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Hydrolysis Correction for Obtaining True Limiting Compressibilities of Amines in Aqueous Solutions

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Limiting apparent molal compressibilities in water of NH_3, $MeNH_2$, $EtNH_2$, n-$PrNH_2$, n-$BuNH_2$, t-$BuNH_2$, Me_2NH and Me_3N have been reported at 25°C after correcting for hydrolysis. The procedure for hydrolysis correction has been described. The values thus obtained differ markedly from those obtained by extrapolation from higher concentrations without applying hydrolysis correction.

LIMITING apparent molal compressibilities (ϕ°_{ks}) of some straight chain mono- and dialkylamines have been reported previously[1,2]. For obtaining the limiting values extrapolations are done from higher concentrations (above 0.5 *m*) where the hydrolysis of amines being only of the order of 5 to 6% is regarded to be negligible. However, the lowest concentration (0.5 *m*) is not sufficiently low where solute-solute interactions can be completely ruled out. Moreover, as the concentration of amine is lowered the degree of hydrolysis increases and therefore smooth extrapolations from concentrations where hydrolysis is negligible cannot be considered to give true limiting values of apparent molal compressibility. Therefore, in order to avoid this complexity arising due to hydrolysis it is the common practice to obtain ϕ°_{ks} from measurements in dilute alkaline solutions (0.05 *N* KOH or NaOH) which supress hydrolysis. Evidently, though the addition of alkali avoids complications arising due to hydrolysis, it certainly supresses the basic nature of the $-NH_2$ group thereby preventing one from visualising a true picture of how a 'native' i.e. unhydrolysed amine molecule really interacts with water. The true limiting apparent molal compressibilities of amines in water compared with those obtained[9] for straight chain alcohols are expected to throw light on the difference, if any, on the mode of interaction of the polar groups ($-NH_2$, $-OH$) with water. This information may be useful in understanding the behaviour of amino acids in water.

In order, therefore, to obtain the true values of ϕ°_{ks} with greater reliability it would be necessary to carry out measurements in aqueous solutions at as low a concentration as would be experimentally accessible. Cabani and Conti[4,5] who have successfully applied hydrolysis correction to apparent molal volumes of amines in aqueous solutions have extended their study of volumetric properties of amines, alcohols and ethers down to a concentration of 0.02 *m*. Similar measurements are reported by Franks *et al*[6]. on alcohols at concentrations below 0.1 *m*, and for cyclic ethers[7] down to 0.01 *m*. However, no sound velocity measurements for the determination of compressibilities of organic bases in such dilute solutions are reported till now.

The present work was undertaken to ascertain the true limiting apparent molal compressibilities of amines in aqueous solutions from measurements at still lower concentrations (0.005 to 0.1 *m*) in order to reduce the extrapolation errors[6] and also to test the applicability of the hydrolysis correction procedure to apparent molal compressibilities. The availability of a phase-comparison interferometer[8,9] for the measurements of sound velocity and also its suitability for work at very low concentration (0.005 to 0.1 *m*) were the deciding factors for the range of concentration investigated in the present work. The degree of hydrolysis in some cases is 30 to 40% which is quite high[10].

In this paper an attempt has also been made to evolve a method for correcting ϕ_{ks} for hydrolysis. The amines chosen for study are ammonia, methyl-, ethyl-, *n*-propyl-, *n*-butyl, dimethyl-, trimethyl-, and *t*-butyl-amines.

Procedure for Hydrolysis Correction

Apparent molal compressibilities are first calculated by introducing in Eq. (1) the molecular weight of the hypothetical species $B.H_2O$ where B stands for the amine.

$$\phi^{obs}_{ks} = \frac{1000\,(\beta-\beta^\circ)}{cd^\circ} + \phi_v\beta^\circ \qquad \dots (1)$$

where $\beta = \frac{1}{U^2d}$ and *U*. is the velocity of sound in solution of density '*d*' ϕ_v is the apparent molal volume of the same hypothetical species $B.H_2O$ calculated by inserting in Eq. (2) the molecular weight of $B.H_2O$ for M.

$$\phi_v = \frac{M}{d^\circ} - \left[\frac{d}{d^\circ} - 1\right]\frac{1000}{c} \qquad \dots (2)$$

