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Ultrasonic Investigation on the Structure of Aqueous Solutions of *N*,*N*-Dimethylformamide and Dimethyl Sulfoxide

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The effects of *N*,*N*-dimethylformamide and dimethyl sulfoxide on the temperature of adiabatic compressibility minimum (T_β) and sound velocity maximum (T_u) of water have been studied. The structural contributions to the shift in T_β and T_u, $[\Delta T_{\beta\ \mathrm{str.}}]_{\mathrm{exp.}}$ and $[\Delta T_{u\ \mathrm{str.}}]_{\mathrm{exp.}}$, have been found to be negative for both solutes. Both $[\Delta T_{\beta\ \mathrm{str.}}]_{\mathrm{exp.}}$ and $[\Delta T_{u\ \mathrm{str.}}]_{\mathrm{exp.}}$ are higher for dimethyl sulfoxide than *N*,*N*-dimethylformamide indicating that the sulfinyl group ($\rangle$SO) is more efficient in structure disruption than the formylimino group ($\rangle$F). The results have been explained in the light of hydrogen bonding equilibria by the solutes.

In recent years the effect of nonelectrolytes on the hydrogen-bonded structure of water has been studied extensively by observing the non-ideal thermodynamic behavior such as viscosity composition maxima,1) negative partial molal volumes2–4) and partial molal heat capacity at infinite dilution.5–7) The structure of aqueous nonelectrolyte solution may also be investigated by determining the shift in the extrema in various physical properties of water caused by the addition of nonelectrolytes. Effects of nonelectrolytes on the density maximum temperature (DMT) of water have been studied extensively8–15) and the results have been utilized successfully to classify the solutes as structure promoters and disrupters. Recent studies on the effect of nonelectrolytes on the adiabatic compressibility minimum temperature16–20) (ACMT) and sound velocity maximum temperature21,22) (SVMT) have been found to be useful in understanding their structural behavior.

Aqueous solutions of *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) are known to be the best mixtures and reaction media. DMSO and DMF interact with water through hydrogen-bonding, but details of such interactions are not well characterised. The studies on density maximum by Macdonald *et al.*,11) excess Gibbs free energy by Clever and Piggott23) and the infrared spectroscopy by Brink and Falk24) on aqueous DMSO characterise DMSO as a structure disrupter, while studies on standard free energy by Oakenfull and Fenwick,28) X-ray diffraction and neutron inelastic scattering by Safford *et al.*,26) partial molar enthalpies by Rallo *et al.*25) apparent molar volume and heat capacity by de Visser *et al.*27) on water+DMSO system classify DMSO as a structure promotor. DMF is also representative of a class of solutes29) including dioxane, dimethylsulfoxide and possibly acetone which are only weakly hydrophobic and probably have little overall influence on the structure of water.

In view of the growing importance of sulfoxides and amides as solutes in biochemical and physicochemical investigations involving water as solvent and also of the fact that contraversial conclusions in particular have been drawn regarding the solute-solvent interactions and structural propensity of DMSO, we have taken up the studies on the effect of DMSO and DMF on SVMT and ACMT of water and the results are reported in this paper.

Experimental

Analar grade DMF and DMSO were used after necessary purification.30) The purity of the samples were checked by determining their densities at 25 °C using a bicapillary type pycknometer with an accuracy of 2 parts in 10^5, the values being in good agreement with literature data.4,27) Ultrasonic velocity (u) was determined using a single crystal variable path interferometer working at 3 MHz with an accuracy of ±0.003%. The details of the measurement of ultrasonic velocity were reported in a previous paper.16) Triple distilled degassed water was used to prepare solutions of DMF and DMSO of various concentrations. Ultrasonic velocities and densities were determined at an interval of ≃2 °C over a range of 5 °C on either side of SVMT and ACMT. The velocities were corrected for diffraction effects following the procedure reported.31) The adiabatic compressibilities calculated using the formula $\beta = u^{-2}\rho^{-1}$ are accurate to ±0.01%. At low concentrations of the organic solute, the temperature dependence of the adiabatic compressibility and ultrasonic velocity in solutions is similar to that of the curves for pure water. Transparent templates of the curves of pure water were used to determine SVMT (T_u) and ACMT (T_β) of solutions. The accuracy of the values of T_β and T_u are ±0.4 and ±0.2 °C, respectively.

