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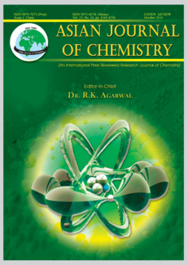

On the Utility of Energy-Volume Coefficient (Internal Pressure) to Study Excess Partial Molar Volumes of Alcohols in Aqueous Solutions at 298.15 K

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Using fine and precise data of density (ρ) at different temperatures, speed of sound (u) and specific heat (C_p) at 298.15 K, available in literature, the calculations of isothermal compressibility (k_T) in the limiting concentration range (0-0.25 M) for aqueous alcohol solutions (methyl to *n*-pentyl and *t*-butyl alcohols) have been made. The coefficient of thermal expansion (α_P) and isothermal compressibility (k_T) of solutions were used to obtain energy-volume coefficient $p_{int} = \left(\frac{\partial U}{\partial V}\right)_T$ property as a function of alcohol concentration. It was found that p_{int} increases with the increase in concentration, the extent becoming more as the chain length of alcohol molecules increase. Applying the Gibson-Trait equation of state, the calculations of excess partial molar volume $(\overline{V}_2^E)$ of alcohols were made, which are negative and again show dependence on chain length. Further calculations of excess internal pressure (p_{int}^E) were made using volume fraction statistics for aqueous alcoholic solutions except for *n*-pentanol-H_2O system. It is observed that solutions of methanol, ethanol and *tert*-butanol exhibit negative p_{int}^E but of *n*-propanol and *n*-butanol show positive p_{int}^E, increasing in magnitude with increase in concentration of alcohol. These results are explained on the basis of hydrophobic hydration of alcohols and persistence of hydrophobic interaction between the non-polar parts of alcohol down to lowest concentration studied in case of higher alcohols. It has been shown that pure liquid as a standard state is inadequate to obtain excess partial molar volumes of solute in water. The p_{int}^E profiles subtly differentiate the mode of interactions of alcohols, either by substitutional dissolution or by interstitial dissolution indicating the importance of structural changes of solvent water.

Key Words: Isothermal compressibility, Internal pressure, Excess partial molar volume, Alcohol.

INTRODUCTION

Aqueous solutions of alcohols are fascinating and are of utility for scientists and technologists. Frank and Ives[1] and Franks and Desnoyers[2] have highlighted the structural properties of alcohol-water mixtures. The study of these systems by many scientists led to development of concept of transfer thermodynamic functions[3,4], NMR-association parameter[5,6], light scattering study[7], application of Kirkwood-Buff theory[8-10] and virial coefficients through McMillan-Mayer theory of solutions[11,12]. The general conclusion from these studies is that, at least in dilute solutions, the predominant interaction is not only due to hydrogen bonding between the two species but also due to alkyl residues.

Solute interactions in dilute aqueous alcohol solutions have been studied with the application of statistical mechanics by Clark *et al.*[13]. They claimed that the results are not compatible with the model of hydrophobic association using the activity and partial molar volume data. Patil *et al.*[14], with the help of Kirkwood-Buff theory have shown that in dilute concentration region, the integrals of solute pair correlation functions (G_{AA}) exhibit extrema and indicate that the strength of hydrophobic interaction decreases (where the properties like isentropic compressibility, apparent molar volume go through a minimum), while these go through a maximum where the properties like excess free energy changes, excess entropy changes, viscosity go through extrema as a function of solute concentration. These observations were attributed to maximization of hydrophobic interaction effects.