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Assuming that the additivity rule of Cabani and Conti[4] for ϕ_v expressed by Eq. (3) for the equilibrium

$$\underset{(1-\alpha)c}{B.H_2O} \rightleftharpoons \underset{\alpha c}{BH^+} + \underset{\alpha c}{OH^-}$$

$$\phi_v^{obs} = (1\text{-}\alpha)\,\phi_v(B.H_2O) + \alpha\,\phi_v(BH^+OH^-) \quad \ldots (3)$$

could analogously be extended to apparent molal compressibility, ϕ_{ks} one can write Eq. (4) as follows :

$$\phi_{ks}^{obs} = (1\text{-}\alpha)\,\phi_{ks}(B.H_2O) + \alpha\,\phi_{ks}(BH^+OH^-) \quad \ldots (4)$$

Assuming linear dependence of ϕ_{ks} (B.H_2O) on concentration with slope S_{ks} and dependence of ϕ_{ks} (BH^+OH^-) on the square root of concentration (corrected for Debye term[11]), we can write for ϕ_{ks}^{obs}

$$\phi_{ks}^{obs} = (1\text{-}\alpha)\,[\phi_{ks}^{\circ}\,(B.H_2O) + (1\text{-}\alpha)c\,S_{ks}] + \alpha\,[\phi_{ks}^{\circ}\,(BH^+OH^-) + \sqrt{\alpha c}\,S_{ks}^{*} + \alpha c b_{ks}] \quad \ldots (5)$$

On dividing Eq. (5) by (1-α) and rearranging one obtains :

$$\frac{\phi_{ks}^{*}}{(1-\alpha)} = \phi_{ks}^{\circ}\,(B.H_2O) + (1\text{-}\alpha)\,cS_{ks} + A \quad \ldots (6)$$

where

$$\phi_{ks}^{*} = \phi_{ks}^{obs} - \alpha\,\phi_{ks}^{\circ}\,(BH^+OH^-) \quad \ldots (7)$$

and

$$A = \frac{\alpha\sqrt{\alpha c}}{(1-\alpha)}S_{ks}^{*} + \frac{\alpha^2 c}{(1-\alpha)}b_{ks} \quad \ldots (8)$$

Since a hypothetical species BH^+OH^- is considered the corresponding value of S_{ks}^{*}, the limiting slope and b_{ks} the deviation constant cannot be known. But their magnitude should be of the same order as in the case of uni-univalent electrolyte, i.e. both S_{ks}^{*} and b_{ks} are of the order of 10^{-10} (ref. 12). Considering these values, A turns out to be less than 10^{-12} as $\frac{\alpha\sqrt{\alpha c}}{(1-\alpha)}S_{ks}^{*}$ is at the worst of the order of 10^{-12} and $\frac{\alpha^2 c}{(1-\alpha)}b_{ks}$ is of the order of 10^{-14}. Therefore A in Eq. (6) can be neglected. Thus Eq. (6) reduces to Eq. (9) which is similar in form to the corresponding equation obtained by Cabani and Conti[4] for hydrolysis correction of ϕ_v.

$$\frac{\phi_{ks}^{*}}{(1-\alpha)} = \phi_{ks}^{\circ}\,(B.H_2O) + (1-\alpha)\,c\,S_{ks} \quad \ldots (9)$$

The limiting partial molal compressibility of the hypothetical electrolyte BH^+OH^- included in the ϕ_{ks}^{*} term in Eq. (7) is obtained from the additivity Eq. (10) valid for strong electrolytes :

$$\phi_{ks}^{\circ}(BH^+OH^-) = \phi_{ks}^{\circ}\,(BH^+Cl^-) - \phi_{ks}^{\circ}\,(Na^+Cl^-) + \phi_{ks}^{\circ}\,(Na^+OH^-) \quad \ldots (10)$$

Quantities on the right hand side of Eq. (10). are determined by extrapolating apparent molal compressibilities of aqueous solutions of NaCl, NaOH and the amine hydrochloride against the square root of concentration. The degree of hydrolysis, α, was calculated using the iterative procedure suggested by Cabani *et al*[4]., which takes into account the activity coefficient of ionic species. The values of the basic dissociation constant (K_b) were calculated using the acid dissociation constant of the bases, taken from Perrin[13], and the pK_w values[14].

It was assumed in the beginning that S_{ks} would be independent of concentration. Accordingly, it was expected that Eq. (9) would represent a straight line with slope S_{ks} and intercept ϕ_{ks}°(B.H_2O). $\frac{\phi_{ks}^{*}}{(1-\alpha)}$ was hence plotted against (1-α)c. But instead of getting linear plots curves were obtained consistently in all the cases, particularly at lower concentration (Fig. 1 methyl amine at 25° and *t*-butyl amine at 5° and 25°C). On specifying the limits of errors (see Fig. 1) to the points at lower concentrations, it was clear that there was no random distribution of points which could have been accounted for by experimental errors, but the points showed a systematic upward trend. As the curves were asymptotic to the ordinate the extrapolation to infinite dilution could not be uniquely carried out and therefore, ϕ_{ks}° (B.H_2O) could not be ascertained reliably.

