

Viscosity B-Coefficients of Amines in Dilute Aqueous Solutions

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Viscosity B-coefficients (B_η) in dilute aqueous solutions of NH_3 , MeNH_2 , EtNH_2 , $n\text{-PrNH}_2$, $n\text{-BuNH}_2$, $t\text{-BuNH}_2$, Me_2NH and Me_3N have been reported at 5°, 15° and 25°C after correcting for hydrolysis (The procedure of hydrolysis correction is also described). A method for obtaining B_η^{sr} , which represents the effect of solute on the structure of solvent, is described. The non-polar part of the molecule enhances water structure, whereas the $-\text{NH}_2$ group has an opposite effect of loosening water structure.

In the previous work¹ from this laboratory, viscosity B-coefficients (B_η) of aliphatic amines, in the concentration range of 0.05 to 1.0 molar were reported. This concentration range, however, is not low enough to rule out solute-solute interaction. Consequently B_η values in this concentration range may not give a true picture of the solute-solvent interaction.

We are reporting here B_η values of amines obtained from measurements of viscosity of very dilute solutions (0.005 M to 0.1 M). Though measurements in this low concentration range eliminate or minimise the uncertainty due to solute-solute interactions, the B-coefficient of unhydrolysed amines will have contributions from the species XH^+ and OH^- as a result of the hydrolysis of the amine (X): $\text{X} + \text{H}_2\text{O} \rightleftharpoons \text{XH}^+ + \text{OH}^-$. In dilute solutions the degree of hydrolysis could be as high as 25-30%.

This difficulty is usually avoided by carrying out measurements in a dilute solution (0.05 M) of a strong alkali (like KOH) as solvent to suppress hydrolysis, a procedure adopted by Conway *et al.*² for obtaining partial molal compressibilities of unhydrolysed amines. An alternative to the use of alkali would be to apply appropriate correction for the contribution of the ionic species, XH^+ and OH^- to the total observed property. Cabani *et al.*³ were the first to work out successfully a procedure for such a hydrolysis correction to determine the true limiting volumes of amines. This was modified and adapted to obtain true limiting partial compressibilities and also limiting volumes for measurements at lower concentrations^{4,5}. Davies and Malpass⁶ applied correction for dissociation of some aliphatic acids for obtaining the B_η of the undissociated acid molecules. In the present work true B_η of amines have been obtained by applying suitable correction for hydrolysis to the relative viscosities of solutions of amines at very low concentration. An appropriate procedure

for hydrolysis correction has also been described. The present treatment though similar in approach to that of Davies and Malpass differs in important aspect that after correcting for the ionic species the method yields the B-coefficient for the hypothetical aggregate $\text{X.H}_2\text{O}$ yielding the hydrolytic products from which one has to subtract the $B_\eta(\text{H}_2\text{O})$ to be obtained by a separate experiment.

Relative viscosities of dilute solutions of the following eight amines, viz. NH_3 , MeNH_2 , EtNH_2 , $n\text{-PrNH}_2$, $n\text{-BuNH}_2$, $t\text{-BuNH}_2$, Me_2NH and Me_3N have been measured at 5°, 15° and 25°C. A new parameter, B_η^{sr} , the structural part of the B_η has been defined and evaluated to enable a meaningful interpretation of viscosity parameters.

As the values of the viscosity B-coefficients of alcohols at different temperatures were available⁷ an attempt has also been made to compare the effect of $-\text{NH}_2$ and $-\text{OH}$ groups of amine and alcohol respectively on the structure of water.

Materials and Methods

$n\text{-PrNH}_2$ (Riedel), $n\text{-BuNH}_2$ (Merck) and $t\text{-BuNH}_2$ (Fluka) were dried over KOH for 48 hr and distilled twice over fresh KOH pellets. The purity of the liquid amines was established by density measurements. The stock solutions of gaseous amines were prepared by dissolving the purified vapours in doubly distilled water. The concentration of the stock solutions was determined by titrating against 0.2 M HCl (AR). Bromocresol purple was used as indicator for titration of all amines except ammonia for which bromophenol blue was used.

