Y \times 10^{-4}$ / Å | $Z \times 10^{-3}$ / kg·m$^2$·s$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| acetonitrile | 4.94 | 0.170 | 1.24 | 4.58 | 632.32 | −3.74 | 0.431 | 5.658 | 21.82 | 1330.81 |
| tetrahydrofuran | 7.66 | 0.197 | 1.91 | 3.45 | 891.72 | 1.57 | 0.536 | 6.612 | 29.22 | 1138.17 |
| 1,3-dioxolane | 6.57 | 0.187 | 1.64 | 3.57 | 771.81 | 1.15 | 0.473 | 5.858 | 26.38 | 1415.41 |
| 1,4-dioxane | 8.07 | 0.200 | 2.02 | 3.57 | 945.32 | 1.37 | 0.477 | 7.197 | 30.26 | 1382.98 |

and structural effects. There is a parallel in the qualitative behavior of the $\Delta K_s$ and the $V^E$ curves (Figures 1 and 3).

Figures 4 and 5 shows that $\Delta L_f$ values are positive for all the binary mixture and that $\Delta Z$ behaves in a manner opposite to $\Delta L_f$. Positive and negative deviations in these functions from linear dependence on composition of the mixtures indicate the extent of association or dissociation between the mixing components.[21] The observed values of $\Delta K_s$ and $\Delta L_f$ can be qualitatively explained by considering the following factors: (i) the mutual disruption of associates present in pure liquids, (ii) dipole-induced interaction between the mixing liquids, and (iii) interstitial accommodation of one component into another. The second two factors contribute negative $\Delta K_s$ and $\Delta L_f$ values. Observed negative value of $\Delta K_s$ and $\Delta L_f$ for the mixtures over the entire range of composition implies that the weak dipole-induced interactions are predominant between the unlike molecules along with interstitial accommodation between the components.[22,15] Thus the graded behaviors of these functions support the results obtained earlier.

In an attempt to explore the nature of the interactions occurring between the mixing components, various thermodynamic parameters[21−25] such as intermolecular free length ($L_f$), specific acoustic impedance ($Z$), van der Waals constant ($b$), molecular radius ($r$), geometrical volume ($B$), molar surface area ($Y$), available volume ($V_a$), molar speed of sound ($R$), relative association ($R_A$), and molecular association ($M_A$) of the binary mixtures have been calculated using

$$L_f = K\sqrt{K_S} \tag{7}$$

$$Z = u\rho \tag{8}$$

$$b = \left(\frac{M}{\rho}\right) - \left(\frac{RT}{\rho^2 u^2}\right)\left\{\left[1 + \left(\frac{Mu^2}{3RT}\right)\right]^{1/2} - 1\right\} \tag{9}$$

$$r = \left(\frac{3b}{16\pi N}\right)^{1/3} \tag{10}$$

$$B = \frac{4}{3}\pi r^3 N \tag{11}$$

$$Y = (36\pi N B^2)^{1/3} \tag{12}$$

$$V_a = V - \left(1 - \frac{u}{u_\infty}\right) \tag{13}$$

$$V_0 = V - V_a \tag{14}$$

$$R = \frac{Mu^{1/3}}{\rho} \tag{15}$$

$$R_A = \left(\frac{\rho_{mix}}{\rho}\right)\left(\frac{u}{u_{mix}}\right)^{1/3} \tag{16}$$

$$M_A = \left(\frac{u_{mix}}{\sum_{i=1}^{2} x_i u_i}\right)^2 - 1 \tag{17}$$

where $K$ is a temperature-dependent constant, $V_0$ is volume at absolute zero, and $u_\infty$ is taken as 1600 ms$^{-1}$. These parameters are listed in Table 4 for the pure components and in Table 5 for the binary mixtures. Plots of $Z$, $L_f$, $R$, $M_A$, and $R_A$ against $x_1$ are shown in Figures 6 to 10.

The plots of $Z$ and $L_f$ for the mixtures behave in opposite manner, and these figures do not exhibit any sudden variation in their behavior. This implies the absence of any complex formation[24] between the mixing components, which is further supported by the linear variations of $R$, $R_A$, and $M_A$ of the binary mixtures against mole fractions of acetonitrile.[24] $M_A$ and $R_A$ values decrease for the mixtures with increasing mole fraction of acetonitrile. This implies strongly dissociative interactions between the unlike molecules in the mixtures.[24,25]