The systematic upward trend of the curves implied that the presumption of S_{ks} being independent of concentration especially in the lower concentration

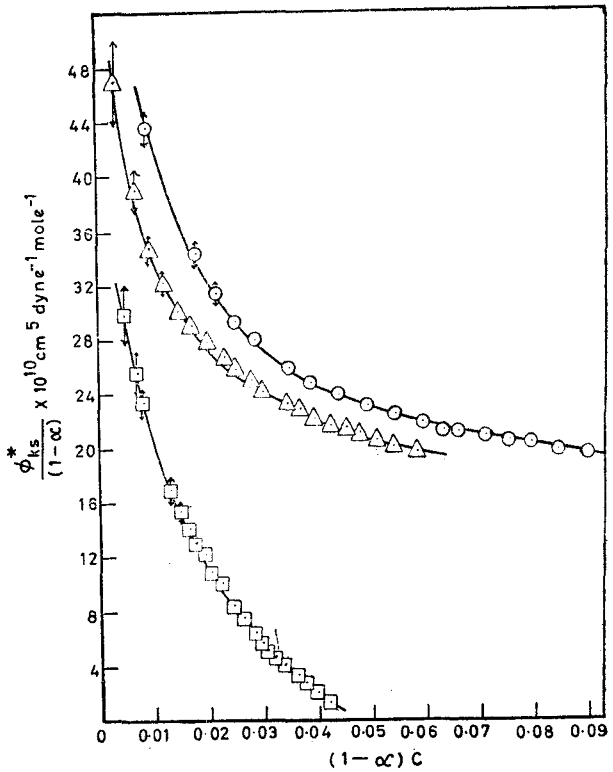

Fig. 1—Plots of $\phi_{ks}^{*}/(1\text{-}\alpha)$ against (1-α)c for aqueous solutions of $MeNH_2$ at 25°C (—⊙—⊙—) *t*-$BuNH_2$ at 25°C (—△—△—) and *t*-$BuNH_2$ at 5°C (—□—□—).

region was unfounded and Eq. (9) could not, therefore, be treated as an equation of a straight line. In order to obtain reliable ϕ^*_{ks} (B.H$_2$O), it was therefore necessary to recast Eq. (9) in a linear form.

After a large number of trials the relation finally tried for extrapolation was :

$$\phi^*_{ks}\, c = (1-\alpha)c\, \phi^\circ_{ks}\ (\mathrm{B.H_2O}) + (1-\alpha)^2 c^2 S_{ks} \quad ..(11)$$

obtained by multiplying Eq. (9) throughout by$(1-\alpha)c$. When S_{ks} and /or $(1-\alpha)^2\ c^2$ is small then the second term on R.H.S. of Eq. (11) can be neglected resulting into a linear equation for $\phi^*_{ks}\, c$ versus $(1-\alpha)\ c$ with slope ϕ°_{ks} (B.H$_2$O) (Fig. 2). It can be said here that the relationship for apparent compressibility ought to have been obtained more appropriately by taking the pressure derivative of expression (3). However, the final expression obtained after differentiating Eq. (3) with respect to pressure and rearranging gave Eq. (11) with an additional term:

$$\frac{d\alpha}{d\rho}\left[\left\{\phi^\circ_v\ (\mathrm{B.H_2O}) - \phi^\circ_v\ (\mathrm{B + HOH^-})\right\}c + \frac{c^2h}{(1-\alpha)} - c\sqrt{\alpha c}\, S_v - \alpha^2ch^*\right]$$

on the right hand side. It was numerically evaluated taking pressure derivative of the approximate relation $\alpha = \sqrt{\frac{K_b}{c}}$ and it was found that the last three terms in the square bracket are almost negligible while the first term gives a finite intercept of the order of 1 cm^2 dyne^{-1}. The evaluated intercepts were found to increase with temperature and were almost negligible for ammonia. The sefacts are consistent with the trend of the intercepts obtained from the actual plots (Fig. 2). The presence of a finite intercept does not, however, change the slopes of the plots (Fig. 2) appreciably hence Eq. (11) can be taken as reasonably correct for the determination of ϕ°_{ks} (B.H$_2$O) as slopes.