Results and Discussion

Results of the measurement of adiabatic compressibility and ultrasonic velocity as a function of temperature at different concentrations of dilute aqueous solutions of DMF and DMSO are shown graphically in Figs. 1—4.

Expressions for T_u and T_β in aqueous solutions are obtained by considering the basic expressions for u and β in pure components as a function of temperature and the expression for the β of the solution in terms of the compressibilities of pure components. The details of the derivation were reported.19) The final expressions are as follows.

$$
\begin{aligned}
T_{\beta\ \mathrm{sol.}} = {} & \left[64 - \frac{\phi_2\alpha_\beta}{\phi_1 0.0032\times10^{-11}}\right] \\
& \times\left[1+\frac{\phi_2\alpha_\beta^1}{\phi_1 0.0016\times10^{-11}}\right]^{-1} \\
& -\frac{\mathrm{d}\beta^{\mathrm{E}}}{\mathrm{d}t}(\phi_1 0.0032\times10^{-11})^{-1} \\
& \times\left[1+\frac{\phi_2\alpha_\beta^1}{\phi_1 0.0016\times10^{-11}}\right]^{-1},
\end{aligned}
\tag{1}
$$

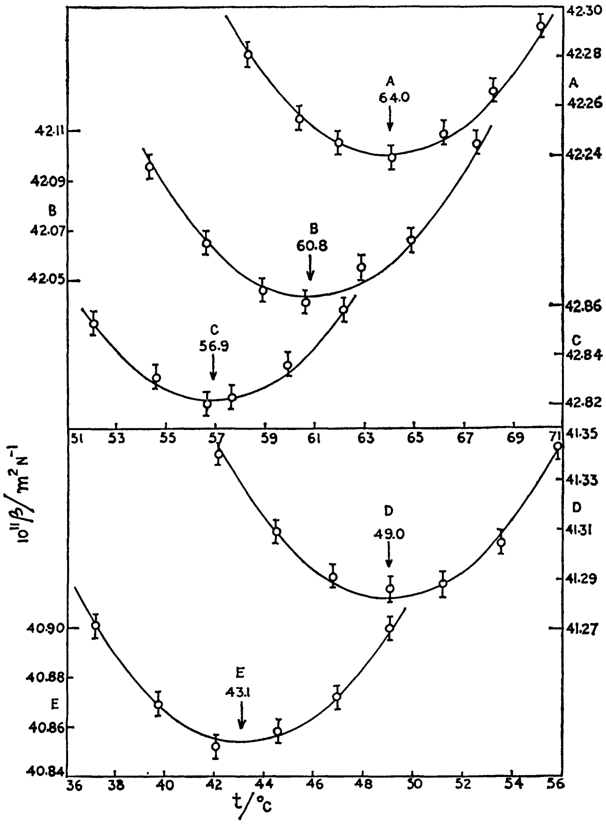

Fig. 1. Adiabatic compressibility, β, plotted against temperature of solutions of aqueous *N*,*N*-dimethylformamide.

A: $X_2=0.0000$, B: $X_2=0.0046$, C: $X_2=0.0095$, D: $X_2=0.0201$, E: $X_2=0.0279$.

