Apparent molal compressibilities of alcohols in aqueous solutions at different temperatures

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Apparent molal compressibilities (ϕ_k) of methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and tert-butyl alcohols in aqueous solutions are reported at 2, 4, 6, 8 and 10°C. The variation of ϕ_k with concentration (m) has been interpreted in terms of effect of dissolved solute (alcohol) on water structure. The limiting apparent molal compressibilities (ϕ_k^0) of alcohols are also reported and interpreted in terms of hydrophobic interactions. In addition, parameter $P_\theta = (\partial/\partial P)(\Delta\theta_{str})$, where $\Delta\theta_{str}$ is the structural contribution of shift in temperature of maximum density ($\Delta\theta$), has been calculated as a function of concentration. It has been observed that P_θ can very well be used as a tool to express the relative structure strengthening ability of dissolved alcohols in water.

Aqueous solutions of alcohols have been studied extensively[1-11]. Particularly, considerable work has been done at and around 25°C. But very little work has been done at low temperature[10-13]. It is more interesting to study aqueous solutions around temperature of maximum density (TMD), as changes in the extent of hydrogen bonding between water molecules on dissolution of solute become more predominant at this temperature. The volumetric properties of aqueous alcohols have been reported in our earlier communication[13] at low temperatures (0-10°C). The present work deals with the compressibility properties of aqueous solutions of these alcohols between 0-10°C.

Compressibility property is fairly sensitive to structural changes especially in a highly structured solvent like water and is hence expected to throw interesting light. Another property TMD of water (3.98°C) is also sensitive to change on addition of solutes. Considerable work has been done on TMD of aqueous solutions of nonelectrolytes[15-18] and subjected to suitable structural analysis to yield information on structure making and structure breaking solutes. It was shown by Kaulgud[14] that the relative structure strengthening ability of solutes can be nicely expressed with the help of

pressure derivative of change in TMD ($\Delta\theta = \theta - \theta_0$ where θ_0 is TMD of water) i.e. $\frac{\partial}{\partial P}\Delta\theta$. Pressure derivatives of $H\Delta\theta$ are experimentally more difficult to measure directly. However, in the above work[14], an expression was deduced linking $\frac{\partial}{\partial P}(\Delta\theta)$ with temperature coefficient of apparent molal compressibility $\frac{\partial}{\partial T}(\phi_{kT})$.

Change in TMD, can arise due to volume effect and structural effect ($\Delta\theta_{str}$). The parameter $\frac{\partial}{\partial P}(\Delta\theta_{str})$ which is of importance in the present work is related to $\frac{\partial}{\partial T}(\phi_{kT})$ as follows[14].

$$P_\theta = \frac{\partial}{\partial P}(\Delta\theta_{str})$$

$$= x_2 \times 3.55 \times 10^3 \left[\frac{\partial}{\partial T}(\phi_{kT}) - \frac{\partial}{\partial T}(\beta_2^0 \cdot V_2^0)\right] \qquad \ldots (1)$$

where, $\Delta\theta_{str}$ is the structural contribution of shift in temperature of maximum density ($\Delta\theta$), x_2 is mole fraction of the solute, ϕ_{KT} is apparent molal isothermal compressibility of the solute and β_2^0 and V_2^0 are the isothermal compressibility and molar volume of pure solute at 4°C.

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In order to use Eq. (1) for structural elucidation one needs data on ϕ_{KT} around TMD. However, such measurements are not available, as most of the work is generally reported at and around 25°C. It was hence thought interesting to investigate compressibility behaviour of aqueous alcohol solutions to evaluate the P_θ parameter as a function of concentration. In order to have reliable slopes of ϕ_{KT} with respect to temperature the measurements were carried out at 2, 4, 6, 8 and 10°C.

Materials and Methods

The alcohols, namely, methyl, ethyl, n-propyl, isopropyl, n-butyl, s-butyl, isobutyl and t-butyl were A.R. grade. These were further purified by standard methods[19]. The densities agreed to ± 0.0001 g/ml and with literature[20]. The measurements were made in doubly distilled water. The density measurement were carried out by using a single float method. The details have been described elsewhere[13,21].

The sound velocity measurements were made by using an Ultrasonic Interferometer model SI-2 (M/s Dr. Steeg and Reuter, Germany) at a fixed frequency of 2 MHz. The measuring cell was a specially designed double walled cell for maintaining a constant temperature by circulating thermostated water. The least count of micrometer screw attached to it was 0.01 mm. The cell was packed up with thermocole balls and kept in an insulated box. The temperature of experimental liquid was kept constant by circulating coolant liquid at constant temperature from MK-70 cryostat (accuracy ± 0.02°C) through the double walled jacket.

