

## Application of Kirkwood-Buff theory of liquid mixtures to binary aqueous solutions of alcohols

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The various integrals over the pair correlation functions,  $G_{AA}$ ,  $G_{WW}$  and  $G_{AW}$  (A=alcohol, W=water) have been calculated for aqueous solutions of methanol, ethanol, 1-propanol and *tert*-butanol at 25°C by utilizing the thermodynamic properties like the isothermal compressibility, partial molar volumes and vapour pressure and by the application of an inverse procedure for Kirkwood-Buff theory of solutions as suggested by Ben-Naim. It is observed that as a function of concentration,  $G_{AA}$ ,  $G_{AW}$  and  $G_{WW}$  have extremas in the studied concentration range. The results are compared with similar systems reported earlier and are interpreted on the basis of solvent structural effects and hydrophobic interaction amongst the solute molecules. The behaviour of  $G_{AA}$  in dilute concentration indicates that the strength of hydrophobic interaction decreases initially in all the studied water-alcohol systems. The mean square concentration fluctuation parameter  $N \langle (\Delta x)^2 \rangle$  as a function of concentration has been estimated using  $G_{ij}$  values. These results are in agreement with the available scattering data, suggesting further that the main effect of alcohol is to interfere destructively with low density domains in water in dilute concentration of alcohols in water.

The Kirkwood-Buff theory is a powerful tool for solution studies<sup>1</sup> and the parameters relate macroscopic quantities to the microscopic structure of the system. The theory involves the calculations of integrals  $G_{ij}$ 's of the orientation averaged pair distribution functions with the help of thermodynamic parameters like partial pressures, partial volumes of the solute and compressibility of the solutions. Such calculations have been reported for some alcohol-water and other non-electrolyte-water systems<sup>2-8</sup>.

Recently Iijima *et al.*<sup>9</sup> from X-ray small angle scattering measurements have successfully shown that the concentration fluctuation parameter  $N \langle (\Delta x)^2 \rangle$  can be correlated with the KB parameters and further established the importance of complementary information obtained through the analysis of spectroscopic and thermodynamic data at molecular level.

In this paper, we report our analysis of the thermodynamic data available in literature about vapour pressure, compressibility and volume of systems: MeOH-H<sub>2</sub>O (0 to 100%), EtOH-H<sub>2</sub>O (0 to 100%), *n*-PrOH-H<sub>2</sub>O (0 to 100%) and *t*-BuOH-H<sub>2</sub>O (0 to 40%) at 25°C. By applying the KB theory and the inverse procedure suggested

by Ben-Naim, the integrals over pair correlation functions,  $G_{AA}$ ,  $G_{AW}$ ,  $G_{WW}$  and  $N \langle (\Delta x)^2 \rangle$  were calculated as a function of concentration of alcohol molecules. These are reported here and compared with the data of other workers mentioned earlier.

### Conceptual aspects of the theory and analysis

The KB integrals ( $G_{ij}$ ) are defined by Eq. (1) (ref. 10)

$$G_{ij} = \int_0^{\infty} (g_{ij}(r) - 1) 4\pi r^2 \cdot dr \quad \dots (1)$$

where  $g_{ij}(r)$  is the radial distribution function or pair correlation function between the species *i* and *j*. The  $G_{ij}$  is the average excess over the bulk average of the number of molecules of type *j* (or *i*) around a molecule of type *i* (or *j*) per unit number density of molecules of type *j* (or *i*). For a two component system of species A (organic solute) and W (water), the KB equations are:

$$\eta = \rho_A + \rho_W + \rho_A \rho_W (G_{AA} + G_{WW} - 2G_{AW}) \quad \dots (2)$$

$$\xi = 1 + \rho_A G_{AA} + \rho_W G_{WW} + \rho_A \rho_W (G_{AA} \cdot G_{WW} - G_{AW}^2) \quad \dots (3)$$

where  $\eta$  and  $\xi$  are the functions that appear in the equations below and  $\rho_A$  and  $\rho_W$  are the number densities of A and W respectively<sup>11</sup>.