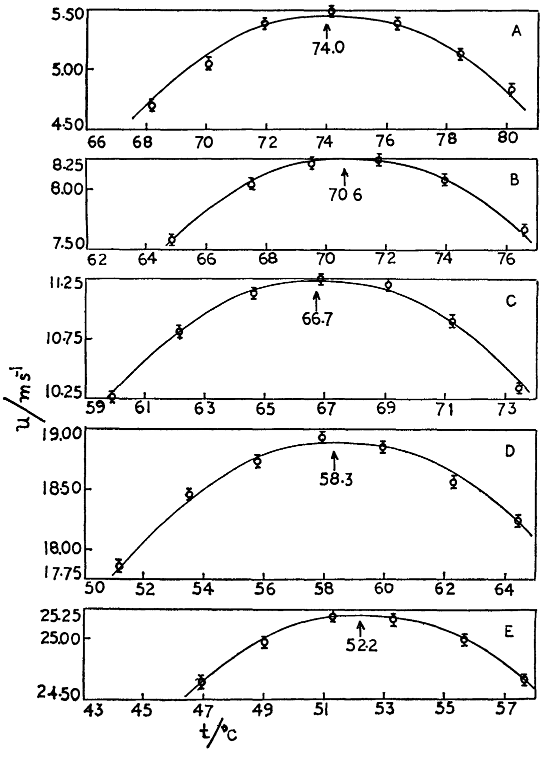

Fig. 2. Ultrasonic velocity, *u*, plotted against temperature, in solutions of aqueous *N*,*N*-dimethylformamide. The values given in the ordinate have to be added to 1550 ms^{-1}. A: $X_2=0.0000$, B: $X_2=0.0046$, C: $X_2=0.0095$, D: $X_2=0.0201$, E: $X_2=0.0279$.

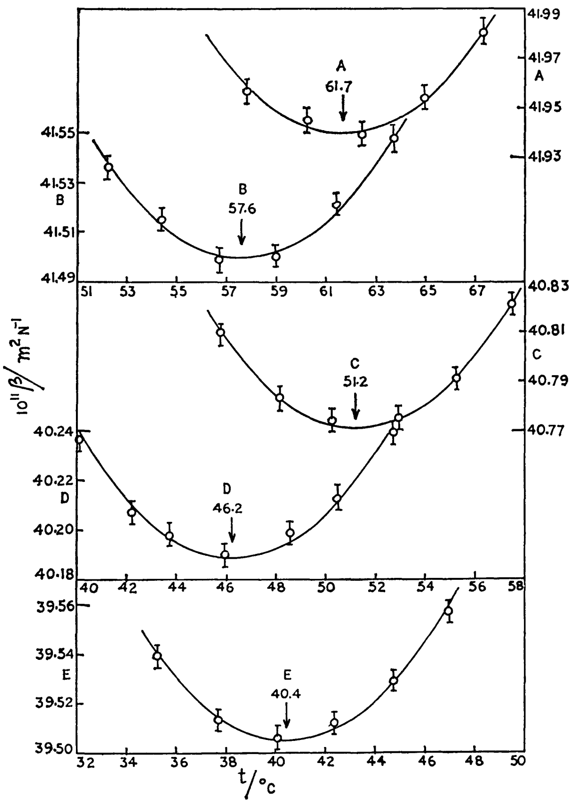

Fig. 3. Adiabatic compressibility, β, plotted against temperature of solutions of aqueous dimethyl sulfoxide. A: $X_2=0.0044$, B: $X_2=0.0115$, C: $X_2=0.0225$, D: $X_2=0.0308$, E: $X_2=0.0402$.

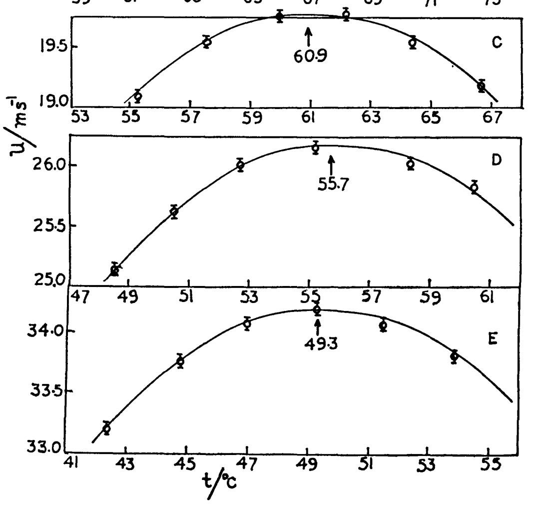

Fig. 4. Ultrasonic velocity, *u*, plotted against temperature, in solutions of aqueous dimethyl sulfoxide. The values given in the ordinate have to be added to 1550 ms^{-1}. A: $X_2=0.0044$, B: $X_2=0.0115$, C: $X_2=0.0225$, D: $X_2=0.0308$, E: $X_2=0.0402$.

