

Temperature of maximum density behaviour of SO₂, H₂S and CO₂ in water

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Temperatures of maximum density (TMD) of aqueous SO₂, H₂S and CO₂ solutions at low concentrations (0.003-0.03 mol kg⁻¹) have been measured to study the effects of these gases on the structure of water. Due to large degree of dissociation of SO₂ in water yielding H⁺ and HSO₃⁻ ions, dissociation corrections are applied to evaluate the structural part ($\Delta\theta_{\text{str}}^{\text{mol}}$) of the change in TMD exclusively due to undissociated SO₂ molecules. This correction is not found necessary for H₂S and CO₂ which on account of their small degree of dissociation produce very small number of ions. The structural part of the change in TMD ($\Delta\theta$) at various concentrations for these gases has been used to evaluate the characteristic constant 'a' from the sign and magnitude of which the gases SO₂, H₂S and CO₂ are shown to be water-structure stabilisers. This is corroborated by the positive ΔC_p^∞ for these gases dissolved in water. These findings are also supported by the formation of stable hydrates of SO₂ and H₂S from phase diagram and X-ray study respectively.

The influence of various dissolved solutes on the TMD of water (3.98°C) has been extensively investigated¹⁻⁹, to determine the effect of dissolved solute on the structural properties of water. This method is particularly useful since the observed effects are readily attributed to a change in the extent of hydrogen bonding between water molecules caused by the dissolved solute molecules.

Though work on TMD of electrolytes^{6,10} and nonelectrolytes^{1,2,3} is available, little or no work on gases dissolved in water is known, probably due to difficulties in handling gases. However, such studies are important from the point of view of the interactions between the dissolved gases and water molecules and certainly most useful in understanding problems of water pollution caused by hazardous gases like SO₂ and H₂S. The present work on TMD of aqueous solutions of SO₂, H₂S and CO₂ is in continuation with the earlier work on TMD of ammonia¹¹ in water and forms a part of the studies of gas-water interactions using TMD method.

In order to express the structural effect in a quantitative way the well known^{1,2} Eq. (1)

$$\Delta\theta_{\text{obs}} = \theta - \theta_w$$

$$= -\frac{x_2\alpha_2V_2^*}{2(1-x_2)\alpha_1V_1^*} - \frac{\partial/\partial T(V_{\text{mix}}^E)}{2(1-x_2)\alpha_1V_1^*} \quad \dots (1)$$

$$\text{or} \quad \Delta\theta_{\text{obs}} = \Delta\theta_{\text{id}} + \Delta\theta_{\text{str}}$$

is used and has been obtained by equating the temperature derivative of molar volume of solution to

zero, remembering the fact that molar volume of water has a parabolic dependence on temperature near TMD.

In Eq. (1) θ and θ_w are the TMDs of solution and pure water; x_2 , α_2 , V_2^* are the molefraction, coefficient of cubic expansion and molar volume at 0°C of pure solute and α_1 and V_1^* are the expansion coefficient and molar volume of pure water at θ_w ($= 3.98^\circ\text{C}$). V_{mix}^E is the excess volume of mixing. The first term in Eq. (1), $\Delta\theta_{\text{id}}$ represents the decrease in TMD caused due to accommodation of the solute in a cavity of suitable size, when the solution behaves ideally ($V_{\text{mix}}^E = 0$, Despretz rule). If $V_{\text{mix}}^E \neq 0$ and $\partial/\partial T(V_{\text{mix}}^E)$ is negative then one gets positive $\Delta\theta_{\text{obs}}$ if $|\partial/\partial T(V_{\text{mix}}^E)| > x_2\alpha_2V_2^*$.