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From thermodynamic considerations

$$\rho/\eta = x_A \left( \frac{d \ln p_A}{dx_A} \right) \quad \dots (4)$$

where  $p_A$  is the partial pressure of A and  $\rho$  is the total number density. Using Eq. (4), the values of  $\eta$  at different concentrations can be computed. Similarly,  $\xi$  can be obtained by using Eq. (5)

$$\beta_T = \xi/kT\eta \quad \dots (5)$$

where  $\beta_T$  is the isothermal compressibility,  $k$  is Boltzmann constant and  $T$  is temperature.

The three KB integrals  $G_{AW}$ ,  $G_{WW}$  and  $G_{AA}$  can be calculated from Eqs (6-8)

$$\bar{V}_A \cdot \bar{V}_W = (\xi - \eta G_{AW})/\eta^2 \quad \dots (6)$$

$$\bar{V}_A = [1 + \rho_W (G_{WW} - G_{AW})]/\eta \quad \dots (7)$$

$$\bar{V}_W = [1 + \rho_A (G_{AA} - G_{AW})]/\eta \quad \dots (8)$$

where  $\bar{V}_A$  and  $\bar{V}_W$  are the respective partial molal volumes of species A and W.

Using the three KB integrals, the parameter  $\Delta_{AW}$ , the degree of similarity can be calculated by using Eq. (9), the magnitude of which may serve to indicate the extent of deviation from a symmetrical ideal behaviour<sup>11</sup>.

$$\Delta_{AW} = G_{AA} + G_{WW} - 2G_{AW} \quad \dots (9)$$

The mean square concentration fluctuation  $N \langle (\Delta x)^2 \rangle$  can be expressed in terms of  $G_{ij}$  as<sup>4</sup>,

$$N \langle (\Delta x)^2 \rangle = x_A \cdot x_W [1 + \rho \cdot x_A \cdot x_W \cdot \Delta_{AW}] \quad \dots (10)$$

Equation (10) is useful for understanding the meaning of  $N \langle (\Delta x)^2 \rangle$ . If the affinity between the like species and that between unlike species are same ( $G_{AA} = G_{WW} = G_{AW}$ ),  $N \langle (\Delta x)^2 \rangle$  is equal to  $x_A x_W$  ( $F = N \langle (\Delta x)^2 \rangle / x_A \cdot x_W = 1$ ). When the affinity between the like species is stronger than that between unlike species ( $G_{AA} + G_{WW} > G_{AW}$ ),  $N \langle (\Delta x)^2 \rangle$  is larger than  $x_A \cdot x_W$  ( $F > 1$ ). When the affinity between unlike species is stronger than that between like species ( $G_{AA} + G_{WW} < G_{AW}$ ),  $N \langle (\Delta x)^2 \rangle$  is smaller than  $x_A \cdot x_W$  ( $F < 1$ ). Kato has discussed the usefulness of these parameters to understand the state of mixing in aqueous solution<sup>4</sup>.

The partial molal volumes  $\bar{V}_A$  and  $\bar{V}_W$  for the aqueous solutions of methanol, ethanol, 1-propanol and *tert*-butanol were obtained from the analysis of density data reported by Benson *et al.*<sup>12</sup> and Desnoyers *et al.*<sup>13</sup>. The partial pressure data required for the calculation of  $\eta$  values for the aqueous solutions of ethanol and *tert*-butanol were obtained from the vapour pressure data of Vaslow *et al.*<sup>14</sup> and given in the book of Rock<sup>15</sup>

and Ives and Brown<sup>16</sup> respectively, while, for aqueous solutions of methanol and *n*-propanol the corresponding data were taken from the Butler *et al.*<sup>17</sup>. Recently Koga *et al.*<sup>18</sup> have reported total vapour pressure of aqueous *tert*-butanol solutions, which has not been used by us (see below). The values of  $\eta$  can also be calculated by utilizing the activity coefficient or excess free energy or partial vapour pressure of solvent. However, we prefer to calculate  $\eta$  using partial pressure of solute ( $p_A$ ). The reasons for adopting this approach are:

(i) The use of activities in the place of partial pressure brings in the question of standard state of the solute. There is no consensus amongst scientific workers about this as in literature one finds use of Henry's law or Raoult's law (i.e. pure solvent as a standard liquid and use of Gibb's Duhem equation).