The relative viscosities of the aqueous solutions were determined by Eq. (1)

$$\frac{\eta}{\eta_0} = \left(\frac{\tau \rho}{\tau_0 \rho_0} \right) K \quad \dots (1)$$

Table 1—Viscosity B-Coefficients of NaCl and NaOH in Water at 5°, 15° and 25°C

	B-coefficients (dm ³ /mol) at		
	5°	15°	20°C
NaCl	0.046†	0.066*	0.079*
NaOH	0.184†	0.194†	0.205*

*Ref. 8

†This work

where, η , τ and ρ are respectively viscosity, time of flow and density of the solution and η_0 , τ^0 and ρ^0 are respectively the viscosity, time of flow and density of solvent; K is the kinetic energy correction factor⁸. Differential method⁸ was used in which two almost identical Ubbelohde viscometers fabricated with calibrated capillaries (tolerance $\pm 0.4\%$) were simultaneously suspended by special levelling device in a thermostatic bath. The bath was driven by MK-70 cryostat ($\pm 0.02^\circ\text{C}$) for 5° and 15° and U-10 thermostat for 25°C. Because of the large volume (27 dm³) of the viscosity bath it was possible to control its temperature within $\pm 0.005^\circ\text{C}$. The reproducibility in the flow time of about 1000s was ± 0.1 s. Kinetic energy corrections⁸ were applied. Relative viscosities of NaCl solutions measured at 15° and 25°C, were in agreement with the literature⁸ values within $\pm 0.02\%$.

The amine hydrochlorides were prepared according to the procedure given by Campbell and Lam¹⁰. The purity of the salts, checked by conductometric estimation of the halide was found to be 99.9%. The concentration of the solutions was varied *in situ* by adding weighed quantity of solution of known concentration to a known mass of water in the viscometer.

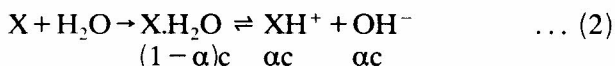
To prevent carbonisation of amines due to atmospheric CO₂ an atmosphere of N₂ was maintained over the solution in the viscometer using sodalime traps.

All solutions were filtered through sintered disc (No. 4) before use to eliminate particulate matter if any.

Densities⁴ were measured with an accuracy of 3 in sixth place of decimal using a differential bouyancy balance with float volume of about 180 ml.

Procedure for hydrolysis correction

It is assumed that the hydrolysis takes place from a hypothetical³ aggregate X.H₂O as follows:



In Eq. (2) X is the amine molecule, α is the degree of hydrolysis and c the stoichiometric concentration.

According to the Jones-Dole equation¹¹ the observed relative viscosity η/η_0 can be written as

$$\left(\frac{\eta}{\eta_0}\right)_{\text{obs}} = 1 + A_\eta(\text{XH}^+ \text{OH}^-)\sqrt{\alpha c} + B_\eta(\text{XH}^+ \text{OH}^-)\alpha c + A_\eta(\text{X.H}_2\text{O})\sqrt{(1-\alpha)c} + B_\eta(\text{X.H}_2\text{O})(1-\alpha)c \quad \dots (3)$$

where $A_\eta(\text{XH}^+ \text{OH}^-)$ and $A_\eta(\text{X.H}_2\text{O})$ are respectively the viscosity A_η -coefficients of $\text{XH}^+ \text{OH}^-$ and $\text{X.H}_2\text{O}$. Also $B_\eta(\text{XH}^+ \text{OH}^-)$ and $B_\eta(\text{X.H}_2\text{O})$ are viscosity B-coefficients of $\text{XH}^+ \text{OH}^-$ and $\text{X.H}_2\text{O}$ respectively. $A_\eta(\text{X.H}_2\text{O}) = 0$ by definition¹² since $\text{X.H}_2\text{O}$ is a non-electrolyte, we thus get:

$$\left(\frac{\eta}{\eta_0}\right)_{\text{obs}} = 1 + A_\eta(\text{XH}^+ \text{OH}^-)\sqrt{\alpha c} + B_\eta(\text{XH}^+ \text{OH}^-)\alpha c + B_\eta(\text{X.H}_2\text{O})(1-\alpha)c \quad \dots (4)$$