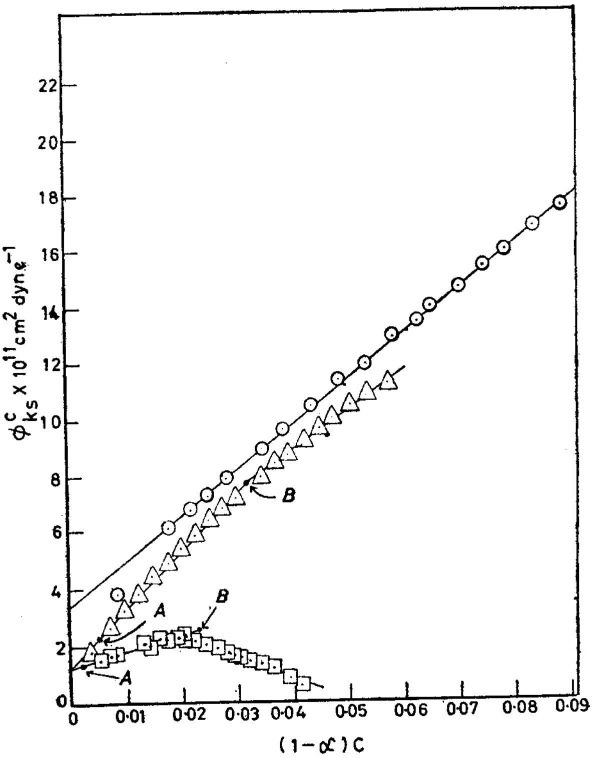

Fig. 2— Plots of $\phi^*_{ks}c$ against $(1\text{-}\alpha)c$ for aqueous solutions of MeNH$_2$ at 25°C (—◎—◎—), t-BuNH$_2$ at 25°C (— △—△ —) and t-BuNH$_2$ at 5°C (—□——□).

A second point which needsc onsideration is the deviation from linearity at higher concentrations observed in certain cases [more pronounced at 5° for t-butylamine. (Fig. 2)]. This is accounted for by the influencing magnitude of S_{ks} (see discussion) Rewriting Eq. (11) in the form(12).

$$\phi^*_{ks}\, c = (1-\alpha)c\,[\phi^\circ_{ks}\ (\mathrm{B.H_2O}) + 1-\alpha)\, c\, S_{ks}] \quad ..(12)$$

it is clear that in cases of non-linearity the contribution of $(1-\alpha)cS_{ks}$ to ϕ°_{ks} (B.H$_2$O) is appreciable. In such cases the slopes were obtained from those portions AB of the curves (Fig. 2) which were linear and corresponded to the lowest concentration region. Finally, the limiting compressibility of the neutral amine molecule ϕ°_{ks} (B) was obtained with good approximation by subtracting ϕ°_{ks} (H$_2$O) for pure water ($\beta^0V^0 = 8\times10^{-10}$ cm^5 dyne^{-1} mol^{-1}) from ϕ°_{ks} (B.H$_2$O) obtained as slopes.

Materials and Methods

Sound velocity (U) in aqueous solutions of amines and amine hydrochlorides was measured by phase-comparison interferometer[10]. Details regarding method of measurement have beend escribed earlier[8,9]. The only additonal precaution taken in the case of amine solutions was to maintain a layer of nitrogen gas over the solution throughout the measurements so as to avoid carbonation of amines due to atmospheric carbon dioxide. Densities of the aqueous solutions of amines and their hydrochlorides needed for the evaluation of ϕ°_{ks} (BH$^+$OH$^-$) in Eq. (10) were measured by differential float balance described earlier[15].

n-Propylamine (Riedel), n-butylamine (Merck) and t-butylamine (Fluka) were dried over KOH for 48 hr and distilled twice. The purity was established by density measurements. The solutions of ammonia methyl-, ethyl-, dimethyl and trimethylamines obtained on dissolution of the purified vapours were used directly as stock solutions. The concentrations of the solutions were determined by first titrating a known volume of stock solution against 0.02 N HCl (AR) using a microburette ($\pm$ 0.01 ml).

Results and Discussion

The corrected and uncorrected values of ϕ°_{ks} are given in Table 1 along with the literature values for comparison. The uncorrected values of ϕ°_{ks} are obtained by extrapolation to zero concentration from plots of ϕ_{ks} against c. It is found that except for trimethylamine the uncorrected values are greater than

TABLE 1 — VALUES OF ϕ°_{ks} OF AMINES IN AQUEOUS SOLUTIONS AT 25°C.