(ii) Kato<sup>4</sup> has shown that the calculation of  $N \langle (\Delta x)^2 \rangle$  using partial pressure of solute and other thermodynamic parameters as input gives values which agree very well with the values obtained from measurements of Rayleigh scattering.

We have not attempted to express the data of volumes, compressibility and vapour pressure in the form of any equations having various constants. The calculation of concentration derivatives of the volume ( $\phi_v$ ) and vapour pressure ( $p_A$ ) were made by drawing appropriate curves graphically and the required derivatives were obtained by drawing tangents using mirror method. The validity of the method of estimating  $\bar{V}_A$  and  $\bar{V}_W$  was verified by making the calculations of  $\bar{V}_A$  and  $\bar{V}_W$  for THF-H<sub>2</sub>O system at 25°C, the comparison of which over the whole concentration region was found to be in excellent agreement with the values reported by Zaitsev *et al.*<sup>19</sup>. Similarly, the calculations of the parameter  $d \ln p_A / dx_A$  for methanol at low concentrations (0 to 10%) were made using Butler *et al.*<sup>18</sup> data as well as the data of Tucker *et al.*<sup>20</sup>. The two sets of data were found to be in close agreement with each other. Isothermal compressibilities for ethanol-water were computed by using expansivity, adiabatic compressibility, density and specific heat<sup>21</sup>. For other systems, adiabatic compressibilities were used instead of isothermal as this parameter does not affect  $G_{ij}$  parameters appreciably<sup>22</sup>.

The KB integrals  $G_{AA}$ ,  $G_{AW}$  and  $G_{WW}$  were computed by using Eqs (6-8). The errors involved in various  $G_{ij}$ 's at different concentrations were estimated following the method suggested by Zaitsev *et al.*<sup>19</sup>. The magnitude of the errors in low concentration region <10 mole % are comparat-

ively less than in the region of 10 to 40 mole % of alcohols which is mainly because of large errors involved in the parameter  $d \ln p_A / dx_A$ . The estimated errors in the  $G_{ij}$  parameters are indicated by showing vertical bars over the corresponding points in figures. The variations of KB integrals as a function of concentration for the systems MeOH-H<sub>2</sub>O, EtOH-H<sub>2</sub>O, *n*-PrOH-H<sub>2</sub>O and *t*-BuOH-H<sub>2</sub>O are shown in Figs 1, 2, 3 and 4 respectively. The variation of degree of similarity parameter,  $\Delta_{AW}$  with mole % of alcohol is shown in Fig. 5.

The values of mean square concentration fluctuation,  $N \langle (\Delta x)^2 \rangle$  for various alcohol-water mixtures were calculated using Eq. 10 and are shown in Fig. 6. In order to compare the deviations from symmetrical ideal solution for various alcohol systems, the values of calculated parameters,  $F$  as a function of  $x_A$  are exhibited in Fig. 7.