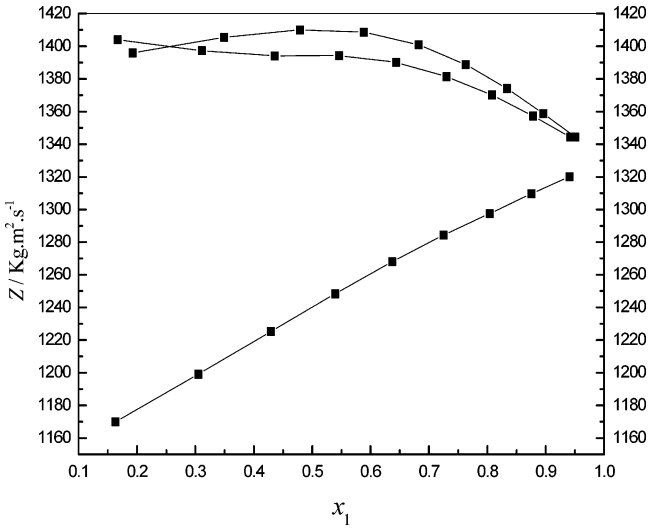


**Figure 6.** $Z$ values for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

**Table 5. Intermolecular Free Length $L_f$, Molar Speed of Sound $R$, Relative Association $R_A$, Molecular Association $M_A$, Available Volume $V_a$, and Specific Acoustic Impedance $Z$ of Binary Mixtures at 298.15 K**

| $x_1$ | $L_f$ / Å | $R \times 10^6$ / m$^3$·mol$^{-1}$·(m·s$^{-1}$)$^{1/3}$ | $R_A$ | $M_A$ | $V_a \times 10^5$ / m$^3$ | $Z \times 10^{-3}$ / kg·m$^2$·s$^{-1}$ |
|---|---|---|---|---|---|---|
| | | Acetonitrile + Tetrahydrofuran | | | | |
| 0.1633 | 0.5186 | 911.85 | 1.2147 | −0.5911 | 1.18 | 1169.94 |
| 0.3052 | 0.5029 | 842.69 | 1.1848 | −0.634 | 8.72 | 1199.17 |
| 0.4295 | 0.4890 | 791.88 | 1.1565 | −0.6681 | 6.26 | 1225.29 |
| 0.5394 | 0.4768 | 753.03 | 1.1295 | −0.6961 | 4.19 | 1248.36 |
| 0.6372 | 0.4664 | 722.31 | 1.1043 | −0.7193 | 2.43 | 1268.15 |
| 0.7249 | 0.4575 | 697.28 | 1.0809 | −0.7389 | 9.41 | 1284.37 |
| 0.8039 | 0.4500 | 676.55 | 1.059 | −0.7558 | −3.58 | 1297.58 |
| 0.8754 | 0.4431 | 659.27 | 1.0385 | −0.7703 | −1.55 | 1309.65 |
| 0.9405 | 0.4369 | 644.61 | 1.0189 | −0.7831 | −2.65 | 1320.03 |
| | | Acetonitrile + 1,3-Dioxolane | | | | |
| 0.1670 | 0.4654 | 937.98 | 1.3773 | −0.4928 | 8.64 | 1403.98 |
| 0.3109 | 0.4587 | 860.66 | 1.3224 | −0.5567 | 6.26 | 1397.31 |
| 0.4361 | 0.4523 | 804.77 | 1.2715 | −0.6074 | 4.32 | 1394.09 |
| 0.5461 | 0.4462 | 762.5 | 1.2241 | −0.6487 | 2.66 | 1394.22 |
| 0.6435 | 0.4412 | 729.26 | 1.1801 | −0.6831 | 1.25 | 1390.11 |
| 0.7302 | 0.4378 | 702.28 | 1.1391 | −0.7124 | 7.42 | 1381.30 |
| 0.8081 | 0.4354 | 679.94 | 1.1013 | −0.7373 | −9.61 | 1370.15 |
| 0.8783 | 0.4335 | 661.37 | 1.0652 | −0.7591 | −1.93 | 1357.24 |
| 0.9420 | 0.4319 | 645.71 | 1.0317 | −0.7779 | −2.85 | 1344.40 |
| | | Acetonitrile + 1,4-Dioxane | | | | |
| 0.1926 | 0.4654 | 1039.22 | 1.3739 | −0.5033 | 9.08 | 1395.94 |
| 0.3492 | 0.4555 | 917.01 | 1.3179 | −0.5677 | 6.05 | 1405.44 |
| 0.4791 | 0.4475 | 837.8 | 1.2667 | −0.6173 | 3.84 | 1409.99 |
| 0.5886 | 0.4416 | 782.14 | 1.2199 | −0.6569 | 2.15 | 1408.67 |
| 0.6822 | 0.4378 | 740.65 | 1.1769 | −0.6897 | 8.45 | 1400.95 |
| 0.7630 | 0.4354 | 708.61 | 1.1370 | −0.7173 | −2.21 | 1388.82 |
| 0.8336 | 0.4341 | 683.07 | 1.1002 | −0.7407 | −1.12 | 1374.1 |
| 0.8957 | 0.4331 | 662.64 | 1.0648 | −0.7611 | −2.00 | 1358.79 |
| 0.9508 | 0.4320 | 645.97 | 1.0317 | −0.7788 | −2.85 | 1344.32 |