TABLE 1. β_2^0, α_β, α_β^1, u_2^0, AND α_u FOR *N,N*-DIMETHYLFORMAMIDE AND DIMETHYL SULFOXIDE

Solute	$\beta_2^0\times10^{11}$ / $\mathrm{m^2\,N^{-1}}$	$\alpha_\beta\times10^{11}$ / $\mathrm{m^2\,N^{-1}\,°C^{-2}}$	$\alpha_\beta^1\times10^{11}$ / $\mathrm{m^2\,N^{-1}\,°C^{-2}}$	u_2^0 / $\mathrm{ms^{-1}}$	α_u / $\mathrm{ms^{-1}\,°C^{-1}}$
N,N-Dimethylformamide	43.046	0.21816	0.001740	1556.77	3.82470
Dimethyl sulfoxide	36.007	0.17048	0.000985	1576.98	3.34693

TABLE 2. $T_{\beta\ \mathrm{id.}}$, $T_{\beta\ \mathrm{exp.}}$, $(\mathrm{d}\beta^E/\mathrm{d}t)$, AND $\Delta T_{\beta\ \mathrm{str.}}$ AT DIFFERENT MOLE FRACTION X_2 OF *N,N*-DIMETHYL FORMAMIDE AND DIMETHYL SULFOXIDE IN WATER

Solute	X_2	$T_{\beta\ \mathrm{id.}}$ / °C	$T_{\beta\ \mathrm{exp.}}$ / °C	$(\mathrm{d}\beta^E/\mathrm{d}t)\times10^{14}$ / $\mathrm{m^2\,N^{-1}\,°C^{-1}}$	$\Delta T_{\beta\ \mathrm{str.}}$/°C	
					Exptl	Calcd
N,N-Dimethylformamide	0.0046	61.3	60.8	0.7±0.3	−0.5±0.4	−0.2±0.1
	0.0095	58.5	56.9	2.1±1.1	−1.6±0.4	−0.7±0.3
	0.0201	52.8	49.0	9.2±4.1	−3.8±0.4	−2.9±1.3
	0.0279	48.9	43.1	17.0±8.5	−5.8±0.4	−5.3±2.6
Dimethyl sulfoxide	0.0044	62.4	61.7	1.0±0.6	−0.7±0.4	0.3±0.2
	0.0115	59.8	57.6	4.3±2.2	−2.2±0.4	−1.4±0.7
	0.0225	55.9	51.2	10.6±5.3	−4.7±0.4	−3.4±1.7
	0.0308	53.1	46.2	18.3±8.2	−6.9±0.4	−6.0±2.7
	0.0402	50.0	40.4	28.2±14.1	−9.6±0.4	−9.3±4.7

TABLE 3. $T_{\mathrm{u\ id.}}$, $T_{\mathrm{u\ exp.}}$, $(\mathrm{d}\rho/\mathrm{d}t)$, $(\mathrm{d}\beta^E/\mathrm{d}t)$, AND $\Delta T_{\mathrm{u\ str.}}$ AT DIFFERENT MOLE FRACTIONS X_2 OF *N,N*-DIMETHYLFORMAMIDE AND DIMETHYLSULFOXIDE IN WATER

Solute	X_2	$T_{\mathrm{u\ id.}}$ / °C	$T_{\mathrm{u\ exp.}}$ / °C	$(\mathrm{d}\rho/\mathrm{d}t)\times10^3$ / $\mathrm{kg\,m^{-3}\,°C^{-1}}$	$(\mathrm{d}\beta^E/\mathrm{d}t)\times10^{14}$ / $\mathrm{m^2\,N^{-1}\,°C^{-1}}$	$\Delta T_{\mathrm{u\ str.}}$/°C	
						Exptl	Calcd
N,N-Dimethylformamide	0.0046	71.0	70.6	−59	−0.9±0.4	−0.4±0.2	0.2±0.2
	0.0095	67.9	66.7	−59	−0.5±0.2	−1.2±0.2	−0.1±0.1
	0.0201	61.7	58.3	−57	2.9±1.3	−3.4±0.2	−1.8±0.5
	0.0279	57.6	52.2	−57	8.7±3.9	−5.4±0.2	−4.5±1.6
Dimethyl sulfoxide	0.0044	72.2	71.5	−60	0.7±0.4	−0.7±0.2	−0.4±0.2
	0.0115	69.4	67.3	−60	2.2±1.1	−2.1±0.2	−1.1±0.4
	0.0225	65.2	60.9	−57	7.2±3.2	−4.3±0.2	−3.4±1.3
	0.0308	62.2	55.7	−58	11.2±5.6	−6.5±0.2	−5.4±2.4
	0.0402	59.0	49.3	−58	19.1±8.6	−9.7±0.2	−9.2±3.8