## Results and Discussion

It can be seen from Figs 1-4 that  $G_{AA}$  goes through a minimum at about 6-8 mole %, 10 mole %, 2.5 mole % and 4 mole % of methanol, ethanol, *n*-propanol and *tert*-butanol respectively, while, with further increase in concentration of alcohol it goes through a maximum at about 30 mole %, 20 mole % and 10 mole % of ethanol, *n*-propanol and *tert*-butanol respectively. However, in the case of methanol it remains almost constant. The positive slope of  $G_{AA}$  with concentration (in the range of 10 to 30 mole % of alcohols) is in agreement with the observation of Ben-

Naim<sup>1</sup>, Donkersloot<sup>2</sup>, Matteoli<sup>5</sup> etc. The initial minimum in low concentration region is in agreement with Patil's observation for *tert*-butanol<sup>3</sup> and the prediction of Ben-Naim for ethanol-water system<sup>1</sup>. It is also pleasing that  $G_{AA}$  data of *tert*-butanol in the concentration range of 5-30 mole % is in very good agreement with the data of Iijima *et al.* obtained from X-ray scattering analysis and which has already been compared graphically by Iijima and coworkers<sup>9</sup>.

The  $G_{WW}$  (Figs 1-4) parameter for all the studied systems increases slowly initially and goes through a maximum at about 30 mole %, 20 mole % and 25 mole % of ethanol, *n*-propanol and *tert*-butanol respectively. In the case of methanol-water system, this maximum cannot be established conclusively. These observations are also in agreement with those of other workers.

The interesting observation from this work seems to be variation of  $G_{AW}$  (Figs 1-4) with concentration. It increases initially (becomes less negative) and then goes through a minimum at the concentration, where  $G_{AA}$  goes through a maximum. We feel that there is a feeble maximum in  $G_{AW}$  in low concentration region for EtOH-H<sub>2</sub>O system but the same cannot be established for *n*-propanol and *tert*-butanol as there are limited number of data points in low concentration region. In the case of methanol solutions  $G_{AW}$  increases distinctly up to 12 mole % and thereafter remains constant. It is quite likely that the concentration of maximum in  $G_{AW}$  may be same as

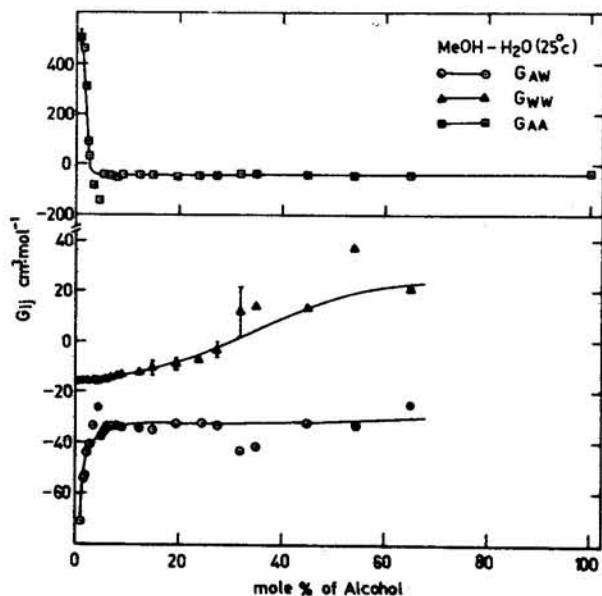


Fig. 1—The concentration dependence of  $G_{ij}$ , for methanol-water system at 25°C.

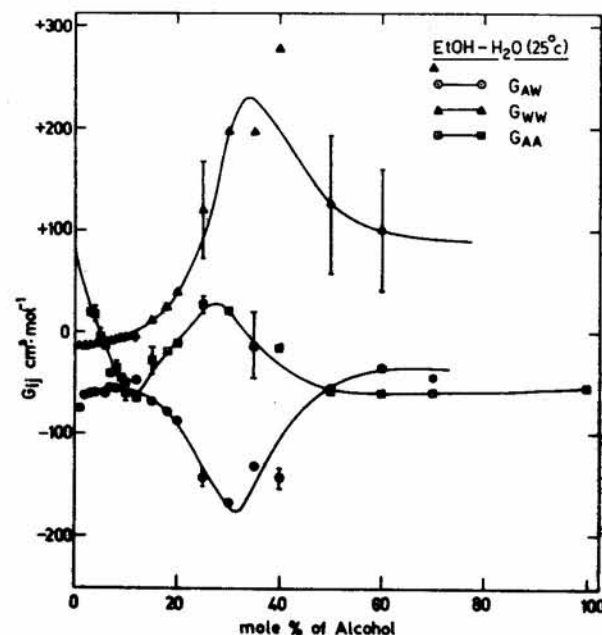


Fig. 2—The concentration dependence of  $G_{ij}$ , for ethanol-water system at 25°C.