The energy volume coefficient, $p_{int} = \left(\frac{\partial U}{\partial V}\right)_T$ property for solutions depends upon the expansive pressure due to thermal energy and the cohesive pressure due to temperature independent attractions between the molecules[15]. Marczak[16], Zorebski[17], Dack[18], Hyne *et al.*[19], as well as Patil *et al.*[20,21] and Dack[22] have described the utility of this parameter to understand the liquid structure and the water structure making and breaking effects due to solute in aqueous solutions. Recently Dhondge and coworkers[23,24] have obtained internal pressure for several aqueous solutions of non-electrolytes and interpreted the results in terms of hydrophobic interactions. Patil and Raut[20] have shown that for aqueous *t*-butanol solutions, initially p_{int} is insensitive to concentration changes and then increases going through a maximum where properties like excess free energy change for solution exhibit extrema. Such an observation is correlated with the variation of excess ultrasonic absorption as a function of mole-fraction (x_2) of alcohols[25]. Thus the p_{int} variation allows us to differentiate between hydrophobic hydration effect (solute induced-solvent interaction) and hydrophobic interaction (solute-solute attraction) effect subtly. In case of aqueous electrolyte solutions, there is always a contraction in volume due to electrostriction[26] (charge dipole interaction). Mukherjee[27] as well as Gardas *et al.*[28], have studied electrostriction in aqueous solutions at infinite dilution for a large number of electrolytes and obtained excess partial molar volumes by applying Gibson Trait equation to the high pressure compression data. Such data of internal pressure in dilute concentration range (especially of p_{int}) is non-existent for alcohol-water solutions [dipole-dipole and hydrophobic interaction (HI)]. However it has been now obtained using isentropic compressibility, volume and specific heat data. The data of variation of p_{int} in the concentration range of 0 to 0.25 M for aqueous methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol and *tert*-butanol have been calculated. For the alcohols discussed in this work, the excess limiting partial molar volume, $\overline{V}_2^{0E} = (\overline{V}_2^0 - V_{liq}^0)$ is calculated, where V^0_{liq} is the molar volume of the pure liquid solute and $\overline{V}_2^0$ is partial molar volume of solute at infinite dilution using Gibson-Tait equation. $\overline{V}_2^{0E}$ is always negative[29,30]. Unfortunately for a comparison involving range of solutes, partial molar expansivity must be related to reference states because they contain sizeable contribution due to the intrinsic volumes of the solute molecules. Since alcohols are known to associate through hydrogen bonding in pure liquid state, the liquid as a standard state is questionable[30]. We have also obtained excess internal pressure (p^E_{int}) assuming pure liquid as standard state and using volume fraction statistics. The results of both the approaches are presented and discussed from the point of view of hydrophobic hydration and interactions.

EXPERIMENTAL

Density (ρ) for aqueous alcohols (MeOH to *n*-PentOH) at 278.15, 298.15 and 318.15 K were obtained from Nakajima *et al.*[31] and speed of sound (u) for aqueous solutions of above alcohols at 298.15 K were obtained from Nakajima *et al.*[32]. Density data (ρ) were used to obtain coefficient of thermal expansivity (α_P) at 298.15 K and has been computed by using the relation:

$$\alpha_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \tag{1}$$

Isentropic compressibility (k_S) for solutions were obtained using Newton-Laplace equation:

$$k_S = \frac{1}{u^2 \rho} \tag{2}$$

where, ρ is density of solution and u is speed of sound in solution.

The specific heat at constant pressure (C_p) data for solutions has been obtained from the apparent molar specific heat of solutes (ϕ_{C_P}) data reported by Jolicour and Lacroix[33]. The data were normalized to whole figure concentrations (in molality) by appropriate fitting and using appropriate polynomial equations. These are listed in the form of coefficients of equations for ρ, C_p, u and k_s in Table-1.

The calculations of isothermal compressibility (k_T) were made by using, k_s, α_P and C_p data and using the equation:

$$k_T - k_s = \delta = \frac{\alpha_P^2 T}{\sigma} = \frac{\alpha_P^2 T}{C_P \rho} \tag{3}$$

The variation of δ is the main contributing factor in obtaining k_T from k_S values[34]. The parameters, k_S, α_P and σ for pure water used were 44.755 × 10^{-11} Pa^{-1}, 2.55 × 10^{-4} K^{-1} and 4.1670 J K^{-1} cm^{-3}, respectively. The C_p value for water used was 4.1793 J K^{-1} g^{-1}, while that of speed of sound used was 1497.0 m s^{-1}. The use of all these resulted in calculated values of k_T and δ as 45.226 × 10^{-11} Pa^{-1} and 0.4714 × 10^{-11} Pa^{-1} for