$$T_{\mathrm{u\ sol.}}=\left[74-\left(\frac{\phi_2}{\phi_1}\right)^2\left(\frac{W_1}{W_2}\right)\left(\frac{\alpha_u}{0.049}\right)\frac{(u_1)^3}{(u_2)^3}\right]-\left(\frac{W_1}{\phi_1^{\,2}}\right)\left(\frac{u_1^{\,3}}{0.098}\right)\left[\rho\frac{\mathrm{d}\beta^E}{\mathrm{d}t}+\beta^E\frac{\mathrm{d}\rho}{\mathrm{d}t}\right]. \tag{2}$$

Where ϕ_1, ϕ_2 and W_1, W_2 represent the volume fractions and weight fractions of pure water and organic solute, respectively, in solution. α_β and α_β^1 are the coefficients involved in the relation for the adiabatic compressibility as a function of temperature (t) of organic solute given below:

$$\beta_2=\beta_2^0+\alpha_\beta\,t+\alpha_\beta^1\,t^2. \tag{3}$$

Where α_u represents the coefficient involved in the expression for temperature dependence of velocity in the organic solute, namely

$$u_2=u_2^0-\alpha_u{}^t. \tag{4}$$

Where u_1 and u_2 are velocities in pure water and organic solute, respectively. β^E represents the excess adiabatic compressibility. The values of β_2^0, α_β, α_β^1, u_2^0, and α_u for DMF and DMSO are evaluated using ultrasonic velocity determined experimentally and density data at different temperatures. The values are given in Table 1.

The shifts produced $\Delta T_\beta=(T_{\beta\ \mathrm{sol.}}-T_{\beta\ \mathrm{water}})$ and $\Delta T_u=(T_{\mathrm{u\ sol.}}-T_{\mathrm{u\ water}})$ may be divided into an ideal contribution ($\Delta T_{\mathrm{u\ id.}}$ and $\Delta T_{\beta\ \mathrm{id.}}$) and structural contribution ($\Delta T_{\mathrm{u\ str.}}$ and $T_{\beta\ \mathrm{str.}}$) according to Eqs. 1 and 2. The ideal contribution is always negative, but the structural contribution can either be positive or negative, indicating either structure promotion or structure disruption by the solute.

The second terms on the right hand side of Eqs. 1 and 2 represent $\Delta T_{\beta\ \mathrm{str.}}$ and $\Delta T_{\mathrm{u\ str.}}$, respectively. They can also be obtained experimentally using the following relations.

$$[\Delta T_{\beta\ \mathrm{str.}}]_{\mathrm{exp.}}=T_{\beta\ \mathrm{exp.}}-T_{\beta\ \mathrm{id.}}, \tag{5}$$

$$[\Delta T_{\mathrm{u\ str.}}]_{\mathrm{exp.}}=T_{\mathrm{u\ exp.}}-T_{\mathrm{u\ id.}}, \tag{6}$$

where $T_{\beta\ \mathrm{id.}}$ and $T_{\mathrm{u\ id.}}$ are given by the first terms of the right hand sides of Eqs. 1 and 2, respectively. These temperatures correspond to those at which adiabatic compressibility minimum of and sound velocity maximum in the solution would take place if ideal mixing occurs. Since the temperature dependence of ϕ_1 and ϕ is small, ϕ_1 and ϕ_2 used to determine $T_{\beta\ \mathrm{id.}}$