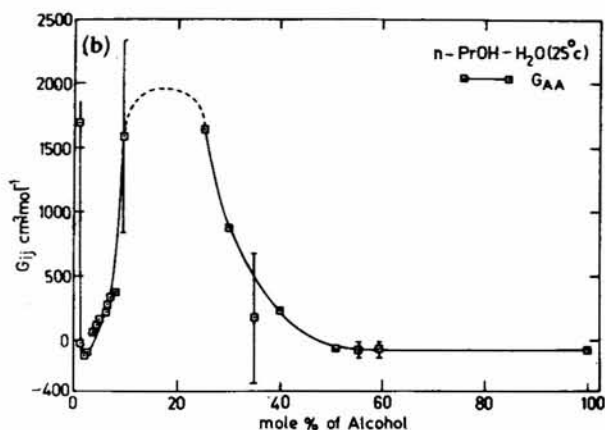
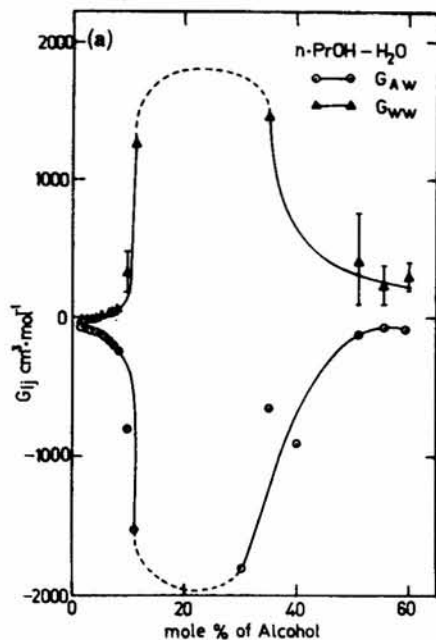


Fig. 3—(a) and (b) The concentration dependence of  $G_{ij}$ , for *n*-propanol-water system at 25°C.

the concentration where  $G_{AA}$  goes through a minimum. In Figs 1-4 the blips in  $G_{WW}$  and  $G_{AW}$  appear to match. We cannot offer satisfactory explanation for this at the moment but feel that this may be due to structural changes in solvent brought about by solute molecules as the compressibility of the solutions goes through a minimum at about the same concentration. The calculations of these parameters at  $x_2 \rightarrow 0$  or  $x_1 \rightarrow 0$  were avoided as in the limit  $x_2 \rightarrow 0$ , the chemical potential ( $\mu_2 = -\infty$  (ref. 7).

Our observations of initial minimum in  $G_{AA}$  in the case of alcohols probably suggest that alcohol molecules which are associated with each other in liquid state (or to a certain extent in gaseous state also) get dissociated in large environment of solvent molecules. The probable mechanism of

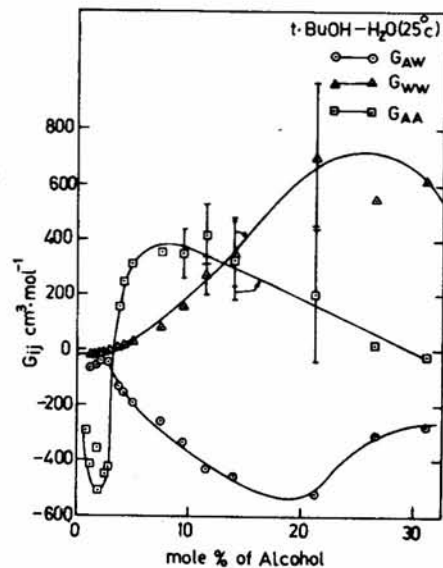


Fig. 4—The concentration dependence of  $G_{ij}$ , for *tert*-butanol-water system at 25°C.