TABLE-1
POLYNOMIAL COEFFICIENTS OF, ρ, u, C_p, k_S, k_T, α_P AND p_{int} AS A FUNCTION OF MOLALITY (m) FOR AQUEOUS ALCOHOL SOLUTIONS AT 298.15 K

	10^{-3} ρ/Kg m^{-3}	u/m s^{-1}	Cp/J K^{-1}	10^{11} k_S/Pa^{-1}	10^{11} k_T/Pa^{-1}	10^4 α_P/K^{-1}	10^{-5} p_{int}/Pa (eqn. 5)
Water (y_o)	0.997048	1497.0	4.1793	44.755	45.226	2.55	1681
MeOH (g)	-0.0059	12.0	0.0229	-0.453	-0.450	0	16.9
(h)	–	–	–	–	–	–	–
EtOH (g)	-0.0061	30.9	0.0673	-1.452	-1.472	-0.0284	29.9
(h)	-0.0176	–	–	–	–	-0.0769	–
n-PrOH (g)	-0.0102	49.8	0.0986	-2.512	-2.488	0.0135	146.4
(h)	–	–	–	–	–	0.7847	–
n-BuOH (g)	-0.012	65.4	0.1297	-3.358	-3.237	0.1337	341.6
(h)	–	–	–	–	–	2.4302	–
n-PentOH (g)	-0.0138	80.5	0.1544	-4.168	-3.994	0.1901	468.2
(h)	–	–	–	–	–	3.3195	–
t-BuOH (g)	-0.0131	61.1	0.1488	-3.156	-3.171	-0.1332	105.1
(h)	–	–	–	–	–	1.2955	–

water at 298.15 K. These are in good agreement with those obtained by Desnoyers and Philip[34].

The energy volume coefficient (internal pressure) *i.e.*, values at different alcohol concentrations were evaluated using the equation of state:

$$p_{int} = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p_{int} = T\beta_V - p \quad (4)$$

where, β_V is thermal pressure coefficient. Assuming p (1 atm = 101325 Pa) is negligible and using $\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha_p}{k_T}$, equation 4 becomes

$$p_{int} = T\left(\frac{\partial p}{\partial T}\right)_V = T\beta_V = \frac{\alpha_p T}{k_T} \quad (5)$$

The internal pressure p_{int} data reported by Patil and Raut[20] was directly used for *tert*-BuOH-H_2O solutions, while for straight chain alcohol solutions; the above methodology was used. The data of α_P, κ_T and p_{int} were fitted with following polynomial equations:

$$y = y_0 + gm + hm^2 \quad (6)$$

where, y is the value for given property, m is the molality of solution and y_0 is the value of property for pure water, g and h are the coefficients. These coefficients are listed Table-1. The variation of p_{int} at 298.15 K as a function of molality of alcohols is shown in Fig. 1. The estimated errors in κ_T and p_{int} values are of the order of ± 0.01 × 10^{-11} Pa^{-1} and ± 2 × 10^5 Pa for aqueous solutions of alcohols. The details about Gibson-Tait equation are given elsewhere[15]. The useful equation is:

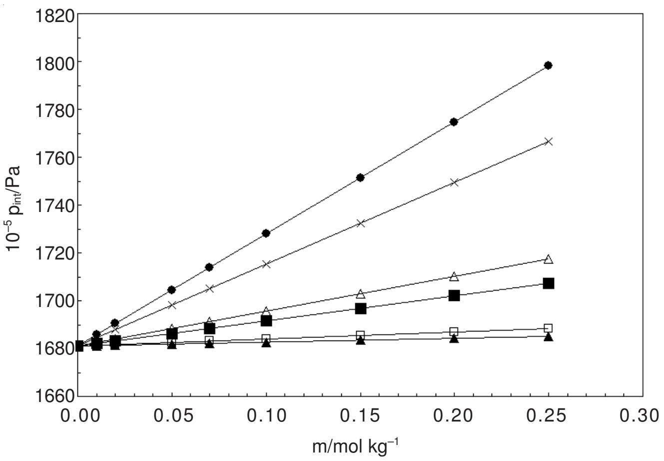

Fig. 1. Variation of the internal pressure (p_{int}) as a function of molality (m) of alcohols at 298.15 K ▲-▲, MeOH; □-□, EtOH; Δ-Δ, *n*-PrOH; ×-×, *n*-BuOH; ●-●, *n*-PentOH; ■-■, *t*-BuOH

