

942-5

547.2

Temperature of maximum density of aqueous solutions of aliphatic amines

M V Kaulgud*, V S Bhagde & V K Mate

Department of Chemistry, Nagpur University, Nagpur 440 010

Received 3 October 1988; revised and accepted 13 January 1989

Temperature of maximum density (TMDs) in water at low concentrations for the seven amines: methyl-, ethyl-, *n*-propyl-, *n*-butyl-, *t*-butyl-, dimethyl-, and trimethyl amines have been measured and analyzed by applying hydrolysis correction to evaluate the structural part of the change in TMD ($\Delta\theta_{\text{str}}$) for the unhydrolysed amine molecules. A correction procedure is described for which additional experimental data on TMDs of corresponding amine hydrochlorides have been obtained. The results of amines studied in this work do not fit in the conventional straight line relation ($\Delta\theta_{\text{str}}/x_2 = a + bx_2$), which is obeyed by other non-electrolytes, like alcohols, which show positive intercepts (*a*) and negative slopes (*b*). The slopes of such plots for amines are positive at low concentrations and negative at higher concentrations showing a broad maxima in between. The intercepts *a* which indicate the structure strengthening property of the solute are large negative for MeNH_2 and EtNH_2 , slightly negative for *n*- PrNH_2 , and positive for the rest of the amines. Comparison of *a* values of alcohols and amines indicate the difference in the amine-water and alcohol-water interactions.

In a previous paper¹ we described the results of measurements of temperature of maximum density (TMD) in dilute aqueous solutions of methyl, ethyl, *n*-butyl, and *t*-butyl-amines. From the observed change in TMD of the solutions of from that of water ($\Delta\theta_{\text{obs}}$; Eq. 1), it was possible² to calculate the structural contribution, $\Delta\theta_{\text{str}}$ (see Eq. 1a) arising out of the non-vanishing temperature coefficient of excess volume [$d/dT (\Delta V_x^M) \neq 0$], to TMD due to the dissolved solute molecules.

$$\Delta\theta_{\text{obs}} = (\theta - \theta_0) = \frac{-x_2\alpha_2V_2^{00}}{2(1-x_2)\alpha_1V_1^{0*}} - \frac{\frac{d}{dT}(\Delta V_x^M)}{2(1-x_2)\alpha_1V_1^{0*}}$$

$$= \Delta\theta_{\text{id}} + \Delta\theta_{\text{str}} \quad \dots (1)$$

$$\Delta\theta_{\text{str}} = \Delta\theta_{\text{obs}} - \Delta\theta_{\text{id}} \quad \dots (1a)$$

In Eq. (1) θ and θ_0 are the TMDs for solution and pure water, respectively; x_2 , α_2 and V_2^{00} are respectively the mol fraction, coefficient of cubical expansion and molar volume at 0°C for pure solute; α_1 and V_1^{0*} are the expansion coefficient and molar volume of pure water at θ_0 ($= 3.98^\circ\text{C}$), respectively; and ΔV_x^M is the volume of mixing. The first term in Eq. (1) ($\Delta\theta_{\text{id}}$) represents behaviour of an ideal system ($\Delta V_x^M = 0$) and shows decrease of TMD caused due to accommodation of the solute in a cavity of suitable size.

Wada and Umeda² found a semiempirical equation between $\Delta\theta_{\text{str}}$ and x_2 (see Eq. 2).

$$\Delta\theta_{\text{str}} = ax_2 + bx_2^2 \quad \dots (2)$$

or

$$\frac{\Delta\theta_{\text{str}}}{x_2} = a + bx_2 \quad \dots (2a)$$

In Eq. (2) *a* and *b* are the constants representing respectively the solute-solvent and solute-solute interactions for a given solute and can be evaluated as intercept and slope of the linear plot of $\Delta\theta_{\text{str}}/x_2$ of Eq. (2a) against x_2 . Positive *a* indicates the degree of structure stabilization caused by the dissolved solute, and negative *a* structure disrupting ability of the dissolved solute. The *b* parameter depends on the solute-solute interactions².

Plots of ($\Delta\theta_{\text{str}}/x_2$) versus mol fraction (x_2) of the dissolved amines (MeNH_2 and *n*- BuNH_2) in our work¹ at lower concentrations showed a systematic deviation from linearity envisaged from Eq. (2a) of Wada and Umeda². This was ascribed¹ to the neglect of hydrolysis of amines, which at low concentrations ($x_2 \approx 10^{-3}$ to 10^{-4}) are as high as 15-20%.

