# Thermodynamic Behavior of Mixtures. 3. Mixtures of Acetonitrile with Dimethylacetamide, Dimethyl Sulfoxide, Nitrobenzene, and Methanol at 25 °C

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Ultrasonic velocities ($u$), densities ($\rho$), viscosities ($\eta$), relative permittivities ($\epsilon$), and refractive indicies ($n_D$) of mixtures of acetonitrile with dimethylacetamide, dimethyl sulfoxide, nitrobenzene, and methanol have been measured at 25 °C. From $u$, $\rho$, and $\eta$, isentropic compressibilities ($\kappa_S$), and its deviation from ideal behavior ($\kappa_S^E$), and excess viscosities ($\Delta\eta$) have been computed. From $n_D$ and $\epsilon$, the Kirkwood correlation factor, $g$, has also been evaluated.

## Introduction

In our recent work (Bakshi, 1993a,b), we have been exploring the intermixing behavior of polar organic solvents. Especially nitrogen organic bases were of interest because of their strong basic nature and unique mixing behavior. It has been found that in most of the cases, the results were not obtained as expected (Bakshi, 1993a,b). For example, though pyridine (Py) and its derivatives are highly polar in nature, the binary mixtures of Py with $\beta$- and $\gamma$-picolines showed an ideal intermixing behavior with respect to volumes and compressibilities (Bakshi, 1993a,b). Significant specific interactions have been observed between the components of Py−isoquinoline, acetonitrile (AN)−isoquinoline, and AN−2,6-lutidine binary mixtures (Bakshi, 1993a,b). In the present work AN has been selected once again as a common component in various binary mixtures in order to evaluate such peculiarities over a wide variety of organic liquids consisting of dipolar aprotic as well as protic solvents such as dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), nitrobenzene (NB), and methanol (MeOH). These liquids are quite important organic solvents due to their favorable physicochemical properties such as the broad temperature range corresponding to their liquid state, relatively higher relative permittivity, and good donor and acceptor properties.

## Experimental Section

Ultrasonic velocities ($u$) for acetonitrile (AN)−*N*,*N*-dimethylacetamide, AN−dimethyl sulfoxide, AN−nitrobenzene, and AN−methanol binary mixtures were measured at (25 ± 0.01) °C over the entire composition range by Ultrasonic Time Intervalometer (UTI) 101, from Innovative Instruments, Hyderabad, India, using a pulse echo overlap technique at a fixed frequency of 2 MHz. Densities ($\rho$) were measured by using an Anton Paar (DMA 602 + DMA 60) densimeter.

An Ubbelohde suspended level viscometer with flow time 750.0 s for water at (25 ± 0.01) °C was used for all viscosity measurements. The viscometer was calibrated with water, *N*,*N*-dimethylformamide, benzene, and pyridine having viscosities 0.890, 0.801, 0.602, and 0.882 mPa·s, respectively, which are in good agreement with 0.890, 0.802, 0.603, and 0.884 mPa·s reported already (Riddick and Bunger, 1970).

Refractive indices ($n_D$) were determined by using the Abbe refractometer, which was maintained at (25 ± 0.01) °C by circulating the thermostated water. All the measurements were carried out for sodium-D light.

Static relative permittivities ($\epsilon$) were obtained with the help of a Universal Dielectrometer type OH-301 (Radelkis, Hungry). The cell used for the present study was OH-911-1 (for the relative permittivity range between 10 and 40) and contained 50 cm$^3$ of the solvent or the solvent mixture for each measurement. Thermostated water was circulated through an outer jacket of the cell to maintain a (25 ± 0.01) °C temperature. After the thermal equilibrium was attained, the capacitances of the solutions were recorded. The cell was calibrated with suitable water−dioxane mixtures.

The overall accuracy in the measurement of each variable was better than 0.5%. The uncertainties in the measurement of ultrasonic velocity, density, viscosity, relative permittivity, and refractive index were within $\pm 0.1$ m·s$^{-1}$, $\pm 1 \times 10^{-5}$ g·cm$^{-3}$, 0.001 mPa·s, $\pm 0.1$, and $\pm 0.000\,01$, respectively.

