Temperature of maximum density of aqueous solutions of aliphatic amines

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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 ($\Delta \theta_{str}$) 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 ($\Delta \theta_{str}/x_2 = a + bx_2^2$), 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 structural strengthening property of the solute are large negative for MeNH$_2$ and EtNH$_2$, slightly negative for 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 paper$^1$ 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 ($\Delta \theta_{obs}$; Eq. 1), it was possible$^2$ to calculate the structural contribution, $\Delta \theta_{str}$ (see Eq. 1a) arising out of the non-vanishing temperature coefficient of excess volume $[\frac{d}{dT} (\Delta V^M_x) \neq 0]$, to TMD due to the dissolved solute molecules.

$$\Delta \theta_{obs} = (\theta - \theta_0) = \frac{-x_2 \alpha_2 V_{1p}^{2}}{2(1-x_2)\alpha_1 V_{1p}^{2}} - \frac{d}{dT} (\Delta V^M_x)$$

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

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

In Eq. (1) $\theta$ and $\theta_0$ are the TMDs for solution and pure water, respectively; $x_2$, $\alpha_2$ and $V_{1p}^{2}$ are respectively the mol fraction, coefficient of cubical expansion and molar volume at $0^\circ C$ for pure solute; $\alpha_1$ and $V_{1p}^{2}$ are the expansion coefficient and molar volume of pure water at $\theta_0$ ($= 3.98^\circ C$), respectively; and $\Delta V^M_x$ is the volume of mixing. The first term in Eq. (1) $\Delta \theta_{id}$ represents behaviour of an ideal system ($\Delta V^M_x = 0$) and shows decrease of TMD caused due to accommodation of the solute in a cavity of suitable size.

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

$$\Delta \theta_{str} = a x_2 + bx_2^2 \quad \ldots (2)$$

or

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

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 $\Delta \theta_{str}/x_2$ 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 interactions$^2$.

Plots of $(\Delta \theta_{str}/x_2)$ versus mol fraction $(x_2)$ of the dissolved amines (MeNH$_2$ and n-BuNH$_2$) in our work$^1$ at lower concentrations showed a systematic deviation from linearity envisaged from Eq. (2a) of Wada and Umeda$^2$. This was ascribed$^1$ 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 $(\Delta \theta_{str}/x_2)$ 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-
dure 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 α values so obtained. Rather, it is preferred to numerically correct for the effects due to hydrolytic products (RNH₃⁺ and OH⁻ ions). Such a procedure was first proposed and applied by Cabani et al., for partial volumes of amines, which was later adopted² 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 (MeNH₂, EtNH₂, n-BuNH₂ and t-BuNH₂) 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, Δθstr is first calculated by ignoring hydrolysis using Eq. (1a). Values of Δθobs 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 (B = RNH₂, R₂NH, R₃N etc.),

\[ B + H₂O = B·H₂O \rightleftharpoons BH⁺ + OH⁻ \]  

in which the hydrolytic products are presumed to be formed by the dissociation of the hypothetical intermediate B·H₂O. We can then write:

\[ \Delta \theta_{str}^{obs} = \Delta \theta_{str}^{mol} + \Delta \theta_{str}^{ion} \]  

The assumption of additivity is justified in dilute solution used in the work on TMD. Δθstr is calculated by applying Despretz rule for ionic solutions,

\[ \Delta \theta_{ion} = K_{D ion} \cdot x_{ion} \]  

where \( x_{ion} \) is the mol fraction of the ionic species in the given solution and \( K_{D ion} \) 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).

\[ \Delta \theta_{str}^{mol} = \Delta \theta_{str}^{obs} - K_{D BH⁺,OH⁻} \cdot x_{BH⁺,OH⁻} \]  

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

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**Table 1 - Measured \( K_{D BH⁺,OH⁻} \) of various amines**

<table>
<thead>
<tr>
<th>Amine</th>
<th>( K_{D BH⁺,OH⁻} ) at 5°C</th>
<th>( pK_a ) at 5°C</th>
<th>Amine</th>
<th>( K_{D BH⁺,OH⁻} ) at 5°C</th>
<th>( pK_a ) at 5°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeNH₂</td>
<td>-641.0 3.209</td>
<td>MeNH₂</td>
<td>-944.4 4.3295</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EtNH₂</td>
<td>-762.0 4.339</td>
<td>EtNH₂</td>
<td>-640.0 3.339</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-PrNH₂</td>
<td>-773.4 4.348</td>
<td>n-PrNH₂</td>
<td>-829.4 4.489</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-BuNH₂</td>
<td>-856.4 3.364</td>
<td>n-BuNH₂</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Analysis of literature data on \( K_a \) 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 \( K_{D BH⁺,OH⁻} \) required in the calculations of \( \Delta \theta_{str}^{mol} \) using Eq. (6). Equation (7):