The mixing functions $V^E$, $\Delta\eta$, $\Delta K_s$, $\Delta L_f$, and $\Delta Z$ were represented mathematically by the following type of Redlich−Kister equation[26] (eq 18) for correlating the experimental data:

$$Y_{ij}^E = x_i x_j \sum_{k=1}^{m} a_k (x_i - x_j)^k \tag{18}$$

where $Y_{ij}^E$ refers to an excess property ($V^E$, $\Delta\eta$, $\Delta K_s$, $\Delta L_f$, and $\Delta Z$) for each $i-j$ binary pair, and $x_i$ is the mole fraction of $i$th component, and $a_k$ represents the coefficients. The values of

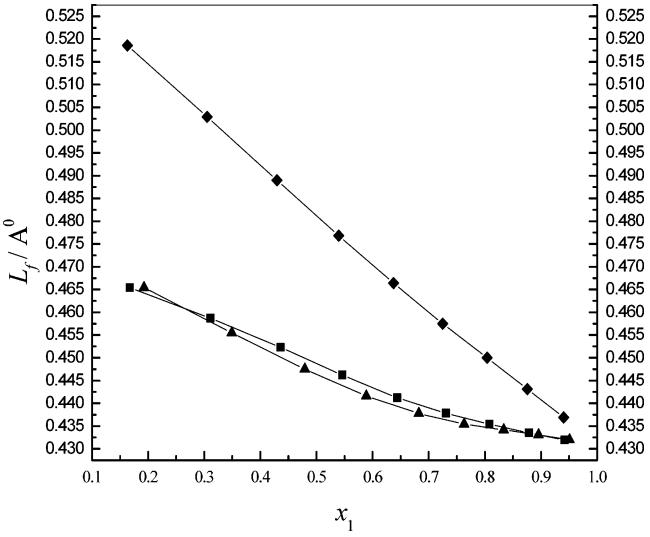


**Figure 7.** $L_f$ values for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

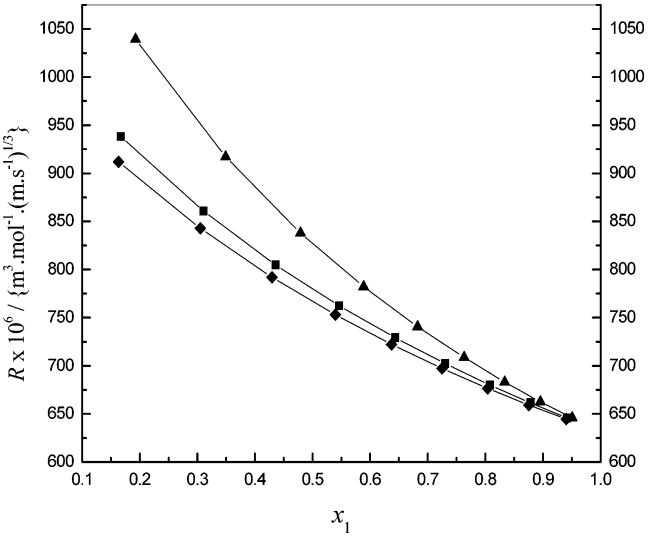


**Figure 8.** $R$ values for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

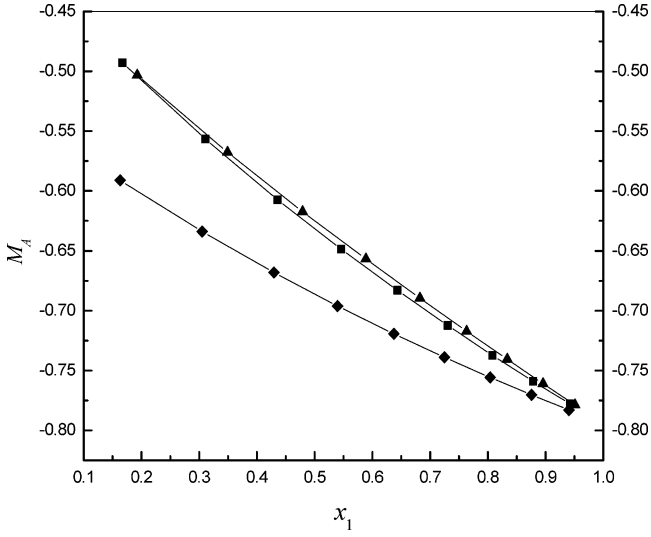


**Figure 9.** $M_A$ values for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

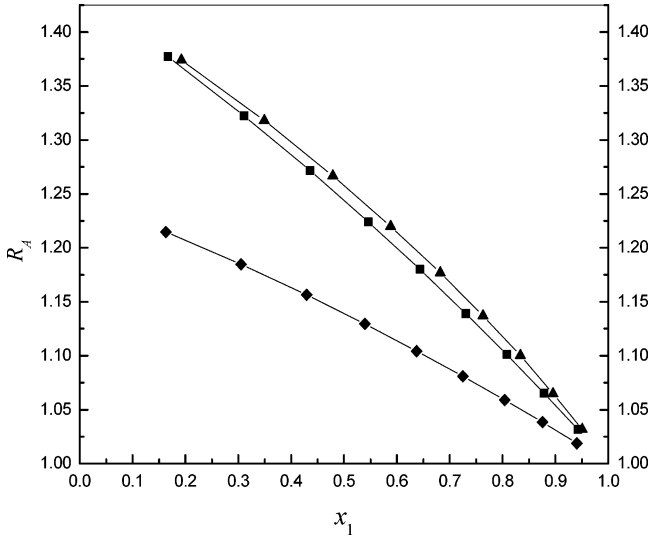


**Figure 10.** $R_A$ values for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

coefficients ($a_k$) were determined by a multiple-regression analysis based on the least-squares method and were summarized along with the standard deviations between the experimental and fitted values of the respective functions in Table 6. The standard deviation was calculated using

$$\sigma = \left[\sum_{i=1}^{n} \frac{(Y^{E}_{i,\mathrm{exp}} - Y^{E}_{i,\mathrm{cal}})^2}{n-p}\right]^{1/2} \tag{19}$$

