J. Chem. Eng. Data **1997,** *42,* 298−300

Thermodynamic Behavior of Mixtures. 4. Mixtures of Methanol with Pyridine and *N*,*N*-Dimethylformamide at 25 °C

Mandeep Singh Bakshi*

Department of Chemistry, Guru Nanak Dev University, Amritsar-143005, Punjab, India

Gurinder Kaur

Department of Physics, Guru Nanak Dev University, Amritsar-143005, Punjab, India

Ultrasonic velocities (u), densities (ρ), viscosities (η), relative permittivities (ϵ_r), and refractive indices (n_D) of mixtures of methanol (MeOH) with pyridine and *N*,*N*-dimethylformamide (DMF) have been measured at 25 °C. From u, ρ, and η, deviation in isentropic compressibilities (κ_s^E), excess volumes (V^E), and viscosities ($\Delta\eta$) have been computed. From n_D and ϵ_r values, the Kirkwood correlation factor, g, has been evaluated. The variation of such properties shows specific interactions between the components of MeOH + pyridine and MeOH + DMF binary mixtures.

Introduction

In our recent work, we have demonstrated the thermodynamic behavior of highly polar organic solvents consisting of a dipolar aprotic solvent as a common component (Bakshi, 1993a,b). However, in our present work, instead of taking a dipolar aprotic solvent, a dipolar protic solvent, methanol (MeOH), has been used as a common component in combination with dipolar aprotic solvents pyridine and *N*,*N*-dimethylformamide (DMF). It has generally been observed that dipolar protic solvents like MeOH mainly undergo electrostatic interactions with other dipolar solvents through the hydrogen bond formation, which subsequently imparts significant structural alterations in the bulk (Bakshi et al., 1996).

Experimental Section

Ultrasonic velocities, densities, viscosities, relative permittivities, and refractive indices of methanol + pyridine (MeOH + pyridine) and methanol + *N*,*N*-dimethylformamide (MeOH + DMF) binary mixtures were measured at (25 ± 0.01) °C over the entire composition range. The experimental procedure for the above mentioned parameters is essentially the same as reported previously (Bakshi et al., 1996).

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 ± 0.1 m s^{-1}, $\pm 1 \times 10^{-5}$ g cm^{-3}, 0.001 mPa s, ± 0.1, and $\pm 0.000\,01$, respectively.

MeOH and pyridine, both 99% pure from E. Merck Bombay, were further purified by the methods reported elsewhere (Riddick and Bunger, 1970). Methanol was first dried over activated molecular sieves and then fractionally distilled thrice. Pyridine was dried on silica gel and fractionally distilled twice from phosphorus pentaoxide before use. *N*,*N*-Dimethylformamide was distilled under reduced pressure of 5 Torr at least twice over calcium hydride before use. 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, ρ, η, ϵ, and n_D values for pure components are reported in Table 1 and compared with those available in the literature and are found to be in good agreement with each other. Such values for MeOH + pyridine and MeOH + DMF binary mixtures have been listed in Table 2.

Table 1. Ultrasonic Velocities (u), Densities (ρ), Viscosities (η), Relative Permittivities (ϵ), and Refractive Indicies (n_D) of Methanol (MeOH), Pyridine, and *N*,*N*-Dimethylformamide (DMF), at 25 °C

	MeOH	pyridine	DMF
u/m s^{-1}	1102.8 (1103)[d]	1481.2	1466.0 (1466.0)[e]
ρ/g cm^{-3}	0.786 80 (0.7868)[b]	0.978 10 (0.978 22)[c]	0.944 00 (0.944 00)[e]
η/mPa s	0.545 (0.545)[a]	0.882 (0.884)[c]	0.796 (796)[f]
ϵ	32.6 (32.7)[c]	12.1 (12.1)[c]	37.6 (37.10)[c]
n_D	1.32601 (1.3265)[c]	1.50701 (1.507 45)[c]	1.42810 (1.428 17)[c]

[a] Bakshi et al., 1996. [b] Nikam et al., 1995. [c] Riddick and Bunger, 1970. [d] Weast, 1988−89. [e] Singh and Bakshi, 1992. [f] Gill and Bakshi, 1988.