To begin with the cell was filled with the solution of known concentration of aqueous alcohol. The solution was allowed to maintain a constant temperature (± 0.01°C) for half an hour, and then velocity measurements were carried out. In this way the sound velocity measurements were carried out for different solution of the same system at the same temperature. The apparatus was calibrated by measuring the sound velocities of water at different temperatures. It was observed that our sound velocity values agreed to better than ± 0.5 m/s with literature.

Observations and calculations of derived parameters

The adiabatic compressibility (β_s) at different concentrations has been computed by using the relation

$$\beta_s = \frac{1}{u^2 . d} \quad \dots (2)$$

where u is sound velocity and d is density of solution.

The apparent molal adiabatic compressibilities (ϕ_{KS}) of solute were determined using Eq. (3).

$$\phi_{KS} = \frac{1000}{m . d . d_0} (d_0\beta - d\beta_0) + \beta . \frac{M_2}{d} \quad \dots (3)$$

where β and β_0 are the adiabatic compressibilities of the solution and solvent respectively, m and M_2 are the molality and molecular weight of the solute and d_0 and d are the densities of solvent and solution respectively.

The isothermal compressibility (β_T) is calculated by using Eq. (4).

$$\beta_T - \beta_s = \frac{\alpha^2 . T}{C_P . d} \quad \dots (4)$$

α is the thermal coefficient of expansion, T is absolute temperature, and C_p is the specific heat of the solution. C_p values have been taken from the literature[22].

The apparent molal isothermal compressibilities (ϕ_{KT}) can be computed by using the following equation:

$$\phi_{KT} = \frac{1000}{m . d . d_0} (\beta_T . d_0 - \beta_{0T} . d) + \beta_T . \frac{M_2}{d} \quad \dots (5)$$

where β_{0T} is the isothermal compressibility of the solvent.

It has been observed that $\phi_{KI} \approx \phi_{KS}$ within the experimental error limits.

Results and Discussion

It has been observed that sound velocity (u) for all alcohols goes through maximum when it is plotted as a function of concentration (m). The adiabatic compressibility (β_s) goes through minimum at around same concentration where sound velocity goes through maximum. The u_{max} or β_{min} shifts towards lower concentration with increase in chain length. Butanols show different values depending upon the geometric configuration of the molecule.

Figure 1 shows the variation of ϕ_K as a function of molality (m) for all alcohols at 2°C. Similar profiles were obtained at other temperatures.

It is observed that (i) for all the alcohols ϕ_K first decreases with concentration, passes through a broad minimum and then increases. The minima shifts towards lower concentration with increase
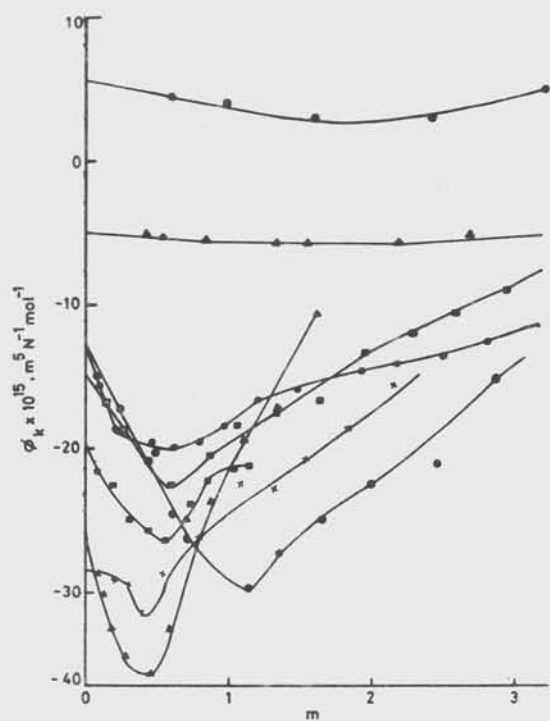
Fig. 1—Plots of apparent molal adiabatic compressibility (ϕ_{KS}) against molality (m) of aqueous alcohols.
○—○ methyl alcohol, △—△ ethyl alcohol, □—□ n-propyl alcohol, ●—● isopropyl alcohol, ▲—▲ n-butyl alcohol, ■—■ isobutyl alcohol, ×—× sec-butyl alcohol and ⊗—⊗ tert-butyl alcohol

Fig. 2—Plots of limiting apparent molal adiabatic compressibility (ϕ_{KS}^0) against temperature (T) of aqueous alcohols.
○—○ methyl alcohol, △—△ ethyl alcohol, □—□ n-propyl alcohol, ●—● isopropyl alcohol, ▲—▲ n-butyl alcohol, ■—■ isobutyl alcohol, ×—× sec-butyl alcohol and ⊗—⊗ tert-butyl alcohol

in chain length. (ii) The initial negative slopes of ϕ_K-m curves become more negative at lower temperatures as obtained from ϕ_K-m curves at different temperatures (not shown).