where $n$ is the number of experimental points and $p$ is the number of adjustable parameters. The small $\sigma$ values for excess properties indicate that the fits are good for the present study.

Several semiempirical models have been proposed from time to time to estimate the dynamic viscosity of the binary liquid mixtures in terms of pure-component data[16,17] and to interpret the molecular interactions in these mixtures. Some of them we examined are as follows:

Grunberg and Nissan[27] have suggested the following logarithmic relation between the viscosity of the binary mixtures and the pure components:

$$\eta = \exp[\sum_{i=1}^{j} (x_i \ln \eta_i) + d_{12} \prod_{i=1}^{j} x_i] \tag{20}$$

where $d_{12}$ is a constant proportional to the interchange energy. It may be regarded as an approximate measure of the strength of molecular interactions between the mixing components. The values of the interchange parameter ($d_{12}$) have been calculated using eq 20 as a function of the composition of the binary liquid mixtures of acetronitrile with tetrahydrofuran (1,3-dioxolane and 1,4-dioxane) and are listed in Table 2.

Tamura and Kurata[28] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{i} x_i \phi_i \eta_i + 2T_{12} \prod_{i=1}^{j} [x_i \phi_i]^{1/2} \tag{21}$$

where $T_{12}$ is the interaction parameter and $\phi_i$ is the volume fraction of $i$th pure component in the mixture.