Results and Discussion

Ultrasonic and Volumetric Behavior. From κ_s (where $\kappa_s = 1/u^2\rho$) and ρ values for MeOH + pyridine and MeOH + DMF systems, deviation in isentropic compressibilities (Douhèret and Pal, 1989) (κ_s^E) and excess volumes (V^E) have been computed using eqs 1−4 and are plotted against

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \tag{1}$$

$$\kappa_s^{id} = \sum \phi_i\{\kappa_s + TV_i\alpha_i^{\,2}/C_{p,i}\} - T\{\sum x_i V_i\}\{\sum \phi_i\alpha_i\}^2/\{\sum x_i, C_{p,i}\} \tag{2}$$

$$\phi_i = x_i V_{mi}/\sum_i x_i V_{mi} \tag{3}$$

$$V^E = (x_1M_1 + x_2M_2)/\rho - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \tag{4}$$

the volume fraction (ϕ) and mole fraction (x) of MeOH in Figures 1 and 2, respectively. In eqs 1−4, ϕ_i, V_i, α_i, and $C_{p,i}$ are the volume fraction, molar volume, coefficient of thermal expansion and heat capacity at constant pressure of the pure component (Riddick and Bunger, 1970), i. T is the absolute temperature. x_1 , x_2, and ρ_1, ρ_2 are the mole

S0021-9568(96)00300-7 CCC: $14.00 © 1997 American Chemical Society

Table 2. Ultrasonic Velocities (u), Densities (ρ), Viscosities (η), Relative Permittivities (ϵ), and Refractive Indicies (n_D) of Methanol + Pyridine (MeOH + Pyridine), Methanol + *N*,*N*-Dimethylformamide (MeOH + DMF) Binary Mixtures at the Corresponding Mole Fraction of MeOH (x) at 25 °C

x	u/m s^{-1}	ρ/g cm^3	η/mPa s	ϵ	n_D
		MeOH + Pyridine			
0.000	1418.2	0.978 10	0.882	12.1	1.507 01
0.1249	1404.5	0.967 60	0.850	14.5	1.495 10
0.2338	1387.7	0.957 92	0.820	16.6	1.487 98
0.4192	1354.3	0.937 79	0.763	20.2	1.466 01
0.5695	1313.9	0.914 83	0.714	23.2	1.442 00
0.6940	1271.4	0.889 04	0.670	25.8	1.425 02
0.7987	1226.4	0.861 28	0.631	28.1	1.396 20
0.8881	1177.6	0.832 39	0.596	30.0	1.372 00
0.9652	1127.8	0.803 13	0.565	31.7	1.341 10
1.000	1102.8	0.786 80	0.545	32.6	1.326 00
		MeOH + DMF			
0.0000	1466.0	0.944 30	0.796	37.6	1.428 10
0.1198	1436.5	0.936 70	0.766	37.8	1.417 98
0.2267	1403.8	0.928 14	0.739	38.1	1.406 01
0.4094	1354.5	0.907 61	0.693	38.3	1.395 00
0.5596	1309.0	0.885 19	0.655	38.1	1.386 02
0.6854	1260.2	0.862 57	0.623	37.5	1.370 01
0.7922	1208.2	0.840 62	0.596	36.4	1.358 03
0.8840	1159.2	0.819 00	0.573	35.0	1.344 01
0.9639	1122.8	0.797 50	0.553	33.5	1.335 05
1.000	1102.8	0.786 80	0.545	32.6	1.326 00

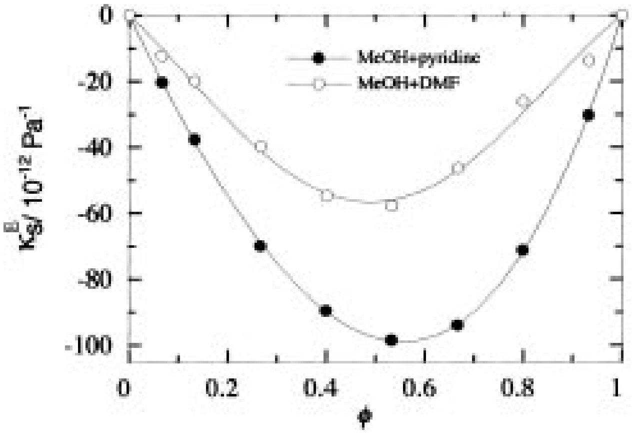

Figure 1. κ_s^E vs volume fraction of MeOH (ϕ).

fractions and densities of MeOH and co-solvent, and κ_s and ρ are the compressibility and density of the mixture, respectively. κ_s^E and V^E values thus obtained are further fitted to a polynomial equation in the following form

$$Y^E = x_1(1 - x_1)\{A_0 + A_1(2x_1 - 1) + A_2(2x_1 - 1)^2\} \quad (5)$$

where Y^E is the excess property. A_0, A_1, and A_2 are the constants characteristic of the system, and their values along with the standard deviations {i.e. $\delta(\kappa_s^E)$ and $\delta(V^E)$} are listed in Table 3. It can be seen from Figures 1 and 2 that both the excess properties show negative deviations for both the mixtures.