$$\overline{V}_2^{(\rho)} - M_2 v_2 = -\frac{434.3C}{v_0(B + p_{int} + p)} \frac{\partial(B + p_{int})}{\partial m} \quad (7)$$

where C and B are positive constants. The $\frac{C}{v_0}$ (v_0 being the apparent specific volume of solvent) term having a value of 0.3150 while the B is 2996 × 10^5 Pa at 298.15 K. The v_2 is specific volume of pure solute (as a liquid). We can call p_{int} as the effective internal pressure created in solution due to dipole-dipole (H-bonding) and hydrophobic interaction between the solute molecules. The equation shows that the magnitude of the partial molar volume of solute is governed by two factors. The term $\frac{\partial(B + p_{int})}{\partial m}$ is the rate of change of total internal pressure with concentration and is a function of both solvent and solute. The term $\frac{434.3C}{v_0(B + p_{int} + p)}$ is related to the compressibility of the solvent at the pressure (p_{int} + p) and is independent of solute. p_{int} is considered to have constant characteristics for a given system at constant composition and temperature.

Gibson[35] derived the equation:

$$\overline{V}_2^0 - V_2^0 = \frac{-1000}{(B + p_{int} + p)} \frac{\partial(B + p_{int})}{\partial m} \quad (8)$$

where m is the molality of solution and V_2^0 is taken to be the hypothetical molar volume of the pure solute in the liquid state at the temperature and pressure of the experiment. The volume change $\overline{V}_2^0 - V_2^0$ is therefore the change in the volume on mixing this hypothetical pure liquid solute and the solvent. To obtain the value of excess partial molar volume $(\overline{V}_2^0 - V_2^0)$ at infinite dilution, we must take the limiting case of eqn. 8. The term $\frac{1000}{v_0(B + p_{int} + p)}$ represents the compressibility of solvent at an external pressure (p_{int} + p). At infinite dilution of the solute this can be replaced by the compressibility of pure water k_T at 1 atm (45.23 × 10^{-11} Pa^{-1} at 298.15 K). eqn. 8, then reduces to

$$\overline{V}_2^0 - V_2^0 = \frac{k_T}{\rho_0} \lim_{m \to 0} \frac{d}{dm}(B + p_{int}) \quad (9)$$

However, this $\overline{V}_2^0 - V_2^0$ can be strictly called the value of excess partial molar volume at infinite dilution only if it arises entirely from changes in the effective pressure (p_{int}) and not in B. The values of $\overline{V}_2^0, \phi_E^0, \frac{\partial p_{int}}{\partial m}, V_2^0$ are collected in Table-2, while the data of excess partial molar volume of alcohols $(\overline{V}_2^{0E})$ are compared with literature data (obtained liquid as a standard state) and are also incorporated in Table-2.

In order to calculate excess internal pressure of solutions (p^E_{int}), we adopted following approach because excess functions have been originally defined for extensive variables. Assuming that the Dalton's law of partial pressures holds good for the mixtures, we write,

$$p_{int}^E = p_{int} - p_{int}^{id} = p_{int}^E - \sum \psi_i p_{int,i}^* \quad (10)$$

where, ψ_i represents the volume fraction of component i and is the internal pressure value of the component, i. For binary solutions, the ideal pressure (p_{int}^{id}) is

TABLE-2

LIMITING PARTIAL MOLAR VOLUME OF SOLUTES ($\overline{V}_2^0$), LIMITING PARTIAL MOLAR EXPANSIVITY (ϕ_E^0), $\frac{\partial(p_{int})}{\partial m}$, MOLAR VOLUMES OF PURE SOLUTES (V_2^0), LIMITING EXCESS PARTIAL MOLAR VOLUME ($\overline{V}_2^{0E}$) CALCULATED USING EQN. 8 AND KNOWN IN LITERATURE ON THE BASIS OF PURE LIQUID AS A STANDARD STATE AT 298.15 K