Extrapolations of the uncorrected curves of ($\Delta\theta_{\text{str}}/x_2$) versus x_2 to zero concentration are likely to give incorrect values of the constant *a* (Eq. 2a), which determines the nature of solute-solvent interaction.

One way to avoid this problem, is to measure the TMD of the amines in dilute solution of a strong alkali (like KOH) to suppress the hydrolysis, as was done by Conway *et al.*³ for determining the partial compressibility of amines. This proce-

ture is not favoured by the authors for TMD on the ground that presence of the strong alkali might modify the native nature of the solvent itself, making it difficult to correctly judge amine-water interactions from the a values so obtained. Rather, it is preferred to numerically correct for the effects due to hydrolytic products (RNH_3^+ and OH^- ions). Such a procedure was first proposed and applied by Cabani *et al.*⁴, for partial volumes of amines, which was later adopted^{5,6}, in this laboratory for determining the apparent molal volume and compressibility of amines.

The present paper describes the hydrolysis correction procedure for TMD of amines. This has been applied to the TMDs of four amines (MeNH_2 , EtNH_2 , $n\text{-BuNH}_2$ and $t\text{-BuNH}_2$) studied earlier¹. In addition, measurements of TMD of n -propyl, dimethyl- and trimethyl-amines are also reported, which are also subjected to the correction procedure developed here.

Method of Hydrolysis Correction

In the procedure for hydrolysis correction proposed here, $\Delta\theta_{\text{str}}$ is first calculated by ignoring hydrolysis using Eq. (1a). Values of $\Delta\theta_{\text{str}}^{\text{obs}}$ thus obtained are conceived as being made up, additively, of contributions by molecules and ions present in the hydrolytic equilibrium (Eq. 3) of the amine B ($\text{B} = \text{RNH}_2$, R_2NH , R_3N etc.).



in which the hydrolytic products are presumed to be formed by the dissociation of the hypothetical intermediate $\text{B} \cdot \text{H}_2\text{O}$. We can then write:

$$\Delta\theta_{\text{str}}^{\text{obs}} = \Delta\theta_{\text{str}}^{\text{mol}} + \Delta\theta_{\text{str}}^{\text{ion}} \quad \dots (4)$$

The assumption of additivity is justified in dilute solution used in the work on TMD. $\Delta\theta_{\text{str}}^{\text{ion}}$ is calculated by applying Despretz⁷ rule for ionic solutions,

$$\Delta\theta_{\text{str}}^{\text{ion}} = K_{\text{D}}^{\text{ion}} \cdot x^{\text{ion}} \quad \dots (5)$$

where x^{ion} is the mol fraction of the ionic species in the given solution and $K_{\text{D}}^{\text{ion}}$ is the Despretz constant (generally negative) characteristic of the electrolyte (BH^+ , OH^-) formed as a result of hydrolysis.

Thus the desired structural effects due to unhydrolysed amine molecules can be obtained by Eq. (6).

$$\Delta\theta_{\text{str}}^{\text{mol}} = \Delta\theta_{\text{str}}^{\text{obs}} - K_{\text{D}(\text{BH}^+, \text{OH}^-)} \cdot x_{(\text{BH}^+, \text{OH}^-)} \quad \dots (6)$$

The constant $K_{\text{D}(\text{BH}^+, \text{OH}^-)}$ is a measure of the extent to which the hydrolytic species affect the TMD of water.

Table 1 – Measured $K_{\text{D}(\text{BH}^+, \text{OH}^-)}$ of various amines

Amine	$K_{\text{D}(\text{BH}^+, \text{OH}^-)}$ °C	pK_{b} at 5°C	Amine	$K_{\text{D}(\text{BH}^+, \text{OH}^-)}$ °C	pK_{b} at 5°C
MeNH_2	-641.4	3.209	$t\text{-BuNH}_2$	-944.4	3.295
EtNH_2	-762.0	3.439	$(\text{Me})_2\text{NH}$	-640.4	3.339
$n\text{-PrNH}_2$	-773.4	3.438	$(\text{Me})_3\text{N}$	-829.4	4.489
$n\text{-BuNH}_2$	-856.4	3.364			