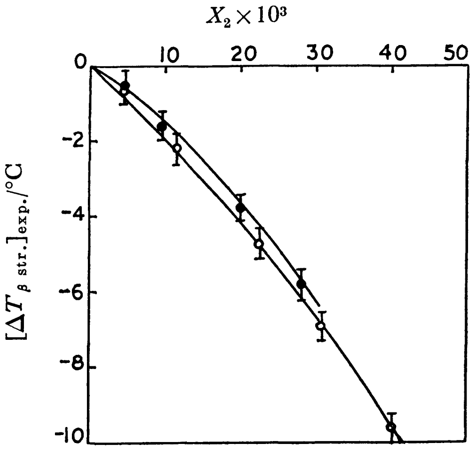

Fig. 5. Structural shifts, $[\Delta T_{\beta\mathrm{str.}}]_{\mathrm{exp.}}$, plotted against X_2 of *N*,*N*-dimethylformamide and dimethyl solfolxide. ●: *N*,*N*-Dimethyl formamide, ○: dimethyl solfoxide.

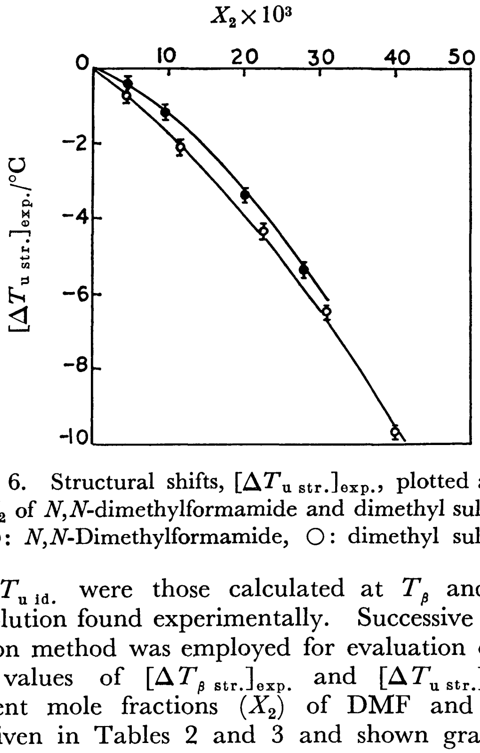

Fig. 6. Structural shifts, $[\Delta T_{\mathrm{u\,str.}}]_{\mathrm{exp.}}$, plotted against X_2 of *N*,*N*-dimethylformamide and dimethyl sulfoxide. ●: *N*,*N*-Dimethylformamide, ○: dimethyl sulfoxide.

and $T_{\mathrm{u\,id.}}$ were those calculated at T_β and T_u of the solution found experimentally. Successive approximation method was employed for evaluation of $T_{\mathrm{u\,id}}$. The values of $[\Delta T_{\beta\,\mathrm{str.}}]_{\mathrm{exp.}}$ and $[\Delta T_{\mathrm{u\,str.}}]_{\mathrm{exp.}}$ at different mole fractions (X_2) of DMF and DMSO are given in Tables 2 and 3 and shown graphically in Figs. 5 and 6, respectively. The negative shifts increase with increasing X_2, indicating that both DMF and DMSO promote disruption of the three dimensional structure of water.