Rearranging Eq. (4) we get

$$\left[\left(\frac{\eta}{\eta_0}\right)_{\text{obs}} - 1\right] - \phi = B_\eta(\text{X.H}_2\text{O})(1-\alpha)c \quad \dots (5)$$

where $\phi = A_\eta(\text{XH}^+ \text{OH}^-)\sqrt{\alpha c} + B_\eta(\text{XH}^+ \text{OH}^-)\alpha c$

The A_η -values for $\text{XH}^+ \text{OH}^-$ were calculated from the limiting equivalent conductances using the equation given by Falkenhagen *et al.*^{8,13}. The values of the limiting conductances of XH^+ and OH^- were taken from literature^{14,16}. $B_\eta(\text{XH}^+ \text{OH}^-)$ were evaluated using the additivity equation (Eq. 6), valid for strong electrolytes in dilute solutions.

$$B_\eta(\text{XH}^+ \text{OH}^-) = B_\eta(\text{XH}^+ \text{Cl}^-) + B_\eta(\text{Na}^+ \text{OH}^-) - B_\eta(\text{Na}^+ \text{Cl}^-) \quad \dots (6)$$

where $B_\eta(\text{XH}^+ \text{Cl}^-)$, $B_\eta(\text{Na}^+ \text{OH}^-)$ and $B_\eta(\text{Na}^+ \text{Cl}^-)$ are the viscosity B-coefficients of amine hydrochloride, NaOH and NaCl respectively. The viscosity B-coefficients of the amine hydrochlorides were determined in this work¹⁷. The values of viscosity B-coefficients of NaCl and NaOH used in Eq. (6) are given in Table 1.

For the evaluation of $B_\eta(\text{X})$, the viscosity B-coefficients of the hypothetical aggregate $\text{X.H}_2\text{O}$ were first evaluated as slopes of the plots of left hand side of Eq. (5) versus $(1-\alpha)c$ which were all linear passing through the origin (Fig. 1). Since similar plots at 5° and 15°C were all linear passing through the origin these have not been reproduced here. The α -values were determined iteratively^{3,4}.

In the case of hydrolysis corrections applied for obtaining limiting compressibilities and volumes in the previous work^{4,5} the respective quantities for pure water, i.e. $\phi_{\text{ks}}^0(\text{H}_2\text{O})$ and $\phi_{\text{v}}^0(\text{H}_2\text{O})$ were sub-

Table 2— B_{η}^{str} and $B_{\eta}(\text{X})$ Values of Amines and Alcohols* at Different Temperatures

Compound	5°		15°		25°	
	$B_{\eta}(\text{X})$	B_{η}^{str}	$B_{\eta}(\text{X})$	B_{η}^{str}	$B_{\eta}(\text{X})$	B_{η}^{str}
NH_3	0.014	-0.021	0.003	-0.032	-0.004	-0.039
H_2O		-0.004		-0.002		
MeNH_2	0.144 (0.170)	0.083	0.119 (0.147)	0.056	0.087 (0.130)	0.026
MeOH	0.121	0.067	0.095	0.040	0.080	0.025
EtNH_2	0.249 (0.307)	0.162	0.238 (0.260)	0.151	0.184 (0.215)	0.097
EtOH	0.245	0.164	0.210	0.129	0.185	0.104
$n\text{-PrNH}_2$	0.372 (0.380)	0.259	0.311 (0.325)	0.198	0.251 (0.275)	0.138
$n\text{-PrOH}$	0.350	0.243	0.290	0.183	0.250	0.143
$n\text{-BuNH}_2$	0.440 (0.480)	0.257	0.344 (0.415)	0.201	0.305 (0.355)	0.162
$n\text{-BuOH}$	0.439	0.302	0.360	0.223	0.305	0.168
$t\text{-BuNH}_2$	0.450 (0.505)	0.313	0.364 (0.440)	0.270	0.303 (0.377)	0.166
$t\text{-BuOH}$	0.515	0.384	0.425	0.294	0.365	0.234
Me_2NH	0.293 (0.290)	0.204	0.254 (0.250)	0.165	0.167 (0.220)	0.087
Me_3N	0.439 (0.470)	0.326	0.394 (0.435)	0.281	0.318 (0.375)	0.205