The initial negative slopes, $\dfrac{d\phi_k}{dm}$ represent the onset of solute molecules entering into natural cavities and thereby imparting some protection to the water structure. The occurrence of minimum in these curves would hence show the maximum occupancy. Further addition of alcohol now leads to gradual breakdown of structured water to make these available for interactions with added solute molecules leading to positive $\dfrac{d\phi_k}{dm}$.

The higher $\dfrac{d\phi_k}{dm}$ slopes at lower temperature indicate the tendency of structured water around solute to remain so on account of lack of sufficient thermal energy required for breakdown of water structure.
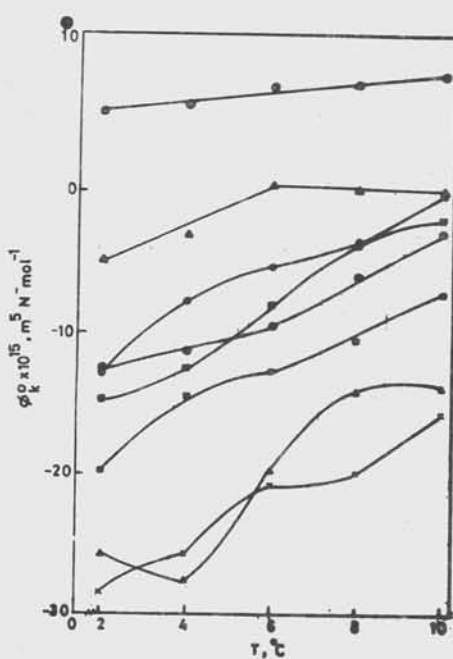
The limiting partial molal compressibilities (ϕ_k^0) of alcohols were obtained with smooth extrapolation of ϕ_K against molality (m) curves to zero concentration. Ideally, reliable ϕ_k^0 would be obtained only by extrapolation of a large number of points in very dilute region. As such our values could be questioned about their reliability. Comparison of ϕ_k^0 at 4°C shows a reasonable agreement with those at 5°C reported from this laboratory from differential measurements done in very dilute region (0-0.5 m, 25 points) as shown in Table 1. Figure 2 shows the variation of ϕ_k^0 as a function of temperature (T). It is seen that ϕ_k^0 increases with temperature for all alcohols. The increase being greater for butanols and smaller for lower alcohols. This suggests temperature labile hydrophobic hydration for higher alcohols, which is least for methanol.

Examination of Table 1 shows that ϕ_k^0 values for all alcohols at all the temperatures are negative or slightly positive except methanol. The negative ϕ_k^0 values suggest the loss in compressibility of solute (alcohol) on dissolution in solvent (water). But positive values of ϕ_k^0 for MeOH which are all around between 6 to 8×10^{-15} m^5 N^{-1} mol^{-1} are very similar in magnitude and sign of

Table 1—Limiting apparent molal compressibilities of alcohols

$\phi_k^0 \times 10^{15}\,(\mathrm{m^5\,N^{-1}\,mol^{-1}})$

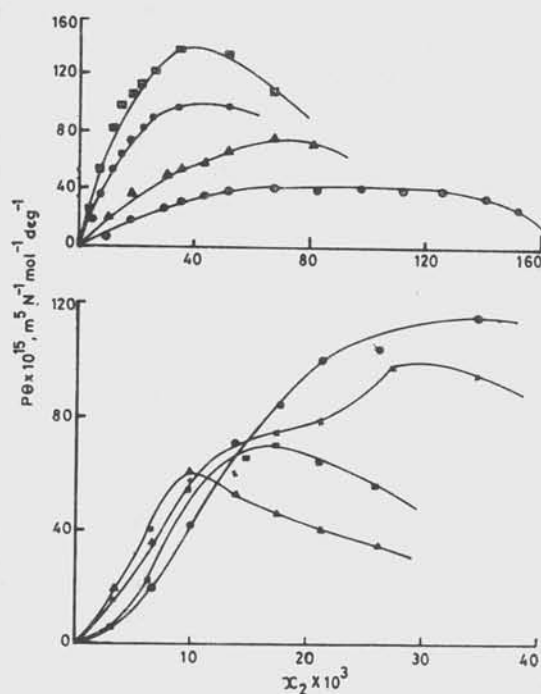| Alcohol	2°C	4°C	6°C	8°C	10°C	5°C (ref. 12)
MeOH	5.6	6.1	7.3	7.5	8.1	6.8
EtOH	− 4.9	− 3.1	0.6	0.0	0.1	− 1.4
n-PrOH	−14.8	−12.5	− 8.0	− 3.9	− 2.0	− 10.7
i-PrOH	−13.0	− 7.8	− 5.3	− 3.7	− 0.1	− 4.7
n-BuOH	−25.8	−27.6	−19.8	−14.4	−14.0	−20.2
i-BuOH	−19.8	−14.3	−12.8	−10.6	− 7.3	−14.7
s-BuOH	−28.4	−25.7	−20.8	−20.0	−15.8	−21.6
t-BuOH	−12.8	−11.4	− 9.5	− 6.0	− 3.0	− 9.7