**Table 6. Redlich−Kister Coefficients $a_k$ and Standard Deviations $\sigma$ for the Binary Mixtures**

| excess property | $T$/K | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| | | | Acetonitrile + Tetrahydrofuran | | | |
| $V^E \times 10^6$/(m$^3$·mol$^{-1}$) | 298.15 | −0.535 | 0.439 | 0.238 | −0.157 | 0.004 |
| | 308.15 | −0.435 | 0.081 | 0.0001 | −0.046 | 0.000 |
| | 318.15 | −1.198 | 0.489 | 0.054 | −0.116 | 0.001 |
| $\Delta\eta$/(mPa·s) | 298.15 | −0.023 | −0.023 | −0.014 | | 0.000 |
| | 308.15 | −0.041 | −0.044 | | | 0.001 |
| | 318.15 | −0.060 | 0.047 | −0.023 | | 0.000 |
| $\Delta K_s \times 10^{12}$/(Pa$^{-1}$) | 298.15 | −46.92 | −20.28 | 16.04 | 28.30 | 0.101 |
| $\Delta L_f$/Å | 298.15 | −0.0097 | −0.0096 | 0.0079 | 0.0125 | 0.000 |
| $\Delta Z$/(kg·m$^2$·s$^{-1}$) | 298.15 | 22.9517 | 33.3804 | −8.6910 | −31.4791 | 0.195 |
| | | | Acetonitrile + 1,3-Dioxolane | | | |
| $V^E \times 10^6$/(m$^3$·mol$^{-1}$) | 298.15 | −1.104 | 0.187 | 0.333 | −0.650 | 0.002 |
| | 308.15 | −1.43 | −0.288 | | | 0.014 |
| | 318.15 | −1.58 | −0.014 | −0.254 | −0.777 | 0.002 |
| $\Delta\eta$/(mPa·s) | 298.15 | −0.195 | −0.080 | −0.108 | −0.059 | 0.001 |
| | 308.15 | −0.141 | −0.090 | −0.090 | | 0.002 |
| | 318.15 | −0.148 | −0.105 | −0.111 | −0.022 | 0.000 |
| $\Delta K_s \times 10^{12}$/(Pa$^{-1}$) | 298.15 | −59.82 | −34.96 | 6.20 | 66.24 | 0.063 |
| $\Delta L_f$/Å | 298.15 | −0.0134 | 0.0150 | | | 0.001 |
| $\Delta Z$/(kg·m$^2$·s$^{-1}$) | 298.15 | 86.9118 | 106.6348 | | | 1.712 |
| | | | Acetonitrile + 1,4-Dioxane | | | |
| $V^E \times 10^6$/(m$^3$·mol$^{-1}$) | 298.15 | −1.069 | −0.714 | 0.219 | 0.424 | 0.005 |
| | 308.15 | −1.38 | −0.368 | −0.180 | | 0.006 |
| | 318.15 | −1.77 | −0.377 | | | 0.009 |
| $\Delta\eta$/(mPa·s) | 298.15 | −0.583 | −0.279 | −0.115 | | 0.003 |
| | 308.15 | −0.365 | −0.112 | 0.131 | 0.102 | 0.001 |
| | 318.15 | −0.408 | −0.168 | 0.066 | 0.332 | 0.001 |
| $\Delta K_s \times 10^{12}$/(Pa$^{-1}$) | 298.15 | −70.22 | −41.53 | 31.13 | 46.67 | 0.101 |
| $\Delta L_f$/Å | 298.15 | −0.0306 | −0.0213 | 0.0143 | 0.0232 | 0.001 |
| $\Delta Z$/(kg·m$^2$·s$^{-1}$) | 298.15 | 213.9833 | 113.6827 | −36.9828 | −77.6469 | 0.163 |

**Table 7. Parameters of McAllister Model, Heric and Brewer Parameters, and Standard Deviations for Kinematic Viscosities at Various Temperatures**

| $T$ | McAllister (three-body model) | | | McAllister (four-body model) | | | | Heric and Brewer parameter | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| K | $u_{12}$ | $v_{21}$ | $\sigma$ | $v_{1112}$ | $v_{1122}$ | $v_{2221}$ | $\sigma$ | $a \times 10^2$/cm$^2$·s$^{-1}$ | $b \times 10^2$/cm$^2$·s$^{-1}$ | c $\times 10^2$/cm$^2$· s$^{-1}$ | $\sigma$ |
| | | | | | Acetonitrile + Tetrahydrofuran | | | | | | |
| 298.15 | 0.4472 | 0.4953 | 0.004 | 0.4422 | 0.4809 | 0.3976 | 0.001 | −0.1092 | −0.0851 | −0.1719 | 0.009 |
| 308.15 | 0.3992 | 0.4621 | 0.004 | 0.3961 | 0.4358 | 0.4554 | 0.001 | −0.6990 | −0.0797 | −0.0048 | 0.002 |
| 318.15 | 0.3481 | 0.4175 | 0.015 | 0.3499 | 0.3967 | 0.1921 | 0.003 | −0.2939 | −0.2417 | −0.4706 | 0.025 |
| | | | | | Acetonitrile + 1,3-Dioxolane | | | | | | |
| 298.15 | 0.3181 | 0.4772 | 0.025 | 0.3339 | 0.4365 | 0.0950 | 0.011 | −0.7160 | −0.5678 | −1.2469 | 0.063 |
| 308.15 | 0.3028 | 0.4280 | 0.021 | 0.3204 | 0.4244 | 0.2383 | 0.005 | −0.4759 | −0.2327 | −0.7290 | 0.026 |
| 318.15 | 0.2541 | 0.3887 | 0.023 | 0.2739 | 0.3861 | 0.1297 | 0.006 | −0.4963 | −0.4096 | −0.9001 | 0.042 |
| | | | | | Acetonitrile + 1,4-Dioxane | | | | | | |
| 298.15 | 0.3131 | 0.8765 | 0.054 | 0.2817 | 0.5868 | 0.0175 | 0.025 | −1.8590 | −2.0151 | −2.7610 | 0.187 |
| 308.15 | 0.4955 | 0.0428 | 0.031 | 0.4467 | 0.2183 | 0.8251 | 0.025 | −0.5120 | −−3.4702 | −2.8854 | 0.154 |
| 318.15 | 0.3815 | 0.2167 | 0.046 | 0.3034 | 0.0921 | 0.6748 | 0.046 | −0.7564 | −5.1889 | −4.3310 | 0.230 |