Wada and Umeda¹ found a semiempirical equation to represent the variation of $\Delta\theta_{\text{str}}$ with concentration x_2 as:

$$\Delta\theta_{\text{str}} = a \cdot x_2 + b \cdot x_2^2 \quad \dots (2)$$

The constants 'a' and 'b' in Eq. (2) represent solute-solvent and solute-solute interactions respectively for a given solute and can be evaluated as intercept and slope of the linear plot of $\Delta\theta_{\text{str}}/x_2$ versus x_2 . They¹ applied Eq. (2) to methanol, ethanol, 1-propanol and 1-butanol and obtained linear plots of $\Delta\theta_{\text{str}}/x_2$ versus x_2 , but did not elaborate as to why Eq. (2) has to be of a quadratic form. Values^{1,2} of 'b' are generally found to be negative, whereas 'a' values are both positive and negative. Positive values of 'a' are interpreted to indicate the degree of water-structure stabilisation caused by the dissolved solute

while negative 'a' denote water structure disrupting ability.

In a recent work¹², it was shown that, in very dilute solutions when the apparent molal volume varies linearly with molefraction x_2 of the solute, the $\Delta\theta_{\text{str}}$ does show a quadratic dependence on x_2 . It further correlates the constant 'a' obtained by using the empirical Eq. (2) of Wada and Umeda exactly to volumetric property of the solute obtained by density measurements around TMD. The value of 'a' was shown to be given by Eq. (3)

$$a = -\frac{d/dT(V_2^{\infty E})_{4^\circ}}{2(1-x_2)\alpha_1 V_1^*} = -\frac{(\alpha_2^{\infty E})_{4^\circ}}{2(1-x_2)\alpha_1 V_1^*} \quad \dots (3)$$

Sign and magnitude of the constant 'a' is governed by the sign and magnitude of the temperature coefficient $(\alpha_2^{\infty E})$ of the limiting excess volume at 4°C. It is also shown¹² that the values of 'a' obtained from Eq. (3) and those from TMD measurements for alcohols and amines are in good agreement. The agreement of 'a' values obtained from TMD and density measurements is also observed for ammonia¹¹.

In the present work it was proposed to carry out TMD measurement of aqueous solutions of SO₂, H₂S and CO₂ at low concentrations (0.003-0.03 mol kg⁻¹), to see if 'a' values are similar to that of ammonia¹¹.

Materials and Methods

The TMD assembly used in this work was fabricated in our laboratory earlier⁸ and consisted of (i) a circulating type cryostat (MK70), (ii) The experimental bath (capacity 60 litres), (iii) heavy duty variable speed stirrer, (iv) a special mercury-in-stainless steel precision thermoregulator fitted with a micrometer screw, (v) heating device, (vi) a double-arm type dilatometer (twisted W-type), (vii) microscope (L.C. = 0.01 mm) and (viii) Beckman thermometer (L.C. = 0.01°C). The procedure for evaluating true TMD was the same as described earlier⁸ in which Eq. (4) is used.

$$\frac{dh}{dT} = \frac{2V_1^*\alpha_1}{A} \left[\frac{T_2 + T_1}{2} - \theta \right] \quad \dots (4)$$

where dh/dT is the rate of change of meniscus heights of both capillaries of the dilatometer taken together with respect to temperature; V_1^* and α_1 have the same meaning as that of Eq. (1); A is cross sectional area of the capillary, and θ is TMD in °C.

At TMD, $dh/dT = 0$ (the h versus T curve being a parabola having a minimum at TMD), hence from Eq. (4) LHS = 0 therefore, RHS is also equal to zero. And since $2V_1^*\alpha_1/A \neq 0$ it follows that intercept on

X (i.e. temperature) axis is TMD $\theta = (T_1 + T_2)/2$. Thus linear plots between dh/dT against mean temperature $(T_2 + T_1)/2$ gave TMD, θ as an intercept on the temperature axis.

A method of generation of SO₂ gas at PPM purity level described by Hashimoto and Tanaka¹³ was adopted in which aqueous sodium bisulphite solution (NaHSO₃) was made slightly acidic in an all-glass assembly and the evolved sulphur dioxide (SO₂) gas was allowed to dissolve into precooled conductivity water to obtain a stock solution.

Concentration of aqueous SO₂ solution was determined using iodimetric method in which known volume of SO₂ solution was added to excess of acidified iodine and then the remaining iodine was titrated against standard sodium thiosulphate solution.