Fig. 3—Plots of P_θ against mole fraction x_2 of aqueous alcohols.
○—○ methyl alcohol, △—△ ethyl alcohol, □—□ *n*-propyl alcohol, ●—● isopropyl alcohol, ▲—▲ *n*-butyl alcohol, ■—■ isobutyl alcohol, ×—× *sec*-butyl alcohol and ⊗—⊗ *tert*-butyl alcohol

that of pure water $(\beta_1^0 . V_1^0 = 8.8 \times 10^{-15}\,\mathrm{m^5\,N^{-1}}$ $\mathrm{mol^{-1}})$. This suggests that MeOH tends to become an indistinguishable partner of the water lattice on being dissolved in water (substitutional dissolution).

With increase in chain length ϕ_k^0 becomes more negative. This is expected because as the chain length increases contribution due to interaction of polar OH group with water molecule remains same but the size of hydrophobic moiety becomes large and the interactions between hydrophobic groups themselves lead to hydrophobic hydration. This results in loss of compressibility of water giving rise to negative ϕ_k^0 values.

Amongst butanols *t*-BuOH shows small negative ϕ_k^0 values. This suggests that *t*-BuOH being symmetrical, causes minimum modifications in the water structure around the solute[12,13].

It has been shown by Kaulgud[14] that relative structure strengthening abilities of molecules belonging to different homologous series can be better understood by studying the pressure derivative of structural effects $(\Delta\theta_{str})$ of the shift in TMD $(\Delta\theta)$ i.e.

$$\frac{\partial}{\partial P}(\Delta\theta_{str}) = P_\theta.$$

P_θ were calculated using Eq. (1), P_θ^0, the P_θ at infinite dilution were obtained by extrapolation of P_θ against x_2 curves to zero concentration.

It has been observed that our P_θ^0 values were little higher in magnitude than reported by Kaulgud[14] excepting for *t*-BuOH, which shows $− 0.025 \times 10^{-15}\,\mathrm{m^5\,N^{-1}\,mol^{-1}\,deg^{-1}}$ value as against $0.27 \times 10^{-15}\,\mathrm{m^5\,N^{-1}\,mol^{-1}\,deg^{-1}}$ reported by Kaulgud. Our values are calculated from ϕ_K values around TMD i.e. at 4°C, whereas Kaulgud

had to extrapolate these from higher temperature. Since the present values are obtained around TMD, these must be regarded as reliable.

It has been observed that MeOH shows a very small value of P_θ^0 $(0.09 \times 10^{-15}\,\mathrm{m^5\,N^{-1}\,mol^{-1}}$ $\mathrm{deg^{-1}})$ which is very close to 0 indicating least disturbance to water structure when it goes into the solution. This is in keeping with our earlier interpretation. The effect of chain length is also distinctly seen. It has also been observed that P_θ^0 increases with increasing chain length. But the effect of chain branching does not seem to influence P_θ^0 both in PrOH and BuOH series. The small value of *t*-BuOH can be again interpreted on the same basis of symmetrical nature of *t*-BuOH i.e. the molecules being symmetrical are accommodated in natural voids present in pure water or else such voids are easily available.

Figure 3 shows the variation of P_θ with concentration (x_2). It is observed that P_θ increases initially with increase in concentration, goes through maxima and then decreases. The magnitude of initial slopes increases with chain length indicating stronger water-water bonds than in water. This observation is supported by Knight's work[22]. He observed that the solvation of MeOH at low temperature is relatively more important than for

higher alcohols where iceberg formation is more predominant. The results of P_θ presented in this work are the first attempt to study the concentration dependence of stabilised network at low temperature. The addition of alcohol strengthens the water structure upto a concentration where maximum P_θ occurs. The nonspecific trend in P_θ maxima for alcohols indicate that the stabilisation of water network is the unique individuality of each alcohol and cannot at present be defined precisely unless further specific experiments are carried out. Further addition of alcohol leads to decrease in P_θ. This could be explained as follows:

The second term in brackets in Eq. 1 on the right hand side is considered as a correction term for solute-solute interactions. Thus decrease in P_θ after passing through maxima indicates the increase in solute-solute interactions and decrease in relative structure strengthening ability of solute and/or formation of new water structure network in the vicinity of solute.

Acknowledgement

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