Values in parantheses are from ref. 1 and 14

* B_{η}^{str} of alcohols corresponding to the amines (column 1) calculated from viscosity B_{η} -coefficients (extrapolated at 15° and 25°C) from ref. 7.

tracted from the composite quantities $\phi_k^0(\text{X.H}_2\text{O})$ and $\phi_v^0(\text{X.H}_2\text{O})$ in order to obtain $\phi_{ks}^0(\text{X})$ and $\phi_v^0(\text{X})$ of unhydrolysed amine molecules. Similarly, in the present case the B_{η} of the unhydrolysed species X was obtained using Eq. (7):

$$B_{\eta}(\text{X}) = B_{\eta}(\text{X.H}_2\text{O}) - B_{\eta}(\text{H}_2\text{O}) \quad \dots (7)$$

Equation (7) is based upon the postulate that the effective volume of the hypothetical aggregate $\text{X.H}_2\text{O}$ is additively made up of the corresponding volume of X and H_2O , which is reasonable in the context of the present work.

Unlike $\phi_{ks}^0(\text{H}_2\text{O})$ and $\phi_v^0(\text{H}_2\text{O})$ which are well known quantities, the $B_{\eta}(\text{H}_2\text{O})$ cannot be determined by direct measurements. $B_{\eta}(\text{H}_2\text{O})$ which represents the effective hydrodynamic volume of water molecules in liquid water cannot be evaluated by using the Stokes-Einstein diffusion equation since water molecules are not sufficiently large to allow the treatment of liquid water as continuum. There is also no established method of obtaining $B_{\eta}(\text{H}_2\text{O})$. In the work of Conway *et al.*² measurements of compressibility of amines dissolved in dil KOH solution enabled them to evaluate limiting compressibilities of unhydrolysed amine molecules. The results obtained were interpreted in terms of amine-water hydration interactions. Presence of KOH is thus to be understood as totally suppressing hydrolytic chemi-

cal interaction with water (Eq. 2) without affecting the hydrophobic hydration effects, if any. It was hence thought that a similar procedure could be adopted for evaluating $B_{\eta}(\text{X})$ for MeNH_2 and EtNH_2 . Subtracting this $B_{\eta}(\text{X})$ from $B_{\eta}(\text{X.H}_2\text{O})$ obtained from Eq. (5) would then enable evaluation of the parameter $B_{\eta}(\text{H}_2\text{O})$. The correctness of this line of thinking is further confirmed by the fact that the difference $[B_{\eta}(\text{X.H}_2\text{O}) - B_{\eta}(\text{X})]$ found experimentally is always positive, as it should be, if this difference has to represent $B_{\eta}(\text{H}_2\text{O})$. The mean values of $B_{\eta}(\text{H}_2\text{O})$ obtained from measurements of viscosity of MeNH_2 and EtNH_2 dissolved in KOH and after subtracting $B_{\eta}(\text{X})$ from the $B_{\eta}(\text{X.H}_2\text{O})$ (Eq. 5) were found to be 0.030 and 0.028 at 25° and 15°C, respectively. The value at 5°C obtained by extrapolation was $0.026 \text{ dm}^3 \text{ mol}^{-1}$. These values were hence used in Eq. (7) to estimate $B_{\eta}(\text{X})$ for all the other amines at different temperatures.

However, this method of using KOH for the determination of $B_{\eta}(\text{X})$ cannot be extended to higher amines (*n*-propylamine onwards) because of the possible increase in the degree of amine-amine-ion interactions with increase in size of the solute. These values of $B_{\eta}(\text{H}_2\text{O})$ so obtained from measurements on methyl and ethyl amines were used subsequently in the case of other amines to obtain $B_{\eta}(\text{X})$.