AN, DMA, DMSO, and MeOH all 99% pure were from E. Merck, Bombay, and NB (98%) was from Sisco Research Laboratories, Bombay. AN was dried on silica gel and fractionally distilled twice from phosphorus pentaoxide

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**Table 1. Ultrasonic Velocities ($u$), Densities ($\rho$), Viscosities ($\eta$), Relative Permittivities ($\epsilon$), and Refractive Indices ($n_D$) of Acetonitrile (AN), *N*,*N*-Dimethylacetamide (DMA), Dimethyl Sulfoxide (DMSO), Nitrobenzene (NB), and Methanol (MeOH) at 25 °C**

| | AN | DMA | DMSO | NB | MeOH |
|---|---|---|---|---|---|
| $u$/m·s$^{-1}$ | 1280.8<br>(1283)$^a$ | 1469.3<br>(1458)$^a$ | 1493.2<br>(1490)$^a$ | 1463.3<br>(1463)$^f$ | 1102.8<br>(1103)$^f$ |
| $\rho$/g·cm$^{-3}$ | 0.77690<br>(0.7766)$^e$<br>(0.7765)$^a$ | 0.93650<br>(0.9366)$^e$<br>(0.9366)$^a$ | 1.09600<br>(1.0958)$^e$<br>(1.0960)$^a$ | 1.19310<br>(1.1984)$^d$ | 0.78680<br>(0.7868)$^d$ |
| $\eta$/mPa·s | 0.341<br>(0.341)$^{b,c}$ | 0.919<br>(0.919)$^c$ | 1.990<br>(1.990)$^b$<br>(1.996)$^e$ | 1.811<br>(1.811)$^c$<br>(1.822)$^d$ | 0.545<br>(0.545)$^b$<br>(0.545)$^e$ |
| $\epsilon$ | 36.0<br>(36.0)$^e$ | 37.8<br>(37.78)$^e$ | 46.6<br>(46.68)$^e$ | 34.3<br>(34.82)$^e$ | 32.6<br>(32.7)$^e$ |
| $n_D$ | 1.34110<br>(1.3416)$^f$<br>(1.3413)$^a$ | 1.43098<br>(1.4356)$^e$<br>(1.4356)$^a$ | 1.47400<br>(1.4769)$^a$<br>(1.4773)$^e$ | 1.54901<br>(1.5499)$^e$ | 1.32601<br>(1.3265)$^e$ |

[a] Aminabhavi and Gopalakrishna (1995). [b] Gill and Bakshi (1988). [c] Gill and Bakshi (1989). [d] Nikam et al. (1995). [e] Riddick and Bunger (1970). [f] Weast (1988–89).

**Table 2. Ultrasonic Velocities ($u$), Densities ($\rho$), Viscosities ($\eta$), Relative Permittivities ($\epsilon$), and Refractive Indices ($n_D$) for the Binary Mixtures at 25 °C**