H₂S gas was obtained by the action of dilute sulphuric acid (A.R.) on iron sulphide using Kipp's apparatus. The gas was then bubbled through aqueous Ba(OH)₂ solution, which was previously purged by N₂ gas, to remove any acidic impurity. This H₂S gas was then allowed to dissolve into precooled conductivity water to obtain the stock solution. The main impurity¹⁴ is hydrogen resulting from the action of acid on uncombined iron in the sticks of ferrous sulphide. However, at 5°C the solubility¹⁵ of hydrogen gas in water (0.18×10^{-3} wt%) is negligible as compared to that of hydrogen sulphide (0.6 wt%). Hence for all practical purposes the H₂S gas was regarded as sufficiently pure.

The concentration of aqueous H₂S solutions was determined using iodimetric method in which known volume of H₂S solution was added to excess of acidified iodine solution and then titrating the remaining iodine against standard thiosulphate solution as is done for SO₂.

CO₂ gas obtained by the action of dilute sulphuric acid (A.R. grade) on calcium carbonate (G.R. grade) was allowed to dissolve into a precooled conductivity water, which was previously purged by N₂ gas, to obtain a stock solution.

Concentration of aqueous CO₂ solution was determined using volumetric method in which known volume of CO₂ solution was added to excess of Ba(OH)₂ solution and then titrating the remaining Ba(OH)₂ against potassium hydrogen phthalate solution.

The change in molefraction of aqueous SO₂, H₂S and CO₂ before and after the TMD measurements was less than 1% and hence negligible. This could be achieved by

- (1) filling of the solution under pressure using nitrogen gas
- (2) very small surface exposed to the atmosphere

owing to capillaries at both ends of dilatometer, and

- (3) keeping the dilatometer having the solution in a bath at 3-5°C, which prevents the gas from escaping out to any considerable extent.

The performance of the TMD assembly was checked and found satisfactory by TMD measurement of sucrose solution. The observed points lies well on the curve drawn through points taken from literature¹⁶ with deviation of less than 0.02°C in $\Delta\theta_{\text{obs}}$.

To convert molarity to molality and then molefraction for aqueous solution of SO₂, H₂S and CO₂, density measurements were carried out using a single float method as described earlier¹⁷ with a Sartorius model 2474 single-pan semimicro-balance having arrangements to weigh below the pan. The glass float with a volume of about 166 cm³ weighted with mercury was used in this work. For density measurements, all necessary cares were taken as described previously¹⁷.

The performance of the assembly was checked and found alright by density measurements of NaCl (recrystallised AR grade). The value of ϕ_v^∞ obtained for NaCl (14.14 ml mol⁻¹) is in good agreement with the literature¹⁸ value (14.17 ml mol⁻¹). Also the coefficients A and B of the polynomial, $d = d_0 + A \cdot m + B \cdot m^2$ (where d_0 , d , m are density of pure water, density of solution and molality of solution respectively) obtained by fitting our data and literature¹⁸ data are very much consistent.

Results and Discussion

Data of all the TMD runs were fitted to a least square programme to obtain correct value of $\Delta\theta_{\text{obs}}$ using Eq. (4). Variation of TMD of water ($\Delta\theta_{\text{obs}}$) due to addition of SO₂, H₂S and CO₂ at various concentrations is shown in Table 1, with deviations of less than 0.02°C in $\Delta\theta_{\text{obs}}$.

SO₂ dissolved in water, which predominantly exist in hydrated form, dissociates into H⁺ and HSO₃⁻ ions considerably. In the concentration range studied, this dissociation is nearly 50-70%, and hence it becomes necessary to account for the presence of ions in order to arrive at the true value of $\Delta\theta_{\text{str}}$ exclusively due to undissociated SO₂ molecules.