Alcohol	$10^6\ \overline{V}_2^0$ / (m³ mol⁻¹)	$10^6\ \phi_E^0$ / (m³ mol⁻¹ deg⁻¹)	$10^{-5}\ \frac{\partial(p_{int})}{\partial m}$ / (Pa mol⁻¹)	$10^6\ V_2^0$ / (m³ mol⁻¹)	$10^6\ \overline{V}_2^{0E(Eq)}$ / (m³ mol⁻¹)	$10^6\ \overline{V}_2^{0E}$ / (m³ mol⁻¹) (liquid as std. state
MeOH	38.25	0.014	16.90	40.73	-2.48	-0.76
EtOH	55.12	0.012	29.26	58.68	-3.56	-1.32
n-PrOH	70.63	0.021	146.48	75.16	-4.53	-6.63
n-BuOH	86.48	0.035	341.24	91.96	-5.48	-15.43
n-PentOH	102.88	0.062	468.24	108.71	-5.83	-21.18
t-BuOH	87.90	0.010	105.19	94.90	-7.00	-4.76

$$p_{int}^{id} = \psi_1 p_{int,1}^{*} + \psi_2 p_{int,2}^{*} \qquad (11)$$

where, ψ_1 and ψ_2 are the volume fractions of solvent and solute in solution, respectively, while $p^*_{int,1}$ and $p^*_{int,2}$ are the internal pressures of pure water (1680×10^5 Pa) and alcohols at 298.15 K, respectively. The $p^*_{int,2}$ values for MeOH, EtOH, *n*-PrOH , *n*-BuOH and *tert*-BuOH used are 2811.8×10^5, 2869.7×10^5, 2840.75×10^5, 2960.5×10^5 and 3344.5×10^5 Pa, respectively. These values were obtained from the compilation made by Dack[18]. We could not obtain pure liquid value for *n*-PentOH and hence for *n*-PentOH-water system the calculations of excess internal pressure could not be made. The volume fractions for water (ψ_1) and for alcohols (ψ_2) were made by using the eqns. 12 and 13 given below. In these calculations, we did not neglect the atmospheric pressure in eqn. 4 as we wanted to have excess internal pressure values, which were expected to be small magnitude.

$$\psi_1 = \frac{x_1 \overline{V}_1}{x_1 \overline{V}_1 + x_2 \overline{V}_2} \qquad (12)$$

$$\Psi_2 = \frac{x_2 \overline{V}_2}{x_1 \overline{V}_1 + x_2 \overline{V}_2} \qquad (13)$$

where, x_1 and x_2 are the mole fractions of water and alcohol, respectively, while, $\overline{V}_1$ and $\overline{V}_2$ represent the partial molar volume of water and alcohol, respectively. These were obtained from the density/apparent molar volume of solute (ϕ_V) data and using Gibbs-Duhem equation. Using eqn. 11, calculations of ideal internal pressures of mixtures were made, while using data solutions, the calculations of excess internal pressure (p_{int}^E) at various concentrations of alcohols were made (eqn. 10). The variations of p^E_{int} as a function of molality (m) are shown in Fig. 2. It is observed that values of p^E_{int} are negative in magnitude for MeOH, EtOH and *tert*-BuOH, while these are positive and increase in magnitude as molality of alcohol increases in case of *n*-PrOH and *n*-BuOH, respectively. It is to be noted that the calculated internal pressure values for ideal mixing based on pure liquid as standard state using mole-fraction additivity give lower values in magnitude than those based on volume fraction additivity. These result into lower p^E_{int} values if one uses volume-fraction statistics as has been done in the present approach.