\[ K_{D BH⁺,OH⁻} = K_{D KH⁺,Cl⁻} + K_{D KH⁺,Cl⁻} - K_{D KH⁺,Cl⁻} \]  

has been used in determining \( K_{D BH⁺,OH⁻} \) from the terms on the right hand side of Eq. (7), which can all be measured experimentally. Values of \( K_{D BH⁺,OH⁻} \) were measured by us separately by preparing the hydrochlorides of the amines. In inserting in Eqn (7) literature values of \( K_{D KH⁺,Cl⁻} \) and \( K_{D KH⁺,Cl⁻} \) we obtained the corresponding values of \( K_{D BH⁺,OH⁻} \) (Table 1). The concentration of ions \( x_{BH⁺,OH⁻} \) 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 \( \alpha_h \) is the true degree of hydrolysis of amine molecules having a molality \( m \) in water it follows:

\[ x_{BH⁺,OH⁻} = \frac{\alpha_h \cdot m}{(1 - \alpha_h) m + \alpha_h \cdot m + 55.51} \]

\[ = \frac{\alpha_h \cdot m}{m + 55.51} \]

The true degrees of hydrolysis were calculated by the iterative method employed by Cabani et al.¹ in their volumetric work on amines. In this, approximate \( \alpha_h \) 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 \( \gamma \) = -0.494 √\( \alpha_h \) c, where \( \gamma \) is the molality. Fresh values of \( \alpha_h \) were next calculated by inserting into Ostwald’s law, activities in place of concentrations. This procedure was repeated till constant values of \( \alpha_h \) were obtained. Generally, \( \alpha_h \) remained constant after third iteration.

**Materials and Methods**

The three amines used in this work were \( n \)-PrNH₂ (AR, Merck, Schuchardt, Germany), 25-30% solution...
of (Me)_2NH (BDH, UK) and 30% solution of Me,N
(Spectrochem Co). n-PrNH_2 was first dried over KOH
pellets and then distilled just before use. Concentra-
tions of the solution were determined by titrating
against standard (0.02N) acid using bromocresol pur-
ple indicator.

The TMDs of different solutions of the above three
amines were measured according to the procedure de-
scribed in the previous work. The TMDs of the corre-
sponding hydrochlorides were determined in the same
way. The changes in TMD (Δθ) were a linear function
of concentration for all the hydrochlorides, whereas
the corresponding amines show non-linear concentra-
tion dependence.

Results and Discussion

Figure 1 shows the Δθ values for the three amines
studied in this work. Values of Δθ for the remaining
four amines were taken from our earlier work. Results
of Δθ_{true}^{mol}, the true structural contribution of unhydro-
lysed amine molecules to Δθ were calculated using Eq.
(6) for all the seven amines. In view of Eq. (3), these may
appear to be due to the B·H_2O species. However, since
water added to water would not cause any change in
TMD, the values given by Eq. (6) may ascribed to the
amine molecules. These have been plotted in Figs 2
and 3 as plots of (Δθ_{true}/x_2) versus x_2 (Eq. 2a). Vertical
bars show the probable uncertainties in the ordinate
arising due to a possible error of ±0.015° in Δθ_{obs}.

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

(i) Plots of (Δθ_{true}/x_2) versus x_2 tend to show nega-
tive slopes at higher concentration which become posi-
tive at lower concentration and show broad maxima in
between. This is in sharp contrast with the behaviour
of almost all nonelectrolytes studied so far, 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
Umeda obtained positive a values for methylamine
by linear extrapolation from points at higher concen-
tration (dotted line in Fig. 2), without considering hy-
drolysis. 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 posi-
tive slopes. The difference in nature of the curves aris-
ing due to neglect of hydrolysis can be seen in Fig. 3,
from a comparison of our results for n-BuNH_2 and
(Me)_2NH 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
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Fig. 3 - Plots of $\Delta \theta_{m}^{\alpha}/x_2$ 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.]

workers\(^2\) (column 3). The difference between these sets of values is 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).

$$a = \frac{\frac{d}{dT}(\bar{V}_n^{\alpha})}{2(1-x_2)\alpha_1 V_1^{\alpha}} = \frac{\alpha_2^{\alpha}}{2(1-x_j)\alpha_1 V_1^{\alpha}} \quad (9)$$

derived elsewhere\(^8\) and using values of $\alpha_2^{\alpha}$ taken from our earlier work\(^3\) 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 too, 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 at\(^4\) 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
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7 Despretz M C, Ann Chim Phys, 70 (1839) 49; 73 (1840) 296.