The second degree of dissociation^{19,20} for hydrated SO₂ being very small, the contribution of corresponding ions (0.2-0.3%) to $\Delta\theta_{\text{str}}$ is negligible. Similarly very small degree of first and second dissociation^{19,21} of H₂S and H₂CO₃ contributes negligibly to their $\Delta\theta_{\text{str}}$. Hence $\Delta\theta_{\text{str}}$ for H₂S and CO₂ need not be corrected for their dissociation (Table 2).

In order to subtract the contribution to $\Delta\theta_{\text{str}}$ of ions formed due to dissociation of hydrated SO₂, a

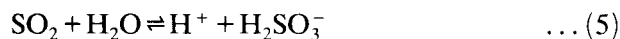
Table 1—Change of TMD of aqueous SO₂, H₂S and CO₂ solutions

Molefraction ($x_2 \cdot 10^4$)	$\Delta\theta_{\text{obs}}$ (°C)	Molefraction ($x_2 \cdot 10^4$)	$\Delta\theta_{\text{obs}}$ (°C)
SO ₂ solutions			
1.509	-0.09	3.143	-0.23
1.601	-0.10	3.285	-0.25
1.956	-0.12	3.958	-0.33
2.019	-0.14	4.214	-0.35
2.801	-0.21	4.406	-0.38
H ₂ S solutions			
0.932	-0.03	3.701	-0.15
1.250	-0.04	4.010	-0.17
1.935	-0.08	4.693	-0.21
2.100	-0.09	5.101	-0.24
2.601	-0.10	5.301	-0.26
CO ₂ solutions			
0.517	-0.05	0.969	-0.10
0.629	-0.06	1.299	-0.14
0.767	-0.08	1.472	-0.16

Table 2—Degree of dissociation of SO₂, H₂S & CO₂ in aq. solution

Gas	Temperature (°C)	Concentration range studied (c)	Range of α in percent Dissociation	
			1st	2nd
SO ₂	20	0.008	74%	0.3%
		0.024	57%	0.2%
H ₂ S	20	0.005	0.4%	$5 \times 10^{-5}\%$
		0.029	0.2%	$2 \times 10^{-5}\%$
CO ₂	5	0.003	1%	0.01%
		0.008	0.6%	0.007%

procedure similar to hydrolysis correction⁹, is applied to the TMD data of aqueous SO₂. To do this, $\Delta\theta_{\text{str}}$ is first calculated by ignoring dissociation, using Eq. (1). The value of α_2 and V_2^* required to evaluate $\Delta\theta_{\text{id}}$ have been calculated from density data^{22,23} of SO₂. Values of $\Delta\theta_{\text{str}}$ thus obtained are conceived as being made up, additively of contributions by molecules and ions present in the equilibrium.



$$\text{Thus } \Delta\theta_{\text{str}} = \Delta\theta_{\text{str}}^{\text{mol}} + \Delta\theta_{\text{str}}^{\text{ion}} \quad \dots (6)$$

$\Delta\theta_{\text{str}}^{\text{ion}}$ is calculated by applying Despretz rule²⁴ for ionic solutions.

$$\Delta\theta_{\text{str}}^{\text{ion}} = K_D^{\text{ion}} \cdot x^{\text{ion}} \quad \dots (7)$$

Where x^{ion} is the molefraction of the ionic species in the given solution which is calculated by regarding

the solution under consideration as a ternary system of solvent water, undissociated SO₂ molecules and the ions present. K_D^{ion} is the Despretz's constant (generally negative) characteristic of the electrolyte (H⁺HSO₃⁻) formed as a result of dissociation.

Thus the desired structural effect due to undissociated SO₂ molecules is obtained by Eq. (8).

$$\Delta\theta_{\text{str}}^{\text{mol}} = \Delta\theta_{\text{str}} - K_D^{\text{ion}}(\text{H}^+\text{HSO}_3^-) \cdot x(\text{H}^+\text{HSO}_3^-) \quad \dots (8)$$