Analysis of literature data on K_{D} values for various strong electrolytes show that it is an additive property and both cations and anions show the same effects irrespective of the nature of counterion. This fact is used to determine $K_{\text{D}(\text{BH}^+, \text{OH}^-)}$ required in the calculations of $\Delta\theta_{\text{str}}^{\text{mol}}$ using Eq. (6). Equation (7):

$$K_{\text{D}(\text{BH}^+, \text{OH}^-)} = K_{\text{D}(\text{BH}^+, \text{Cl}^-)} + K_{\text{D}(\text{K}^+, \text{OH}^-)} - K_{\text{D}(\text{K}^+, \text{Cl}^-)} \quad \dots (7)$$

has been used in determining $K_{\text{D}(\text{BH}^+, \text{OH}^-)}$ from the terms on the right hand side of Eq. (7), which can all be measured experimentally. Values of $K_{\text{D}(\text{BH}^+, \text{Cl}^-)}$ were measured by us separately by preparing the hydrochlorides of the amines. On inserting in Eqn (7) literature values of $K_{\text{D}(\text{K}^+, \text{OH}^-)}$ and $K_{\text{D}(\text{K}^+, \text{Cl}^-)}$ we obtained the corresponding values of $K_{\text{D}(\text{BH}^+, \text{OH}^-)}$ (Table 1). The concentration of ions $x_{(\text{BH}^+, \text{OH}^-)}$ is calculated by regarding the solution under consideration as a ternary system of solvent water, unhydrolysed amine molecules (B) and the hydrolytic products (BH^+ , OH^-). If α_{h} is the true degree of hydrolysis of amine molecules having a molality m in water it follows:

$$\begin{aligned} x_{(\text{BH}^+, \text{OH}^-)} &= \frac{\alpha_{\text{h}} \cdot m}{(1 - \alpha_{\text{h}})m + \alpha_{\text{h}} \cdot m + 55.51} \\ &= \frac{\alpha_{\text{h}} \cdot m}{m + 55.51} \quad \dots (8) \end{aligned}$$

The true degrees of hydrolysis were calculated by the iterative method employed by Cabani *et al.*⁴ in their volumetric work on amines. In this, approximate α_{h} values were first calculated from Ostwald's dilution law using thermodynamic basic dissociation constant of amines (see Table 1). Approximate mean activity coefficients were then calculated using Debye-Hückel limiting law (at 5°C) in the form: $\log \gamma_{\pm} = -0.494 \sqrt{I} = -0.494 \sqrt{\alpha_{\text{h}} \cdot c}$, where c is the molarity. Fresh values of α_{h} were next calculated by inserting into Ostwald's law, activities in place of concentrations. This procedure was repeated till constant values of α_{h} were obtained. Generally, α_{h} remained constant after third iteration.

Materials and Methods

The three amines used in this work were $n\text{-PrNH}_2$ (AR, Merck, Schuchardt, Germany), 25-30% solution

of $(\text{Me})_2\text{NH}$ (BDH, UK) and 30% solution of Me_3N (Spectrochem Co). $n\text{-PrNH}_2$ was first dried over KOH pellets and then distilled just before use. Concentrations of the solution were determined by titrating against standard (0.02N) acid using bromocresol purple indicator.

The TMDs of different solutions of the above three amines were measured according to the procedure described in the previous work¹. The TMDs of the corresponding hydrochlorides were determined in the same way. The changes in TMD ($\Delta\theta$) were a linear function of concentration for all the hydrochlorides, whereas the corresponding amines show non-linear concentration dependence.

Results and Discussion

Figure 1 shows the $\Delta\theta$ values for the three amines studied in this work. Values of $\Delta\theta$ for the remaining four amines were taken from our earlier work¹. Results of $\Delta\theta_{\text{str}}^{\text{mol}}$, the true structural contribution of unhydrolysed amine molecules to $\Delta\theta$ were calculated using Eq. (6) for all the seven amines. In view of Eq. (3), these may appear to be due to the $\text{B}\cdot\text{H}_2\text{O}$ species. However, since water added to water would not cause any change in TMD, the values given by Eq. (6) may be ascribed to the amine molecules. These have been plotted in Figs 2 and 3 as plots of $(\Delta\theta_{\text{str}}^{\text{mol}}/x_2)$ versus x_2 (Eq. 2a). Vertical bars show the probable uncertainties in the ordinate arising due to a possible error of $\pm 0.015^\circ$ in $\Delta\theta_{\text{obs}}$.

A careful examination of the plots in Figs 2 and 3 for the seven amines studied in this work reveals the following features.

(i) Plots of $(\Delta\theta_{\text{str}}^{\text{mol}}/x_2)$ versus x_2 tend to show negative slopes at higher concentration which become positive at lower concentration and show broad maxima in between. This is in sharp contrast with the behaviour of almost all nonelectrolytes studied so far², which all show a negative slope (i.e. negative b values).