| $x_A$ | $u$/m·s$^{-1}$ | $\rho$/g·cm$^{-3}$ | $\eta$/mPa·s | $\epsilon$ | $n_D$ |
|---|---|---|---|---|---|
| Acetonitrile (A) + *N*,*N*-Dimethylacetamide (B) | | | | | |
| 0.0000 | 1469.3 | 0.936 50 | 0.919 | 37.8 | 1.430 98 |
| 0.1117 | 1454.6 | 0.926 86 | 0.855 | 37.7 | 1.426 99 |
| 0.2131 | 1439.4 | 0.918 10 | 0.796 | 37.6 | 1.421 01 |
| 0.3902 | 1408.2 | 0.897 76 | 0.694 | 37.3 | 1.408 00 |
| 0.5399 | 1379.3 | 0.875 61 | 0.607 | 37.1 | 1.395 11 |
| 0.6701 | 1351.7 | 0.852 64 | 0.532 | 36.8 | 1.383 90 |
| 0.7788 | 1328.1 | 0.830 82 | 0.469 | 36.6 | 1.375 89 |
| 0.8756 | 1306.6 | 0.809 36 | 0.413 | 36.3 | 1.356 91 |
| 0.9610 | 1288.0 | 0.788 85 | 0.363 | 36.1 | 1.346 00 |
| 1.0000 | 1280.8 | 0.776 90 | 0.341 | 36.0 | 1.341 10 |
| Acetonitrile (A) + Dimethyl Sulfoxide (B) | | | | | |
| 0.0000 | 1493.2 | 1.096 00 | 1.990 | 46.6 | 1.474 00 |
| 0.0879 | 1487.7 | 1.072 31 | 1.713 | 45.8 | 1.462 09 |
| 0.1719 | 1474.1 | 1.049 11 | 1.493 | 44.9 | 1.453 11 |
| 0.3291 | 1435.5 | 1.003 72 | 1.133 | 43.2 | 1.436 99 |
| 0.4735 | 1400.4 | 0.959 53 | 0.862 | 41.7 | 1.421 01 |
| 0.6066 | 1367.3 | 0.916 79 | 0.663 | 40.3 | 1.401 98 |
| 0.7296 | 1338.6 | 0.875 52 | 0.523 | 38.9 | 1.386 88 |
| 0.8437 | 1312.6 | 0.835 75 | 0.430 | 37.7 | 1.368 12 |
| 0.9497 | 1292.8 | 0.797 48 | 0.376 | 36.6 | 1.356 03 |
| 1.0000 | 1280.8 | 0.776 90 | 0.341 | 36.0 | 1.341 10 |
| Acetonitrile (A) + Nitrobenzene (B) | | | | | |
| 0.0000 | 1463.3 | 1.203 10 | 1.811 | 34.3 | 1.549 01 |
| 0.1219 | 1438.8 | 1.177 61 | 1.550 | 34.7 | 1.540 11 |
| 0.2301 | 1425.7 | 1.152 72 | 1.339 | 34.9 | 1.530 09 |
| 0.4140 | 1390.8 | 1.095 01 | 1.022 | 35.2 | 1.501 90 |
| 0.5644 | 1365.3 | 1.033 51 | 0.799 | 35.4 | 1.471 89 |
| 0.6898 | 1340.4 | 0.972 20 | 0.639 | 35.6 | 1.444 11 |
| 0.7955 | 1317.6 | 0.913 58 | 0.523 | 35.8 | 1.415 02 |
| 0.8860 | 1298.7 | 0.858 32 | 0.436 | 35.9 | 1.384 87 |
| 0.9645 | 1283.9 | 0.806 57 | 0.371 | 36.0 | 1.362 01 |
| 1.0000 | 1280.8 | 0.776 90 | 0.341 | 36.0 | 1.341 10 |
| Acetonitrile (A) + Methanol (B) | | | | | |
| 0.0000 | 1102.8 | 0.786 80 | 0.545 | 32.6 | 1.326 01 |
| 0.0522 | 1116.0 | 0.786 98 | 0.508 | 33.1 | 1.328 01 |
| 0.1059 | 1127.0 | 0.786 73 | 0.482 | 33.4 | 1.328 00 |
| 0.2019 | 1149.5 | 0.786 19 | 0.440 | 33.9 | 1.330 09 |
| 0.3394 | 1175.0 | 0.785 17 | 0.392 | 34.5 | 1.331 98 |
| 0.4683 | 1197.5 | 0.783 97 | 0.359 | 34.9 | 1.332 89 |
| 0.6065 | 1222.0 | 0.782 42 | 0.337 | 35.3 | 1.335 03 |
| 0.7551 | 1244.0 | 0.780 45 | 0.328 | 35.6 | 1.336 01 |
| 0.9891 | 1279.0 | 0.777 40 | 0.346 | 35.9 | 1.337 98 |
| 1.0000 | 1280.8 | 0.776 90 | 0.341 | 36.0 | 1.341 10 |

before use. Methanol was first dried over activated molecular sieves and then fractionally distilled thrice. The middle fraction was collected for use. *N*,*N*-Dimethylacetamide and dimethyl sulfoxide were distilled under a reduced pressure of 5 Torr at least twice over calcium hydride before use. Nitrobenzene was fractionally crystallized and distilled twice at 3 Torr and then finally fractionally crystallized (Riddick and Bunger, 1970). Extra care was taken to protect the solvents and solvent mixtures from atmospheric moisture. All the solutions were made by mass with an accuracy of 3 ppm. Each experiment was carried out at least twice to check the reproducibility. The $u$, $\rho$, $\eta$, $\epsilon$, and $n_D$ values for pure components are reported in Table 1 and compared with the available literature and are found to be in good agreement with each other. Measured values for AN–DMA, AN–DMSO, AN–NB, and AN–MeOH binary mixtures have been listed in Table 2.