The constant $K_{D(\text{H}^+\text{HSO}_3^-)}$ is a measure of the extent to which the ionic species affect the TMD of water and is calculated using the additivity property of K_D valid in dilute solutions of strong electrolytes:

$$K_{D(\text{H}^+\text{HSO}_3^-)} = K_{D(\text{Na}^+\text{HSO}_3^-)} + K_{D(\text{H}^+\text{Cl}^-)} - K_{D(\text{Na}^+\text{Cl}^-)} \quad \dots (9)$$

Values of $K_{D(\text{Na}^+\text{HSO}_3^-)} = -588^\circ\text{C}$, $K_{D(\text{H}^+\text{Cl}^-)} = -285^\circ\text{C}$ and $K_{D(\text{Na}^+\text{Cl}^-)} = -511^\circ\text{C}$ were measured by us separately. On inserting these K_D s in Eq. (9), $K_{D(\text{H}^+\text{HSO}_3^-)}$ is found to be -362° .

To evaluate the true degree of dissociation (α) for aqueous SO₂ by the iterative method employed by Cabani²⁵ the values of dissociation constant are taken from literature^{19,20}.

Figure 1a shows the variation of change in TMD ($\Delta\theta_{\text{obs}}$) of water due to dissolved SO₂ at different concentrations. By adopting the procedure for correction, it has been possible to obtain $\Delta\theta_{\text{str}}^{\text{mol}}$ and make appropriate plot of $\Delta\theta_{\text{str}}^{\text{mol}}/x_2$ versus x_2 (Fig. 1c). Extrapolation of the linear plot in Fig. 1c gives, $a = +94^\circ\text{C}$ with a probable uncertainty owing to the scatter of the points being about $\pm 11^\circ\text{C}$. Not adopting the correction procedure, would have resulted in a plot (Fig. 1b) yielding large negative 'a' value ($-208 \pm 10^\circ\text{C}$), caused apparently due to presence of ionic species. This justifies need for a correction procedure.

This water structure stabilising ability of SO₂ molecule is further supported by positive excess molal heat capacity, $\phi_{\text{cp}}^{\infty\text{E}}$ of SO₂^{26,27} at infinite dilution ($\phi_{\text{cp}}^{\infty\text{E}} = 35.01$, $\phi_{\text{cp}}^{\infty\text{E}} = 46.61$ and $C_{\text{p,gas}}^\circ = 11.6$ all in cal/mol.deg).

For H₂S and CO₂ the structural contribution $\Delta\theta_{\text{str}}$ is calculated as is done for SO₂ by subtracting $\Delta\theta_{\text{id}}$ from $\Delta\theta_{\text{obs}}$ ($\Delta\theta_{\text{obs}} = \Delta\theta_{\text{id}} + \Delta\theta_{\text{str}}$) and ignoring the dissociation of H₂S and CO₂ taking place in aqueous solution of a given concentration. The values of α_2 and V_2^* required in the evaluation of $\Delta\theta_{\text{id}}$ have been calculated using density data from literature¹⁵.

The variation of change in TMD ($\Delta\theta_{\text{obs}}$) of water due to dissolved H₂S and CO₂ at different concentrations are given in Table 1. The plot of $\Delta\theta_{\text{str}}/x_2$ versus x_2 (Fig. 2) gives value of $a = +94 \pm 29^\circ\text{C}$ and $+98 \pm 40^\circ\text{C}$ for H₂S and CO₂ respectively. These