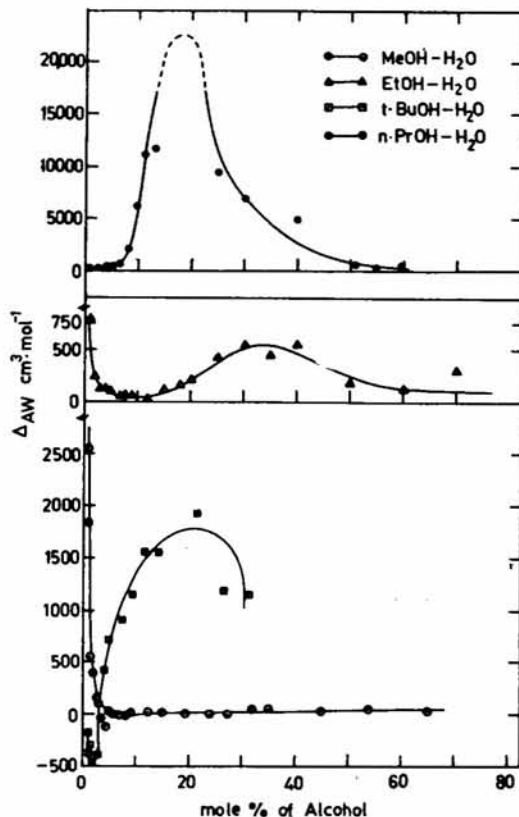


Fig. 5—The concentration dependence of  $\Delta_{AW}$  for aqueous solutions of methanol ( $\circ-\circ$ ), ethanol ( $\Delta-\Delta$ ), *n*-propanol ( $\bullet-\bullet$ ) and *tert*-butanol ( $\square-\square$ ) at 25°C.

this dissociation may be due to the decrease in hydrogen bonding between alcohol molecules ( $-\text{OH}-\text{OH}$  interactions) or due to decrease in strength of hydrophobic association amongst alcohol molecules. Alternatively, this also may be due



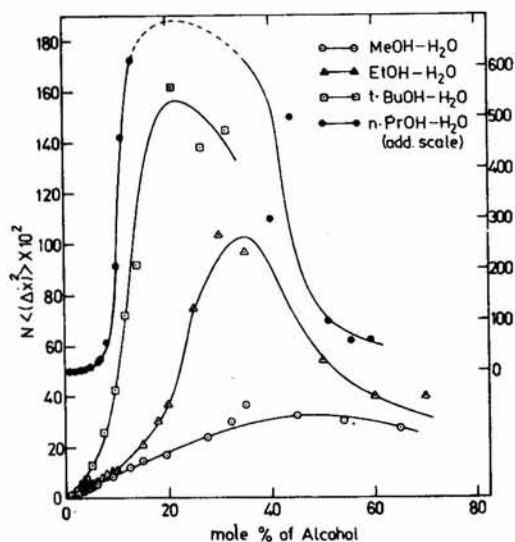


Fig. 6—Variation of  $N\langle(\Delta x)^2\rangle$  as a function of mole % of alcohol [ $\circ$ — $\circ$  methanol,  $\Delta$ — $\Delta$  ethanol,  $\bullet$ — $\bullet$  *n*-propanol and  $\square$ — $\square$  *tert*-butanol] in water at 25°C.