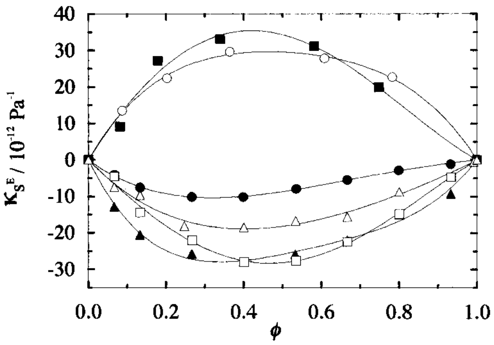

**Figure 1.** $\kappa_s^E$ *vs* volume fraction of AN ($\phi$): AN–DMA (●); AN–DMSO (▲); AN–NB (□); AN–MeOH (△); AN–Py (■); AN–DMF (○).

## Results and Discussion

***Ultrasonic Behavior.*** Isentropic compressibilities ($\kappa_s$) for the above mentioned binary mixtures were computed by the following equation

$$\kappa_s = 1/u^2\rho \tag{1}$$

where $\rho$ is the density of the mixture (Table 2).

From $\kappa_s$, deviations in isentropic compressibilities (Douhèret and Pal, 1989), $\kappa_s^E$, for the binary mixtures of AN with DMA, DMSO, NB, and MeOH were computed by means of eqs 2–4, where $\phi_i$, $V_i$, $\alpha_i$, and $C_{p,i}$ are the volume

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \tag{2}$$

$$\kappa_s^{id} = \Sigma\phi_i\{\kappa_s + TV_i\alpha_i^2/C_{p,i}\} - T\{\Sigma x_iV_i\}\{\Sigma\phi_i\alpha_i\}^2/\{\Sigma x_iC_{p,i}\} \tag{3}$$

$$\phi_i = x_iV_i/\Sigma_i x_iV_i \tag{4}$$

fraction, molar volume, coefficient of thermal expansion, and heat capacity at constant pressure of the pure component, $i$. $T$ is the absolute temperature. Values of $\alpha_i$ and $C_{p,i}$ for the pure components have been taken from the literature (Riddick and Bunger, 1970; Weast, 1988–89). The calculated values of $\kappa_s^E$ obtained from eq 2 are plotted in Figure 1 and compared with those for AN–pyridine and AN–*N*,*N*-dimethylformamide mixtures (Singh and Bakshi, 1992). The values for the present binary mixtures were also fitted by the least squares method to the equation

$$\kappa_s^E = \phi_1(1 - \phi_1)\{A_1 + A_2(2\phi_1 - 1) + A_3(2\phi_1 - 1)^2\} \tag{5}$$

where $A_i$ are constants that are characteristic of the system and their values are listed in Table 3. The standard deviations in the property obtained from eq 5 are also given in Table 3.

***Viscometric Behavior.*** Viscosities of liquid mixtures have great applicability in determining various transport properties. Excess viscosities ($\Delta\eta$) can be designated as

**Table 3. Parameters of Equation 5 along with the Standard Deviation in $\kappa_s^E$ {$\delta(\kappa_s^E)$}/$10^{-12}$ Pa$^{-1}$ and $\Delta\eta$ {$\delta(\Delta\eta)$}/mPa·s for Acetonitrile + *N,N*-Dimethylacetamide (AN + DMA), Acetonitrile + Dimethyl Sulfoxide (AN + DMSO), Acetonitrile + Nitrobenzene (AN + NB), and Acetonitrile + Methanol (AN + MeOH)**

| | AN + DMA | AN + DMSO | AN + NB | AN + MeOH |
|---|---|---|---|---|
| $A_1$ | −34.7 ± 0.5 | −103.3 ± 3.0 | −112.4 ± 2.8 | −72.6 ± 3.1 |
| $A_2$ | 32.9 ± 1.1 | 42.3 ± 6.0 | 18.6 ± 5.5 | 28.7 ± 6.2 |
| $A_3$ | −9.3 ± 2.3 | −73.3 ± 13.0 | 30.0 ± 11.8 | 0.0 |
| $\delta(\kappa_s^E)$ | 0.3 | 9.5 | 7.9 | 9.1 |
| $A_1$ | 0.003 ± 0.002 | −1.357 ± 0.030 | −0.747 ± 0.009 | −0.345 ± 0.008 |
| $A_2$ | −0.008 ± 0.004 | 0.466 ± 0.060 | 0.062 ± 0.018 | 0.170 ± 0.017 |
| $A_3$ | −0.016 ± 0.010 | −0.231 ± 0.151 | 0.0 | −0.127 ± 0.042 |
| $\delta(\Delta\eta)$ | 0.000 | 0.000 | 0.000 | 0.000 |