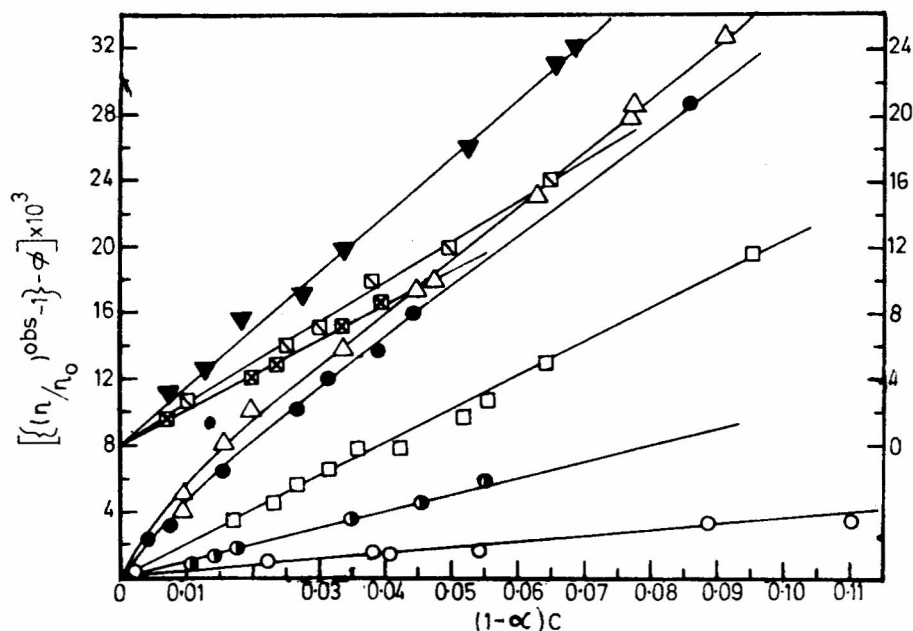


Fig. 1—Variation of $[(\eta/\eta_0)^{obs} - 1] \times 10^3$ with $(1 - \alpha)c$ at 25°C, O, NH_3 ; $\bullet$, MeNH_2 ; $\square$, EtNH_2 ; $\bullet$, $t\text{-BuNH}_2$; Δ , $n\text{-BuNH}_2$ (Left hand scale) $\boxtimes$, Me_2NH ; $\boxtimes$, $n\text{-PrNH}_2$; $\blacktriangledown$, Me_3N (Right hand scale)

For $n\text{-BuNH}_2$ and $t\text{-BuNH}_2$ at 25° the plots between left hand side of Eq. (5) versus $(1 - \alpha)c$ had slight curvature at low concentration (0 to 0.01 M) (Fig. 1). Hence $B_\eta(\text{X.H}_2\text{O})$ of these amines at 25°C were determined from the plots in the amine concentration range of 0.015–0.1M within which the plots were linear.

Results and Discussion

In Table 2 are given the coefficients, $B_\eta(\text{X})$, of amines at 5°, 15° and 25°C, obtained after correction for hydrolysis. For comparison, the B_η -coefficients obtained earlier at high concentration¹ are also given. The B_η -coefficients obtained presently after applying correction for hydrolysis are slightly smaller. The trends in variation with respect to temperature of the present $B_\eta(\text{X})$ and earlier values are, however, similar. In Table 3 are presented the values of $(dB_\eta/dT)_{5^\circ} [\equiv B'_\eta(5^\circ)]$ for amines. For comparison the $B'_\eta(5^\circ)$ of alcohols are also given.

The B_η -coefficients are usually interpreted in the light of the Einstein^{11,19} equations.

$$\left(\frac{\eta}{\eta_0} - 1\right) = v^E \phi_w \quad \dots (8)$$

or

$$\left(\frac{\eta}{\eta_0} - 1\right) = v^E V_h \cdot c \quad \dots (9)$$

Table 3—Values of $B'_\eta(5^\circ) \times 10^3$ at 5°C for Amines and Alcohols

Amine		Alcohol*	
Ammonia	− 1.1		
Methyl	− 2.5	MeOH	− 3.3
Ethyl	− 1.1	EtOH	− 4.0
<i>n</i> -Propyl	− 6.1	<i>n</i> -PrOH	− 6.3
<i>n</i> -Butyl	− 10.4	<i>n</i> -BuOH	− 11.0
<i>t</i> -Butyl	− 10.0	<i>t</i> -BuOH	− 12.5
$(\text{CH}_3)_2\text{NH}$	− 3.9		
$(\text{CH}_3)_3\text{N}$	− 4.5		