The following viscosity model of Hind et al.[29] may also interpret the molecular interactions:

$$\eta = \sum_{i=1}^{j} x_i^2 \eta_i + 2H_{12} \prod_{i=1}^{j} x_i \tag{22}$$

where $H_{12}$ is the Hind interaction parameter.

In the present study, the values of interaction parameters $T_{12}$ and $H_{12}$ have been calculated from eqs 21 and 22, respectively, and are listed in Table 2. It is observed that for a given binary mixture $T_{12}$ and $H_{12}$ do not differ appreciably from each other; this is in agreement with the view put forward by Fort and Moore[15] in regard to the nature of parameters $T_{12}$ and $H_{12}$.

The McAllister multibody interaction model[30] is widely used to correlate the kinematic viscosities ($\upsilon = \eta/\rho$)of the binary mixtures with mole fraction. The three-body model is defined as

$$\ln \upsilon = x_1^3 \ln \upsilon_1 + x_2^3 \ln \upsilon_2 + 3x_1^2 x_2 \ln \upsilon_{12} + 3x_2^3 x_1 \ln \upsilon_{21} - \ln\left[x_1 + \frac{x_2 M_2}{M_1}\right] + 3x_1^2 x_2 \ln\left[\frac{2}{3} + \frac{M_2}{3M_1}\right] + 3x_2^2 x_1 \ln\left[\frac{1}{3} + \frac{2M_2}{3M_1}\right] + x_2^3 \ln\left[\frac{M_2}{M_1}\right] \tag{23}$$

The four-body model is given by

$$\ln \upsilon = x_1^4 \ln \upsilon_1 + 4x_1^3 x_2 \ln \upsilon_{1112} + 6x_1^2 x_2^2 \ln \upsilon_{1122} + 4x_1 x_2^3 \ln \upsilon_{2221} - \ln \upsilon_{2221} + x_2^4 \ln \upsilon_2 - \ln\left[x_1 + x_2\left(\frac{M_2}{M_1}\right)\right] + 4x_1^3 x_2 \ln\left[\frac{3}{4} + \frac{M_2}{4M_1}\right] + 6x_1^2 x_2^2 \ln\left[\frac{1}{2} + \frac{M_2}{2M_1}\right] + 4x_1 x_2^3 \ln\left[\frac{1}{3} + \frac{3M_2}{4M_1}\right] + x_2^4 \ln\left[\frac{M_2}{M_1}\right] \tag{24}$$

where $v$, $v_1$, and $v_2$ are kinematic viscosities of the mixture, the pure acetonitrile and the corresponding second component, respectively. $v_{12}$, $v_{21}$, $v_{1112}$, $v_{1122}$, and $v_{2221}$ are model parameters; $M_i$ and $x_i$ are the molecular weight and mole fraction of the $i$th pure component in the mixture.

Table 7 records the parameters calculated using eqs 23 and 24 along with the standard deviations. It is seen that the values of both the parameters are positive and adequate for all of the binary mixtures.

Heric and Brewer[31] have proposed an equation for the kinematic viscosity of the binary liquid mixtures:

$$v = x_1 v_1 + x_2 v_2 + x_1 x_2 \{a + b(x_1 - x_2) + c(x_1 - x_2)^2\} \quad (25)$$

where $a$, $b$, and $c$ are model parameters and $M_i$ and $x_i$ are the molecular weight and mole fraction of the $i$th pure component in the mixture, respectively.

The percentage standard deviation[24] was calculated using

$$\sigma\,\% = \left[\frac{\sum (100(v_{\text{exptl}} - v_{\text{calcd}})/v_{\text{exptl}})^2}{(n - m)}\right]^{1/2} \quad (26)$$

where $n$ represents the number of experimental points and $m$ is the number of coefficients.