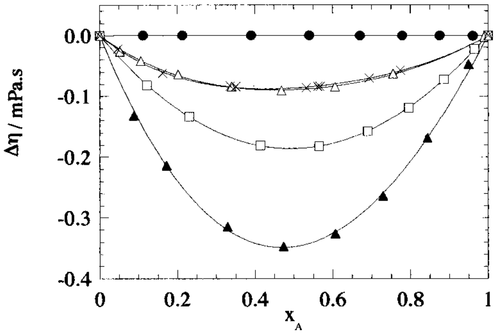

**Figure 2.** $\Delta\eta$ *vs* mole fraction of AN ($x_A$): symbols as for Figure 1. AN−MeOH (×) from Harned and Owen (1943).

the deviations from a rectilinear dependence (Fort and Moore, 1966) of viscosity of the mixture. Such values for the present systems were computed by using eq 6, where

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \qquad (6)$$

$\eta$ is the viscosity of the mixture and $\eta_1$ and $\eta_2$ are the viscosities of the pure components, respectively (Tables 1 and 2). $\Delta\eta$ values for the present binary mixtures have been plotted in Figure 2. In Figure 2, $\Delta\eta$ for the AN−MeOH system has also been compared with those already reported for this system in the literature (Harned and Owen, 1943) and they are found to be in good agreement with each other. $\Delta\eta$ is fitted to eq 5, and the constants characteristic of each system are listed in Table 3.

***Kirkwood Correlation Factor, g.*** In order to elucidate the optical and permittivity behavior on the basis of molecular orientation, the degree of orientation of the dipoles, Kirkwood correlation factor, $g$, has been calculated from the Cole equation (Cole, 1957)

$$g = (9kTV/4\pi N\mu_g^{\,2})\{(\epsilon - \epsilon_\alpha)(2\epsilon + \epsilon_a)/\epsilon(\epsilon_\alpha + 2)^2\} \qquad (7)$$

where $k$ is the Boltzmann constant, $T$ is absolute temperature, $V$ is the molar volume, $N$ is Avrogadro's number, $\mu_g$ is the electric moment of the free molecule, $\epsilon$ and $\epsilon_\alpha$ are the relative permittivity and the high-frequency limiting value which has been assumed (Dannhauser and Bahe, 1964) to be equal to $\epsilon_\alpha = 1.1n_D^2$ (Table 1). The explanation of the variation of the $g$ factor is generally carried out in terms of the specific influence of the hydrogen bonds. The $g > 1$ or $g < 1$ indicates the formation of multimers with large and small dipole moments, respectively. The value of $g$ close to 1 indicates the nonexistence of hydrogen bond formation because the effects of both kinds of multimers with large and small dipoles neutralize each other. $g$ values calculated for AN−DMA, AN−DMSO, AN−NB, and AN−MeOH mixtures are plotted against the mole fraction of AN ($x_A$) in Figure 3. $g$ values for pure AN, DMA, DMSO, NB, and MeOH are 0.74, 1.27, 1.13, 0.86, and 2.81, respectively.

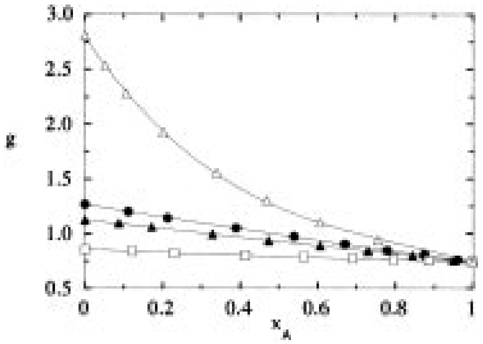

**Figure 3.** $g$ *vs* mole fraction of AN ($x_A$): symbols as for Figure 1.

Figure 3 shows that $g$ values for AN−NB, AN−DMA, and AN−DMSO mixtures have a linear variation from pure CS to AN upon addition of AN. This can be ascribed to the nonexistence of hydrogen bonding between the unlike molecules of these binary mixtures. However, $g$ for the AN−MeOH mixture has a significant large nonlinear variation with $g > 1$ in the MeOH rich region of this mixture. This indicates that the addition of AN in MeOH leads to the breakdown of MeOH structure and results in the formation of large multimers with large dipole moments (Bottcher, 1952) and with predominantly parallel alignment between the unlike molecules.

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