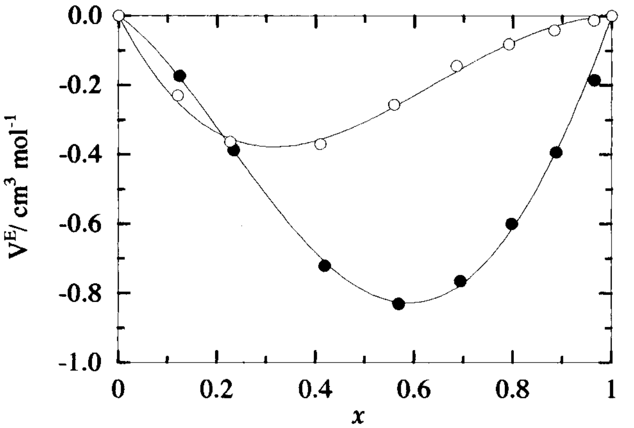

Figure 2. V^E vs mole fraction of MeOH (x): symbols as for Figure 1.

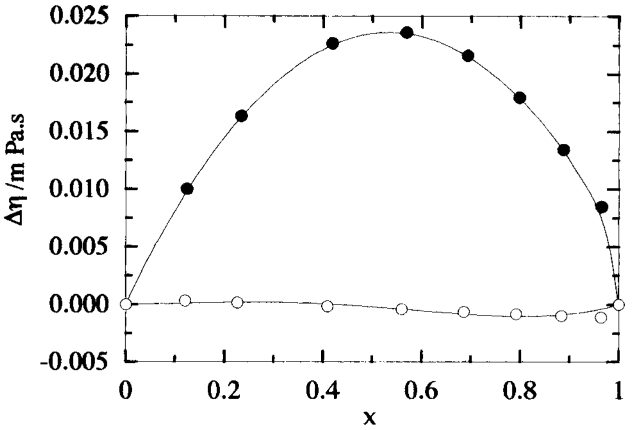

Figure 3. $\Delta\eta$ vs mole fraction of MeOH (x): symbols as for Figure 1.

Viscometric Behavior. Excess viscosities ($\Delta\eta$) for the present systems were computed by using eq 6 and are plotted against the mole fraction of MeOH (x) in Figure 3.

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

where $\Delta\eta$ is simply the extent of deviation of η in the mixture from additivity and η_1 and η_2 are the viscosities of the pure components, respectively. $\Delta\eta$ values are fitted to eq 5, and the constants characteristic of the system are listed in Table 3. Figure 3 shows that variation of $\Delta\eta$ is practically negligible for MeOH + DMF and positive for MeOH + pyridine. It has already been found that the sign of $\Delta\eta$ can be correlated to that of V^E in a number of binary mixtures. $\Delta\eta$ is positive when V^E is negative (Nath and Dubey, 1981; Prolongo et al., 1984). The same is also true for the MeOH + pyridine system herein.

Kirkwood Correlation Factor, g. In order to elucidate the optical and permittivity behavior on the basis of molecular orientation, the degree of orientations of dipoles, Kirkwood correlation factor, g, has been calculated for MeOH + pyridine and MeOH + DMF binary mixtures from the Cole equation (Cole, 1957)

$$g = (9kTV/4\pi N\mu_g^2)\{(\epsilon_r - \epsilon_\alpha)(2\epsilon_r + \epsilon_\alpha)/\epsilon_r(\epsilon_\alpha + 2)^2\} \quad (7)$$

where k is the Boltzmann constant, T is absolute temperature, V is the molar volume, N is the Avogadro number, μ_g is the electric moment of the free molecule, ϵ_r and ϵ_α are the relative permittivity and the high-frequency limiting value which has been assumed (Dannhauser and Bahe, 1964) to be equal to $\epsilon_\alpha = 1.1n_D^2$. g values for MeOH, pyridine, and DMF are 2.81, 0.86, and 1.05, respectively. The explanation of the variation of the g factor is generally carried out in terms of the specific influence of the hydrogen bonds. $g > 1$ or $g < 1$ indicates the formation of multimers with large or small dipole moments with predominantly parallel or antiparallel alignment, respectively (Böttcher, 1952). g values calculated for MeOH + pyridine and MeOH + DMF binary mixtures are large and positive ($g > 1$), which show the presence of large aggregates with large dipole moments with predominantly parallel alignment between the unlike molecules. From g values, the devia-

Table 3. Parameters (A_i) of Equation 5 and Standard Deviations, $\delta(\kappa_s^E/10^{-12}\ Pa^{-1})$, $\delta(V^E/cm^3\ mol^{-1})$, and $\delta(\Delta\eta/mPa\ s)$, for Methanol + Pyridine (MeOH + Pyridine) and Methanol + N,N-Dimethylformamide (MeOH + DMF) at 25 °C

system	A_0	A_1	A_2	$\delta(\kappa_s^E)$
MeOH + pyridine	674.7 ± 6.78	441.5 ± 12.23	257.2 ± 27.2	42.35
MeOH + DMF	545.7 ± 20.10	269.3 ± 36.5	0.0	37.71
system	A_0	A_1	A_2	$\delta(V^E)$
MeOH + pyridine	3.1737 ± 0.0593	1.5030 ± 0.1070	0.6952 ± 0.2388	0.0032
MeOH + DMF	1.2217 ± 0.0349	1.3608 ± 0.0634	0.1836 ± 0.1409	0.0011
system	A_0	A_1	A_2	$\delta(\Delta\eta)$
MeOH + pyridine	0.092 ± 0.004	0.021 ± 0.007	0.039 ± 0.017	0.000
MeOH + DMF	−0.001 ± 0.001	−0.006 ± 0.001	−0.005 ± 0.003	0.000