The values of parameters $a$, $b$, and $c$ have been calculated using eq 25 and are listed in Table 7 along with the standard deviations. A perusal of Table 7 shows that the values of $a$ and $b$ are negative for all of the binary mixtures.

## Literature Cited


(1) Kim, E. S.; Marsh, K. N. Isothermal vapor−liquid equilibria for the ternary ethanol−acetonitrile−chloroform system. *J. Chem. Eng. Data* **1988**, *33*, 288−292.

(2) Roy, M. N.; Sinha, B.; Dakua, V. K. Excess molar volumes and viscosity deviations of binary liquid mixtures of 1,3-dioxolane and 1,4-dioxane with butyl acetate, butyric acid, butyl amine, and 2-butanone at 298.15 K. *J. Chem. Eng. Data* **2006**, *51*, 590−594.

(3) Roy, M. N.; Sinha, A.; Sinha, B. Excess molar volumes, viscosity deviations and isentropic compressibility of binary mixtures containing 1,3-dioxolane and monoalcohols at 303.15 K. *J. Solution Chem.* **2005**, *34* (11), 1311−1325.

(4) Moumouzias, G.; Panopoulos. D. K.; Ritzoulis. G. Excess properties of the binary liquid system propylene carbonate + acetonitrile. *J. Chem. Eng. Data* **1991**, *36*, 20−23.

(5) Das, B.; Saha, N. Electrical conductances of some symmetrical tetraalkylammonium salts in methanol, acetonitrile, and methanol (1) + acetonitrile (2) mixtures at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 2−5.

(6) Brocos, P; Calvo, E; Pineiro, A; Bravo, R; Amigo, A. Heat capacities, excess enthalpies, and volumes of mixtures containing cyclic ethers. 5. Binary systems {1,3-dioxolane + 1-alkanols}. *J. Chem. Eng. Data* **1999**, *44*, 1341−1347.

(7) Leaist, D. G.; MacEwan, K.; Stefan, A.; Zamari, M. Binary mutual diffusion coefficients of aqueous cyclic ethers at 25° C. Tetrahydrofuran, 1,3-dioxolane, 1,4-dioxane, 1,3-dioxane, tetrahydropyran, and trioxane. *J. Chem. Eng. Data* **2000**, *45*, 815−818.

(8) Janz, G. G.; Tomkins, R. P. T. *Nonaqueous Electrolytes Handbook*; Academic Press: New York, 1973; Vol. 2.

(9) Jasinski, R. *High Energy Batteries*; Plenum Press: New York, 1967.

(10) Saha, N.; Das, B. Apparent molar. volumes of some symmetrical tetraalkylammonium bromides in acetonitrile at (298.15, 308.15, and 318.15) K. *J. Chem. Eng. Data* **1997**, *42*, 227−229.

(11) Roy, M. N.; Jha, A.; Dey, R. Study of ion−solvent interactions of some alkali metal chlorides in tetrahydrofuran + water mixture at different temperatures. *J. Chem. Eng. Data* **2001**, *46*, 1327−1329.

(12) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Techniques of Chemistry*, Vol. 2, 4th ed.; Wiley-Interscience: New York, 1986.

(13) Roy, M. N.; Hazra, D. K. Densities and viscosities of the binary aqueous mixture of tetrahydrofuran and 1,2 dimethoxyethane at 298, 308 and 318 K. *Indian J. Chem. Technol.* **1994**, *1*, 93−97.

(14) Roy, M. N.; Jha, A.; Choudhury, A. Densities and viscosities and adiabatic compressibilities of some mineral salts in water at different temperatures. *J. Chem. Eng. Data* **2004**, *49*, 291−296.

(15) Fort, R. J.; Moore, W. R. Viscosities of binary liquid mixtures. *Trans. Faraday Soc.* **1966**, *62*, 1112−1119.

(16) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: 1987.

(17) Irving, J. B. *Viscosities of Liquid Mixtures*; NEL Reports 630 and 631; National Engineering Laboratory: East Kilbride, Glassgow, 1977.

(18) Treszczanowicz, A. J.; Kiyohara, O.; Benson, G. C. Excess molar volumes for *n*-alkanes binary mixtures of decan-1-ol + *n*-pentane, + *n*-hexane, + *n*-octane, + *n*-decane, and + *n*-hexadecane. *J. Chem. Thermodyn.* **1981**, *13*, 253−260.