(ii) In the case of MeNH_2 and EtNH_2 , owing to the asymptotic nature of the curves, it was not possible to extrapolate these to zero concentration for obtaining a values. It is quite clear, that the a parameter for these two amines should be large and negative. Wada and Umeda² obtained positive a values for methylamine by linear extrapolation from points at higher concentration (dotted line in Fig. 2), without considering hydrolysis. However, a values for other amines studied in this work do show positive a values, albeit only through a non-linear extrapolation of curves with positive slopes. The difference in nature of the curves arising due to neglect of hydrolysis can be seen in Fig. 3, from a comparison of our results for $n\text{-BuNH}_2$ and $(\text{Me})_2\text{NH}$ with those of Wada and Umeda (dotted lines). Table 2 gives a values obtained in present work (column 2). Also given are values obtained by other

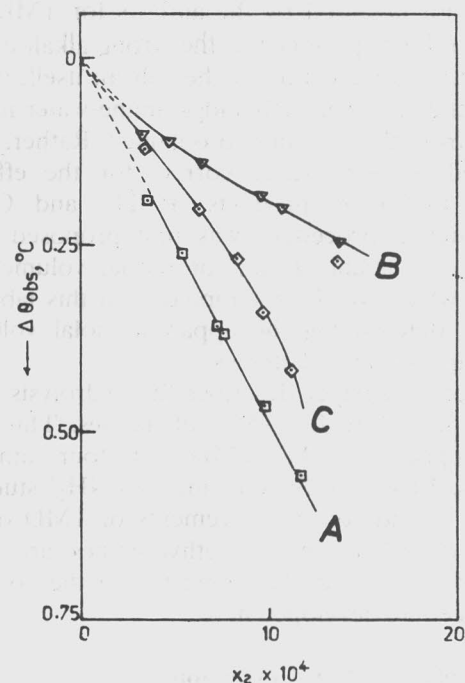


Fig. 1 – Change in temperature of maximum density ($\Delta\theta_{\text{obs}}$) for the amines (this work) [A. n -propylamine; B. dimethylamine and C. trimethylamine]

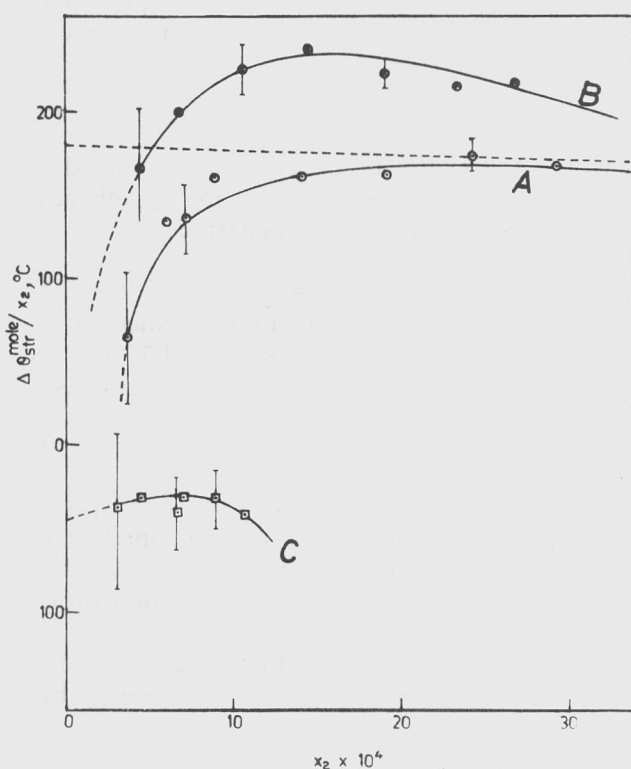


Fig. 2 – Plots of $\Delta\theta_{\text{str}}^{\text{mol}}/x_2$ versus x_2 for the amines. A. methylamine (ref. 1); B. ethylamine (ref. 1); and C. n -propylamine (this work) [Dotted lines show the results of methylamine of Wada & Umeda (ref. 2)]