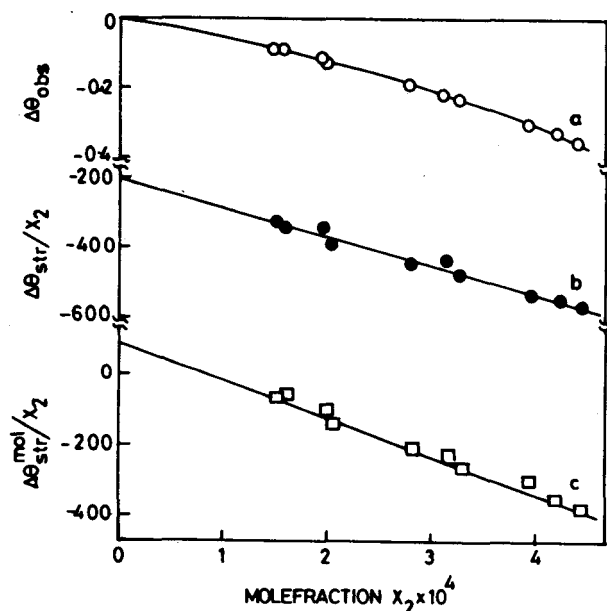


Fig. 1—(a) Plot of $\Delta\theta_{\text{obs}}$ versus x_2 molefraction for aqueous SO₂ solution (b) Plot of $\Delta\theta_{\text{str}}/x_2$ including ionic contribution versus molefraction for aqueous SO₂ solution and (c) Plot of $\Delta\theta_{\text{str}}^{\text{mol}}/x_2$ after subtracting ionic contribution versus molefraction for aqueous SO₂ solution

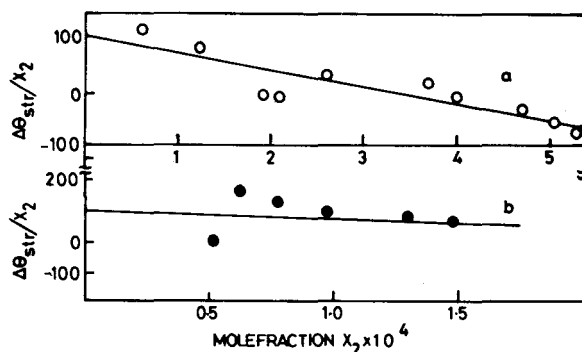


Fig. 2—(a) Plot of $\Delta\theta_{\text{str}}/x_2$ versus molefraction for aqueous H₂S solution and (b) Plot of $\Delta\theta_{\text{str}}/x_2$ versus molefraction for aqueous CO₂ solution

positive values represent their water structure enhancing propensity.

This water structure stabilising ability of H₂S and CO₂ molecule is further supported²⁶⁻²⁸ by their positive excess molal heat capacity, $\phi_{\text{cp}}^{\infty\text{E}}$ at infinite dilution (for H₂S, $\phi_{\text{cp}}^{\infty\text{E}} = 36.61$ obtained from $\phi_{\text{cp}}^\infty = 44.79$ and $C_{\text{p,gas}}^\circ = 8.18$ and for CO₂, $\phi_{\text{cp}}^{\infty\text{E}} = 28.78$ obtained from $\phi_{\text{cp}}^\infty = 58.13$ and $C_{\text{p,gas}}^\circ = 29.35$ all in cal/mol. deg).

The water structure stabilising ability of SO₂, H₂S, CO₂ and NH₃ ($a = +129 \pm 8^\circ\text{C}$ for ammonia¹¹) is ascribed to their polarity and small sizes^{23,29,30} ($r = 1.43, 1.43, 1.16$ and 1.014 Å respectively) which are comparable to that of water. Cage radius in water network ranges³¹ from 2.9 to 4.3 Å. It is there-

fore possible for the molecules of NH_3 , SO_2 , H_2S and CO_2 to fit easily into the cages and form hydrates thereby strengthening water structure. This is evident from the positive values of 'a' for these gases. X-ray study³² proved that the hydrates of most of the gases constitute a class of solids in which small molecules of the gases occupy the holes in ice-like lattices made up of hydrogen bonded water molecules.

From the phase diagram³¹ of $\text{SO}_2 - \text{H}_2\text{O}$ system it is found that sufficiently stable SO_2 hydrates do exist around TMD of water. The region of interest (i.e. around 4°C) is bounded by those equilibrium curves which has stable SO_2 hydrate as one of the phases. Ammonia has ability to form hydrogen bonding. The X-ray structure of the monohydrate of ammonia was found³³ to show chains of water molecules cross-linked in a three dimensional structure by ammonia molecules, all held together by hydrogen bonds. This also supports the structure enhancing ability of these gases discussed herein from the value of characteristic constant a obtained using TMD measurements in the present work.

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