(19) Jain, P.; Singh, M. Density, viscosity, and excess properties of binary liquid mixtures of propylene carbonate with polar and nonpolar Solvents. *J. Chem. Eng. Data* **2004**, *49*, 1214−1217.

(20) Nikam, P. S.; Kharat, S. J. Excess molar volumes and deviations in viscosity of binary mixtures of *N*,*N*-dimethylformamide with aniline and benzonitrile at (298.15, 303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data* **2003**, *48*, 972−976.

(21) Pal, A.; Bhardwaj, R. K. Ultrasonic speeds and volumetric properties of dipropylene glycol monomethyl ether−*n*-alkylamine mixtures at 298.15 K. *Z. Phys. Chem.* **2002**, *216*, 1033−1051.

(22) Ku, H.-C.; Tu, C.-H. Densities and viscosities of binary and ternary mixtures of ethanol, 2-butanone, and 2,2,4-trimethylpentane at $T$ = (298.15, 308.15, and 318.15) K. *J. Chem. Eng. Data* **2005**, *50*, 608−615.

(23) Jacobson, B. Ultrasonic velocity of liquids and liquid mixtures. *J. Chem. Phys.* **1952**, *20*, 927−928.

(24) Mehta, S. K.; Chauhan, R. K.; Dewan, R. K. Excess volumes and isentropic compressibilities of pyrrolidin-2-one-alkanol ($C_1$−$C_5$) binary mixtures. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 1167−1173.

(25) Shastry, N. V.; Patel, S. R. Densities, viscosities, sound speeds and excess properties of binary mixtures of methyl methacrylate with alkoxyethanols and 1-alchohols at 298.15 and 308.15 K. *Int. J. Thermophys.* **2000**, *21*, 1153−1174.

(26) Redlich, O.; Kister, A. T. Algebric representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(27) Grunberg, L.; Nissan, A. H. Mixture law for viscosity. *Nature* **1949**, *164*, 799−800.

(28) Tamura, M.; Kurata, M. Viscosity of binary mixture of liquids. *Bull. Chem. Soc. Jpn.* **1952**, *25*, 32−37.

(29) Hind, R. K.; McLaughlin, E.; Ubbelohde. A. R. Structure and viscosity of liquid-camphor and pyrene mixtures. *Trans. Faraday. Soc.* **1960**, *56*, 328−334.

(30) McAllister, R. A. The viscosity of liquid mixtures. *AIChE J.* **1960**, *6*, 427.

(31) Heric, E. L.; Brewer, J. G. Viscosity of some binary liquid nonelectrolyte mixtures. *J. Chem. Eng. Data* **1967**, *12*, 574−583.

(32) Nikam, P., S.; Kharat, S. J. Densities and viscosities of binary mixtures of *N*,*N*-dimethylformamide with benzyl alcohol and acetophenone at (298.15, 303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data* **2003**, *48*, 1291−1295.

(33) Sinha, A.; Roy, M. N. Studies on viscous antagonism, excess molar volume and isoentropic compressibility in aqueous mixed solvent systems at different temperatures. *Phys. Chem. Liq.* **2006**, *44*, 303−314.

(34) Aminabhavi, T. M.; Patil, V. B. Density, viscosity, refractive index, and speed of sound in binary mixtures of ethenylbenzene with *N*,*N*-dimethylacetamide, tetrahydrofuran, *N*,*N*-dimethylformamide, 1,4-dioxane, dimethyl sulfoxide, chloroform, bromoform, and 1-chloronaphthalene in the temperature interval (298.15−308.15) K. *J. Chem. Eng. Data* **1998**, *43*, 497−503.

(35) Gascon, I.; Mainar, A. M.; Royo, F. M.; Urieta, J. S. Experimental viscosities and viscosity predictions of the ternary mixture (cyclohexane + 1,3-dioxolane + 2-butanol) at 298.15 and 313.15 K. *J. Chem. Eng. Data* **2000**, *45*, 751−755.

(36) Giner, B.; Villares, A.; Gascon, P.; Cea, P.; Lafuente, C. Speeds of sound and isentropic compressibilities of binary mixtures containing cyclic ethers and haloalkanes at 298.15 and 313.15 K. *Int. J. Thermophys.* **2004**, *25* (6), 1735−1746.

(37) Inglese, A.; Groller, J. E.; Wllhelm, E. Excess volumes of mixtures of oxolane, oxane, 1,3-dioxolane, and 1,4-dioxane with *n*-alkanes at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1983**, *28*, 124−127.

(38) Rao, K. P.; Reddy, K. S. Viscosities of trichloroethylene with ketones and i,4-dioxane at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1988**, *33*, 130−133.


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