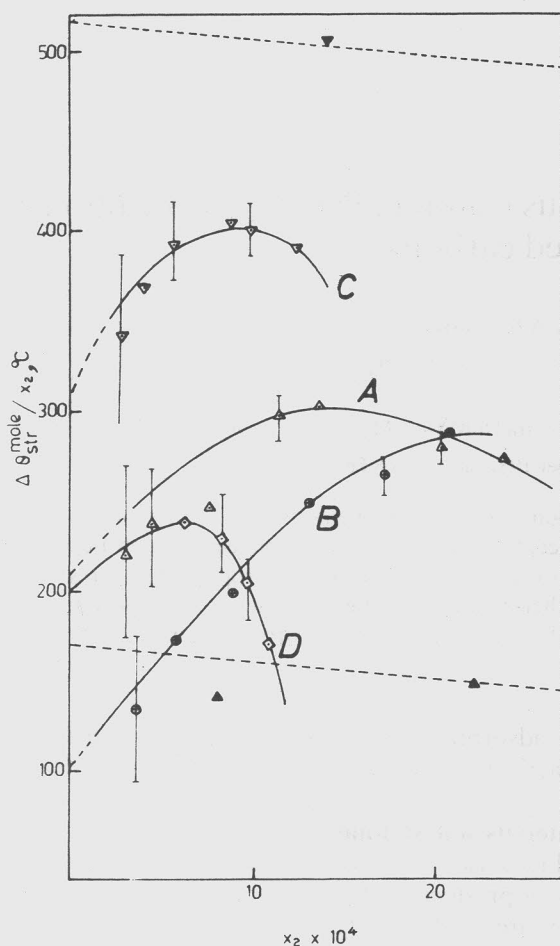


Fig. 3—Plots of $\Delta\theta_{\text{mol}}^0/x_2$ versus x_2 for the amines, [A, *n*-butylamine (ref. 1); B, *t*-butylamine (this work), and D, trimethylamine (this work). Dotted lines represent results of Wada & Umeda (ref. 2) for dimethylamine (C) and *n*-butylamine.]

workers² (column 3). The difference between these sets of values are subtle and must be ascribed to the neglect of hydrolysis by earlier workers and also to the fact that they carried out measurements at higher concentrations. In Table 2 are also listed a values for the corresponding alcohols (last column) to bring out the difference in the nature of alcohol-water and amine-water interactions; all alcohols show positive a values in contrast to the amines, the lower members of which show negative a values.

One can also evaluate the a parameter directly using the relation (9).

$$a = \frac{\frac{d}{dT}(\bar{V}_2^{0E})}{2(1-x_2)\alpha_1 V_1^{0*}} = \frac{\bar{\alpha}_2^{0E}}{2(1-x_2)\alpha_1 V_1^{0*}} \quad \dots (9)$$

Table 2—Values of constant (a) for amines

Amine	a (°C)		a (°C)	
	from TMD this work	W and U (ref. 2)	From (ref. 8)	for alcohols (ref. 2)
Methyl	Large -ve	180	-591	173
Ethyl	Large -ve	—	-324	273
<i>n</i> -Propyl	-53	—	-43	263
<i>n</i> -Butyl	210	173	231	237
<i>t</i> -Butyl	102	—	114	605
Dimethyl	310	515	314	—
Trimethyl	200	—	242	—

derived elsewhere⁸ and using values of $\bar{\alpha}_2^{0E}$ taken from our earlier work⁵ on the density of amines at low temperatures. These values are also given in Table 2 (column 4). As can be seen, the agreement between a values obtained from TMD measurements in this work and those calculated using Eq. (9), both in regard to sign and magnitude is quite satisfactory. This fact underlines the correctness of the method of hydrolysis correction adopted in this work. In the case of alcohols too⁸, a good agreement is seen between a values from TMD results and those calculated using Eq. (9).

The a values for amines in Table 2 clearly indicate that the first few members of the series of aliphatic amines are not structure-stabilizers (negative a) but the higher members are (positive a). Also, chain branching brings about enhancement of structure of water more effectively than chain-lengthening. Similar conclusions were arrived at⁵ on the basis of volumetric work on amines.

It is concluded that while evaluating the a parameter from TMD results in the case of solutes like amines, it is necessary to correct for hydrolysis; the neglect of which can give erroneous a values leading to improper interpretation of solute-solvent interactions. Alcohols and amines show a different trend in the a values, indicating the role of the hydrophilic group in deciding the nature of solute-solvent interactions.

References

- Kaulgud M V, Bhagde V S & Dhondge S S, *Indian J Chem*, 24A (1985) 373.
- Wada G & Umeda S, *Bull chem Soc Japan*, 35 (1962) 646, 1797.
- Conway B E & Verrall R E, *J phys Chem*, 70 (1966) 3952.
- Cabani S, Conti G & Lepori L, *J phys Chem*, 76 (1972) 1338.
- Kaulgud M V, Bhagde V S & Srivastava A, *J chem Soc Faraday Trans I*, 78 (1982) 313.
- Kaulgud M V, Awode M R & Srivastava A, *Indian J pure & appl Phys*, 18 (1980) 864.
- Despretz M C, *Ann Chim Phys*, 70 (1839) 49; 73 (1840) 296.
- Kaulgud M V, *J chem Soc Faraday Trans I*, (communicated).