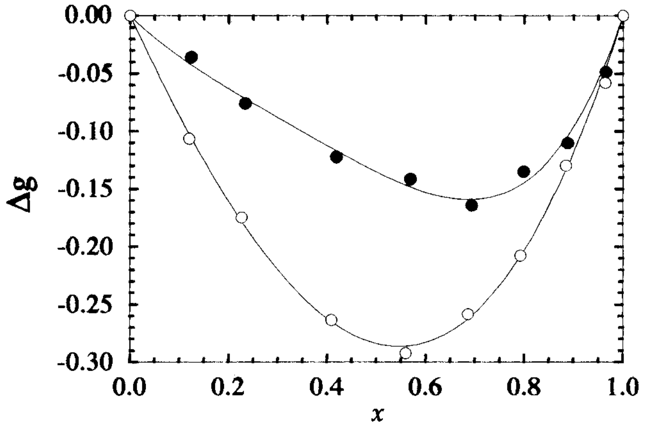

Figure 4. Δg *vs* mole fraction of MeOH (x): symbols as for Figure 1.

tion in the Kirkwood correlation factor (Δg) can be calculated from the following empirical equation (Nath and Saini, 1990)

$$\Delta g = g - (g_1x_1 + g_2x_2) \qquad (8)$$

Δg values have been plotted in Figure 4. Both the binary mixtures show negative deviations which can be attributed to the specific interactions between the unlike molecules and are larger for the MeOH + DMF in comparison to the MeOH + pyridine binary mixture. It seems that the dipole−dipole interactions between the components of MeOH + DMF lead to a much more ordered structure in comparison to MeOH + pyridine which leads to stronger deviations.

Literature Cited

Bakshi, M. S. Thermodynamic Behaviour of Mixtures. Part 1. *J. Chem. Soc., Faraday Trans.* **1993a**, *89*, 2001−2005.

Bakshi, M. S. Thermodynamic Behaviour of Mixtures. Part 2. *J. Chem. Soc., Faraday Trans.* **1993b**, *89*, 3049−3054.

Bakshi, M. S.; Singh, J.; Kaur, H.; Ahmad, S. T.; Kaur, G.; Thermodynamic Behaviour of Mixtures. Part 3. *J. Chem. Eng. Data* **1996**, *41*, 1459−1461.

Böttcher, C. J. F. *Theory of Dielectric Polarisation*; Elsevier Publishing Co.: Amsterdam, 1952.

Cole, R. H. Induced Polarization and Dielectric Constant of Polar Liquids. *J. Chem. Phys.* **1957**, *27*, 33−35.

Douhèret, G.; Pal, A. Excess Thermodynamic Properties. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2723−2736.

Dannhauser, W.; Bahe, W. Dielectric Contants of Hydrogen Bonded Liquids. *J. Chem. Phys.* **1964**, *40*, 3058−3066.

Gill, D. S.; Bakshi, M. S. Transference Number Meaurements. *J. Chem. Soc., Faraday Trans.* **1988**, *84*, 3517−3528.

Nath, J.; Dubey, S. N. Binary Sytems, Viscosities at 303.15 K. *J. Phys. Chem.* **1981**, *85*, 886−889.

Nath, J.; Saini, R. Ultrasonic and Dielectric Behaviour of Binary Mixtures. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 645−650.

Nikam, et al. *J. Chem. Eng. Data* **1995**, *40*, 931−934.

Prolongo, M. G.; Masegosa, R. M.; Hernandez-Fuentes, I.; Horta, A. Viscosities of Binary Mixtures. *J. Phys. Chem.* **1984**, *88*, 2163−2167.

Riddick, J. A.; Bunger, W. B. *Organic Solvents*; Wiley Interscience: New York, 1970.

Singh, J.; Bakshi, M. S. Ultrasonic Velocities, Densities and Refractive Indices. *J. Chem. Res.* **1992**, (S) 218−219, (M) 1701−1739.

Weast, R. C. *CRC Handbook of Chemistry and Physics*, 69th ed.; CRC Press Inc.: Boca Raton, FL, 1988−89.

Received for review September 9, 1996. Accepted November 18, 1996.⊗

JE960300P

⊗ Abstract published in *Advance ACS Abstracts,* January 15, 1997.