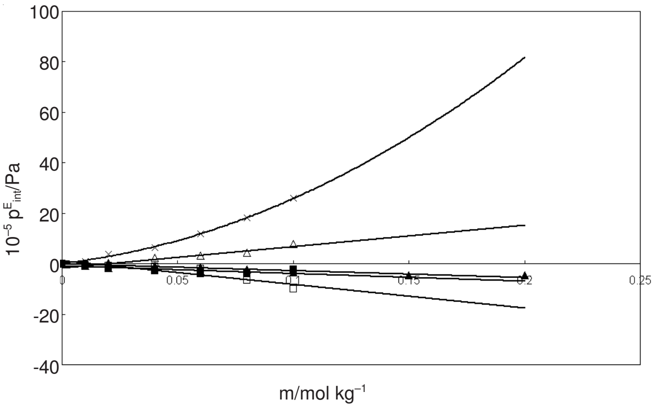

Fig. 2. Variation of the excess internal pressure (p^E_{int}) as a function of molality (m) of alcohols at 298.15 K ▲-▲, MeOH; □-□, EtOH; Δ-Δ, *n*-PrOH; ×-×, *n*-BuOH; ■-■, *t*-BuOH

RESULTS AND DISCUSSION

It is observed from Table-2 that the limiting apparent molar expansivity (ϕ_E^0) for lower alcohols is of small magnitude. This is due to insensitivity of the thermal coefficient of expansion (α_P) of solutions, while the same changes much more in case of higher alcohols (*n*-BuOH and *n*-PentOH). The combination of this with compressibility data allows us to study the variation of internal pressure (p_{int}) which changes little in case of aqueous methanol and aqueous ethanol solutions as a function of concentration, while much more rapidly in case of *n*-BuOH and *n*-PentOH solutions. The case of aqueous *t*-BuOH is intermittent between the two extremes. It is thus observed that although all alcohols studied contain only one functional polar -OH group, the non-polar portion imparts additional attraction showing the importance of hydrophobic interaction. We have studied p_{int} in the limiting concentration range where generally solute-solute interactions are assumed to be neglected and the effects are accounted in terms of solute-solvent interactions. Present studies reflect that even in limiting concentration range, solute-solute association effect persists in case of higher alcohols. The trend of p_{int} of homologous series of mono functional alcohols (p_{int}) is in the order MeOH < EtOH < *t*-BuOH < *n*-prOH < *n*-BuOH < *n*-PentOH suggesting that it is a reasonable approximation to consider these quantities as a sum of two contributions: first due only to the hydrocarbon-water interaction and the second arising at least in part due to the interaction between hydrophilic centre (OH group) allowing the lower alcohols forming H bonds to be incorporated in water clusters. Probably in this way the structure of water is preserved against the breaking up caused by thermal energy and the expansive pressure due to compression. This is amply evident in case of MeOH and EtOH and to some extent in case of *t*-BuOH solutions while the trends for higher alcohols show the predominance of alkyl group interaction.

The excess partial molar volume at an infinite dilution, is defined as:

$$\overline{V}_2^0 = V_2^0 + \overline{V}_2^{0E} \qquad (14)$$

The application of Gibson-Tait equation gives the values of $\overline{V}_2^{0E}$ without any assumption about V_2^0. The values are collected in Table-2 and reveal that for lower alcohols these are negative and small in magnitude, comparing reasonably well with those obtained from the assumption of pure liquid as a standard state. The data for higher alcohols show large negative values and do not compare with liquid state standard values. Therefore $\overline{V}_2^E$ increases in magnitude (with contraction) as the hydrophobicity increases. These facts can be interpreted by the idea that the structural change cannot be assessed as pure alcohol standard state. The shape of the molecule (in case of *t*-BuOH) as well as the extent of non-polar groups for which hydrophobic (alkyl-alkyl group) interaction contributes additionally, resulting in the increase of p_{int} as well as of $\overline{V}_2^{0E}$. We do not claim much accuracy in calculated $\overline{V}_2^{0E}$ values but it is assumed to be of the order of 0.5×10^{-6} m^3 mol^{-1}. Considering this, the variation of $\overline{V}_2^{0E}$ with number of carbon atoms is significant. Kaulgud and Patil[36] have interpreted the apparent molar compressibility values for amines in aqueous solutions in terms of substitutional dissolution of the lower amines and interstitial dissolution for other higher amines[1]. We can extend the same analogy for aqueous alcohol solutions. Accordingly the interstitially dissolved amines or alcohols (*n*-PrOH, *n*-BuOH, *n*-PentOH) can be thought of as occupying either the cavities existing in the open structure or else such cavities or created on demand to suit the size and shape of the solute. The latter case will lead to strengthening of water structure in the vicinity of solute molecules giving large negative values of $\overline{V}_2^{0E}$. In substitutional dissolution (MeOH, EtOH, *t*-BuOH) an alcohol molecule at infinite dilution occupies one of the so called "Framework sites"[1] displacing one water molecule into the bulk. Formation of one or two hydrogen bonds with alcohol thus leads to the breakdown of a few others formed originally by the oxygen atom of the displaced water molecules. The overall scheme thus seems to consist of breakdown of H-bonded aggregate of lower alcohols (as pure liquid solutes), formation of new H-bonds with the framework water molecules and stabilizing effect on water structure causing small volume contraction and hence lower values for excess partial molar volume, $\overline{V}_2^{0E}$. In the light of all these facts we emphasize that the values obtained in the present study can only be rationalized in terms of well established three dimensional nature of water, the clathrate like nature of hydrophobic hydration (MeOH, EtOH), the pair wise nature of hydrophobic attractive interaction (for *n*-PrOH to *n*-PentOH) even in limiting concentration region and the H-bonding interaction between water and alcohols.

The above arguments can be supported by examining Fig. 2, wherein, excess internal pressure of solutions (p^E_{int}) profiles are depicted as a function of molality (m) of alcohols. It is observed that MeOH, EtOH and *t*-BuOH, there are negative p^E_{int}, the magnitudes increase with increase in concentration, while for *n*-PrOH and *n*-BuOH these are positive. Thus, the dissolution mode of lower alcohols are distinct from those of higher alcohols, which can be attributed to succinct structural changes in solvent around these alcohol molecules.

The energy volume coefficient *i.e.*, p_{int} has been the most fundamental property of liquid system and relates the susceptibility of the internal energy to isothermal volume change which in turn are sensitive to intermolecular interactions. Macdonald and Hyne[37] discussed this parameter for MeOH and *t*-BuOH systems for the entire mole-fraction region. They have discussed p_{int} in terms of sum of intermolecular attraction and repulsion and dependence on intermolecular distance. The maxima in p_{int} were attributed to minimum of free volume effect. Our results of p_{int} in very dilute concentration region highlight the effect of chain length of alcohol molecules as well the interactions of alcoholic OH group with the lattice sites of water structure, more distinctly as compared to the maximum in p_{int} at high concentration. A detailed molecular interpretation of these observations, however, await more detailed investigation of the highly aqueous other systems as well about the problems of liquid state structure, specification of standard state and interaction of molecules in flickering clusters and hence the stabilization and breaking of open hydrogen bonded liquid water structure against disruption by compression.

Conclusion

We have obtained isothermal compressibility (k_T) and internal pressure (p_{int}) data in dilute concentration region for aqueous solutions of alcohols. The application of Gibson-Tait equation of state to the p_{int} data allowed to determine excess partial molar volumes of alcohols at infinite dilution at 298.15 K. The results show that the volume contraction is small for lower members of the homologous series while large for higher members. Therefore H-bonding interaction present in pure alcohols makes the assumption of pure liquid as a standard state questionable and not in accordance with the data obtained using Gibson-Tait equation of state. Excess internal pressure (p^E_{int}) values have been obtained using volume fraction statistics and literature values of internal pressure of pure liquids. The results of $\overline{V}_2^{0E}$ values as well the excess internal pressure (p^E_{int}) profiles indicate a possible distinction of the way alcohol molecules exert their stabilizing influence. The lower members of the homologous series appear to dissolve predominantly substitutionally and thus strengthening the native water structure (hydrophobic hydration) whereas the higher members dissolve by occupying with creation of larger cavities and forcing water into an ordered arrangement through exertion of pair-wise hydrophobic attraction between alkyl groups in combination with the hydrophobic hydration H-bonding influence.

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