The spectroscopic and thermodynamic studies of aqueous DMSO by Fox and Whittingham[32] indicate hydrophobic hydration of DMSO in water, only when DMSO is present in a small amount *i.e.* $X_2 \leq 0.005$. At higher concentration complex formation is predominant. The extrema that have been observed in the excess enthalpy,[32] isothermal compressibility,[33] viscosity[34] and activation volume for benzyl chloride solvolysis[35] around $X_2 \simeq 0.35$ indicate the formation of 2:1 (H_2O:DMSO) complexes, and do not correspond to hydrophobic hydration. As such, DMSO cannot be described as a structure promoter. The structural contribution to the shift in MDT of water for DMSO has been found to be negative,[11] indicating the structure disrupting character of DMSO which supports the present study. Studies on X-ray diffraction and neutron inelastic scattering by Safford *et al.*[26] indicate DMSO as structure promoter. The studies by Brink and Falk[24] show that addition of a few mol% of DMSO to water does not change the average value or the width of distribution of hydrogen-bond energies derived from infrared spectroscopy. The studies on the apparent molar volumes[4,27,36] and heat capacities[27,37] indicate both DMSO and DMF to be weakly hydrophobic. The minimum in the standard free energy of hydrophobic interaction ($\Delta G^\circ_{\mathrm{HI}}$) for both DMSO and DMF around $X_2 \simeq 0.25$ and 0.1 indicates that these solutes strengthen hydrophobic interaction.[28] DMF is weakly hydrophobic. However, the present study indicates that it does not enhance the long-range interaction in water. Ultrasonic velocity and adiabatic compressibility measurements carried out by Endo[38] on water+DMF system over the temperature range 20—50 °C indicate some complex formation, where the number of molecules of water per DMF molecule are 22.8, definitely not of clathrate hydrate type.[39] Thus DMF–water interactions are not of hydrophobic nature. Also ultrasonic absorption measurements made by Kawaizumi *et al.*[40] on this system indicate that added DMF molecules have the same effects as the temperature rise upon the ultrasonic absorption coefficient, and DMF has been characterized as a structure disrupter. The structural contribution to the shift in MDT is negative[12] which further confirms the structure disrupting nature of DMF. Since the structure promoting interactions are sensitive to temperature[20,41–44] different conclusions drawn only reflect the different experimental temperatures, *i.e.* 64 and 74 °C for ACMT and SVMT studies carried out in the present work, 4 °C for MDT studies, and 25 °C for the other studies. It is possible that various experimental techniques correspond to different phenomena.

One may regard the ability of the solute to perturb the structure of water as a sum of group effects as proposed by Wada and Umeda.[8] We see in Figs. 5 and 6 that the structure disrupting tendency of DMSO is greater than that of DMF. Since both solutes have a common dimethyl group, it is clear that the sulfinyl group (>SO) is more efficient in disrupting the structure of water than the formylimino group (>F).

The structural contribution to the shifts in T_β and T_u has also been calculated using the values of $\dfrac{\mathrm{d}\beta^\mathrm{E}}{\mathrm{d}t}$ at each concentration. The excess adiabatic compressibility β^E was evaluated[11] at each temperature using experimental velocities of pure components and the mixtures. At all concentrations β^E was found to be a linear function of temperature within experimental error. The calculated structural shifts $[\Delta T_{\beta\,\mathrm{str.}}]_{\mathrm{cal.}}$ and $[\Delta T_{\mathrm{u\,str.}}]_{\mathrm{cal.}}$, are also given in Tables 2 and 3 and these values compare well with the experimental ones.

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References

1) W. Hertz and E. Lorentz, *Z. Phys. Chem.*, *A*, **140**, 406 (1929).

2) V. S. Griffiths, *J. Chem. Soc.*, **1952**, 860.

3) G. N. Malcolm and J. S. Rowlinson, *Trans. Faraday Soc.*, **53**, 921 (1957).

4) F. Kawaizumi, M. Ohno, and Y. Miyahara, *Bull. Chem. Soc., Jpn.*, **50**, 2229 (1977).

5) R. K. Mohanty, S. Sunder, and J. C. Ahluwalia, *J. Phys. Chem.*, **76**, 2577 (1972).

6) E. M. Arnett, W. B. Kover, and J. V. Carter, *J. Am. Chem. Soc.*, **91**, 4028 (1969).

7) G. C. Kresheck and I. Benjamin, *J. Phys. Chem.*, **68**, 2476 (1964).

8) G. Wada and S. Umeda, *Bull. Chem. Soc. Jpn.*, **35**, 646, 1797 (1962).

9) F. Franks and B. Watson, *Trans. Faraday Soc.*, **63**, 329 (1967).

10) M. Sakurai, T. Komatsu, and T. Nakagawa, *Bull. Chem. Soc. Jpn.*, **45**, 1038 (1972).

11) D. D. Macdonald, M. D. Smith, and J. B. Hyne, *Can. J. Chem.*, **49**, 2817 (1971).

12) D. D. Macdonald, M. E. Estep, M. D. Smith, and J. B. Hyne, *J. Solution Chem.*, **3**, 713 (1974).

13) G. Wada and M. Miura, *Bull. Chem. Soc. Jpn.*, **42**, 2498 (1969).