*From ref. 7

where ϕ_w is the volume fraction, v^E is a constant depending upon the size and shape of the solute particles in a solution of concentration c and V_h is the hydrodynamic volume of the solute. The net effect of the solute on the structure of a solvent can be understood appropriately if the shape and size effect B_η^E is subtracted from the experimental viscosity B -coefficients. We define a new parameter, B_η^{str} by Eq. (10)

$$B_\eta^{\text{str}} = B_\eta^{\text{Tot}} - B_\eta^E \quad \dots (10)$$

where B_η^E is evaluated from Eq. (11)

$$B_\eta^E = v^E V_w = v^E \cdot V_h \quad \dots (11)$$

In Table 2 are given the values of B_η^{str} computed from the van der Waal's volumes $(V_w)^{20}$ and the values of v^E given by Herskovits²¹, for alcohols assuming that the axial ratio of the amines and correspond-

ing alcohols will not differ much. B_{η}^{sr} increases with increase in the chain length of the molecule (Table 2). This is expected since non-polar groups enhance²² water structure due to hydrophobic hydration. The ability of structure promotion therefore increases with increase in chain length as is to be expected. In the case of isomeric amines (Table 2), the B_{η}^{sr} values of the branched isomers Me_2NH and Me_3N are greater than those of the straight chain isomers EtNH_2 and $n\text{-PrNH}_2$, respectively, especially at lower temperatures. Similarly the B_{η}^{sr} of $t\text{-BuNH}_2$ is greater than that of $n\text{-BuNH}_2$. This suggests that the branching of the hydrocarbon chain has greater influence on water structure. The negative B_{η}^{sr} for ammonia and for water at 5° and 15° should not be interpreted as showing structure breaking tendency, but rather it may be looked upon as indicating the inadequacy of the Einstein relation for molecules which are of size comparable to the molecules of the medium in which they move.

In Table 2 are also given the B_{η}^{sr} of alcohols evaluated by us using the B-coefficients of alcohols determined by Alexander⁷. The values of B_{η}^{sr} of the amines do not differ significantly from those of the corresponding alcohols (Table 2) indicating that the difference in the degree of structure promotion of water by the $-\text{OH}$ and the $-\text{NH}_2$ groups is too subtle to be differentiated on B_{η}^{sr} values alone.

The temperature dependence of viscosity B_{η} -coefficients can be more useful for understanding the solvent interaction. In Table 3 are given the B_{η}' (5°) at sufficiently low temperature where thermal disordering effects do not obliterate the structural stabilisation, if any, induced by the solute in its neighbourhood. Negative B_{η}' (5°) can be meaningfully attributed to the structural melting and the degree of structure promotion by the solute. It is seen that though the B_{η}' (5°) of amines and alcohols become more negative as the hydrophobic chain length increases the B_{η}' (5°) of amines are always less negative than the B_{η}' (5°) of the corresponding alcohols (Table 3). This suggests that $-\text{OH}$ group causes greater water structure stabilisation than the $-\text{NH}_2$ group. This corroborates the observation of Kaulgud²³, who has shown on the basis of the relation between compressibilities (of alcohols and of amines) and the change in temperature of maximum density of water caused by the solutes that $-\text{NH}_2$ group has a loosening effect on water structure while $-\text{OH}$

group, because of its ability to enter into cooperative bonding with water molecules, promotes it. Similar conclusion has been drawn from the study of volumetric properties⁵ of dilute solutions of amines and alcohols.

The B_{η} -coefficients obtained from measurements at higher concentration are systematically higher than those obtained from present measurements at very low concentration (Table 2). This can be due to solute-solute interactions at higher concentration causing an increase in the effective volumes of solutes.

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