[Values in cm^5 $dyne^{-1}$ mol^{-1}]

Solute	ϕ°_{ks} (B) $\times 10^{10}$ (corrected) This work	ϕ°_{ks} $\times 10^{10}$ (uncorr.) This work	$\Delta\phi^{\circ}_{ks}$ $\times 10^{10}$	ϕ°_{ks} $\times 10^{10}$ (literature[2] at 20°C)	ϕ°_{ks} $\times 10^{10}$ (literature[3])
NH_3	4.22	5.0	—0.78	—	—
$MeNH_2$	7.72	20.0	—12.28	4.5	7.5
$EtNH_2$	13.32	19.0	—5.68	—2.5	—
n-$PrNH_2$	13.40	23.0	—9.60	—9.5	—
n-$BuNH_2$	15.42	27.0	—11.58	—16.0	—
t-$BuNH_2$	12.92	25.0	—12.08	10.0	—
Me_2NH	21.06	23.0	—1.94	2.5	5.0
Me_3N	15.52	7.0	8.52	—	2.0

the corrected ones. The magnitude of the differences $\Delta\phi^{\circ}_{ks} = (\phi^{\circ}_{ks\ \mathrm{corr}} - \phi^{\circ}_{ks\ \mathrm{uncorr.}})$ (Table 1) indicates that the presence of the ionic species (BH^+ & OH^-) produced by the hydrolysis of amine prevents to a large extent the bare —NH_2 group from revealing its true nature of interaction. On comparing the corrected values with those obtained by supressing hydrolysis it is seen that only for methylamine ϕ°_{ks} (B) agrees closely with Conway's[3] value (Table 1). The marked differences between the present ϕ°_{ks} (B) and those obtained by extrapolation to zero concentration from points at higher concentrations without applying hydrolysis correction reveal the importance of hydrolysis correction.

The influence of solute-solute interactions resulting in the non-linearity of the curves at higher concentration can be understood in the light of Eq. (12). The terms on R. H. S. of Eq. (12) given in the square bracket represent $\phi_{ks}(B.H_2O)$ at a given concentration c. In the event of weaker solute-solute interaction the contribution of $(1-\alpha)c\ S_{ks}$ to ϕ°_{ks} $(B.H_2O)$ is negligible which is evident from the linearity of the plots (methylamine at 25°C. Fig. 2). Where solute-solute interactions are appreciable, especially at lower temperatures the contribution of $(1-\alpha)cS_{ks}$ to ϕ°_{ks} $(B.H_2O)$ increases with increasing concentration thereby introducing non-linearity in the plots showing the advent of solute-solute interaction. The pronounced non-linear nature of the plots at lower temperature than at higher temperature (compare *t*-butylamine at 5 and 25°, Fig. 2) also supports this fact. Detailed interpretation of the results of ϕ°_{ks} (B) at different temperatures, especially the two slopes at lower temperature, will be published elsewhere[16].

Coming to the effect of chain length on ϕ°_{ks} it is found that ϕ°_{ks} (B) increases as the length of the hydrophobic chain increases (Table 1). Alcohols[9] show an opposite trend at 25°. At 45°, however, alcohols[9] also show a similar tendency of increasing ϕ°_{ks} with chain length as shown by amines at 25°. Since the hydrophobic groups are expected to behave similarly whether attached to —OH or —NH_2, the above result strongly suggests that —NH_2 group may be causing a disruptive influence on the hydrophobically structured solvent molecules or may be lowering the 'structure promoting' ability of the hydrophobic group. ϕ°_{ks} (B) of *t*-$BuNH_2$ is observed to be lower than that of *n*-$BuNH_2$, a result found to be true for alcohols[9] also, indicating that the compact geometry and the symmetry of the molecule helps its easy accommodation into the natural cavities of water.

Concluding, it could be said that the hydrolysis procedure proposed by Cabani and Conti[4] for volumetric properties could be in principle extended or compressibility too provided it is ascertained from ϕ°_{ks} c vs $(1-\alpha)c$ plots that they are reasonably linear, which means that the solute-solute interactions are small or negligible. Otherwise, the values of ϕ°_{ks} (B) have to be obtained from measurements at still lower concentration, or if such measurements are not immediately available, from the linear part at the lowest concentration as has been done in the case of *t*-$BuNH_2$ at 5° and 25°C. (Fig. 2).

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