14) D. D. Macdonald, B. Dolan, and J. B. Hyne., *J. Solution Chem.*, **5**, 405 (1976).

15) D. D. Macdonald and J. B. Hyne, *Can. J. Chem.*, **54**, 3073 (1976).

16) S. V. Subrahmanyam and N. Manohara Murthy, *J. Solution Chem.*, **4**, 347 (1975).

17) N. Manohara Murthy and S. V. Subrahmanyam, *J. Acoust. Soc. India*, **5**, 88 (1977).

18) N. Manohara Murthy and S. V. Subrahamnyam, *Acustica.*, **40**, 263 (1978).

19) N. Manohara Murthy and S. V. Subrahmanyam, *Can. J. Chem.*, **56**, 2412 (1978).

20) N. Manohara Murthy and S. V. Subrahmanyam, *J. Chem. Soc., Faraday Trans. 1*, **75**, 2067 (1979).

21) S. V. Subrahmanyam and N. Manohara Murthy, *Z. Phys. Chem. (Neue Folge)*, **88**, 116 (1974).

22) N. Manohara Murthy and S. V. Subrahmanyam, *J. Acoust. Soc. India*, **7**, 79 (1979).

23) H. L. Clever and S. P. Piggott, *J. Chem. Thermodyn.*, **3**, 221 (1971).

24) G. Brink and M. Falk, *J. Mol. Struct.*, **5**, 27 (1970).

25) F. Rallo, F. Rodante, and P. Silvestroni, *Thermochim. Acta.*, **1**, 311 (1970).

26) G. J. Safford, P. C. Schaffer, P. S. Leung, G. F. Doebbler, G. W. Brady, and E. F. X. Lyden, *J. Chem. Phys.*, **50**, 2140 (1969).

27) C. de Visser, W. J. M. Heuvelsland, L. A. Dunn, and G. Somsen, *J. Chem. Soc., Faraday Trans. 1*, **74**, 1159 (1978).

28) D. Oakenfull and D. E. Fenwick, *J. Chem. Soc., Faraday Trans. 1*, **75**, 636 (1979).

29) J. E. Desnoyers, O. Kiyohara, G. Perron, and L. Avedikian, *Adv. Chem. Ser.*, **155**, 274 (1976).

30) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon, Oxford (1966).

31) S. V. Subrahmanyam, V. Hyderkhan, and C. V. Raghavan, *J. Acoust. Soc. Am.*, **46**, 272, (1969).

32) M. F. Fox and K. P. Whittingham, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1407 (1975).

33) K. H. Jung and J. B. Hyne, *Can. J. Chem.*, **48**, 2423 (1970).

34) S. A. Schichman and R. L. Amey, *J. Phys. Chem.*, **75**, 98 (1971).

35) D. D. Macdonald and J. B. Hyne, *Can. J. Chem.*, **48**, 2494 (1970).

36) A. R. Giaquinto, R. E. Lindstrom, J. Swarbrick, and A. LoSurdo, *J. Solution Chem.*, **6**, 687 (1977).

37) C. de Visser, G. Perron, J. E. Desnoyers, W. J. M. Heuvelsland, and G. Somsen, *J. Chem. Eng. Data.*, **22**, 74 (1977).

38) H. Endo, *Bull. Chem. Soc. Jpn.*, **46**, 1106 (1973).

39) A. D. Potts and D. W. Davidson, *J. Phys. Chem.*, **69**, 996 (1965).

40) F. Kawaizumi, H. Nomura, M. Ohno, and Y. Miyahara, *Bull. Chem. Soc. Jpn.*, **52**, 3135 (1979).

41) F. Franks and D. J. G. Ives, *Quart. Rev.*, **20**, 1 (1960).

42) F. Franks, "Hydrogen Bonded Solvent Systems" Taylor and Francis, London (1968).

43) R. K. Mohanty, T. S. Sarma, S. Subramanian, and J. C. Ahluwalia, *Trans. Faraday Soc.*, **67**, 305 (1971).

44) B. Kingston and M. C. R. Symons, *J. Chem. So . Faraday Trans. 2*, **69**, 978 (1973).