to hydrogen bond formation between alcohol and solvent (water) molecules. Out of these two, which mechanism is operating and to what extent is difficult to decide but most probably the solute-solvent hydrogen bond formation interaction should give rise to this effect, as in the same concentration region  $G_{AW}$  does not vary appreciably with concentration. This amounts to a decrease in solute-solute interaction in this concentration range as predicted by Ben-Naim and Yaacobi on the basis of solubility of argon in aqueous alcoholic solutions<sup>23</sup>. Further increase in solute concentration increases the solute-solute association, reflecting a steep rise in  $G_{AA}$  values up to a certain concentration and then normal solute dilution effect by solvent molecules should prevail in the solutions. We summarize that the initial minimum in  $G_{AA}$  corroborates with the minimum in partial volume, compressibilities and other derived properties, while, the maximum in  $G_{AA}$  corresponds to the extremas in the case of ultrasonic absorption, viscosity, heat of mixing and excess entropy of mixing for aqueous alcoholic solutions<sup>24</sup>. This is in contradiction with the usual belief that these extremas are because of strong solute-solvent interactions. Our observations about minimum in  $G_{AW}$  corroborates with the interpretation given above indicating further that at 15 to 30 mole % of alcohols, the solute-solvent interactions are minimum and may even lead to phase separation in suitable cases.

In all the cases,  $\Delta_{AW}$  (Fig. 5) are positive (except *tert*-butanol) initially and become very small in magnitude in the region, where many investiga-

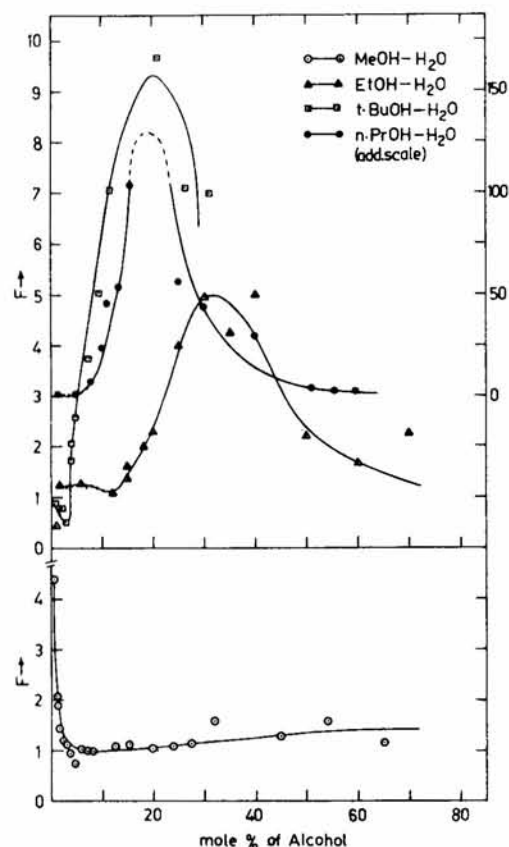


Fig. 7—Variation of  $F$  as a function of mole % of alcohol [ $\circ$ — $\circ$  methanol,  $\Delta$ — $\Delta$  ethanol,  $\bullet$ — $\bullet$  *n*-propanol and  $\square$ — $\square$  *tert*-butanol] in water at 25°C.

tors have postulated clathrate like equilibria. The positive values in higher concentration range again can be ascribed to hydrophobic interaction in solution. The information given by  $\Delta_{AW}$  can be converted in  $N\langle(\Delta x)^2\rangle$  and where one can note that the mean square fluctuations are very small in dilute concentration region. We find that  $N\langle(\Delta x)^2\rangle$  increase after the concentration 10 mole %, 10 mole %, 5-7 mole % and 5 mole % for methanol, ethanol, *n*-propanol and *tert*-butanol respectively. The variation of  $N\langle(\Delta x)^2\rangle$  with concentration and the magnitudes agree very closely with the data reported by Iijima *et al.*<sup>9</sup> for *tert*-butanol- $H_2O$  system.

The  $F$  value decreases initially and after 10 mole % remains more or less constant in the case of methanol, while, in other alcohol systems it goes through a small minimum initially and then through a large maximum. Franks and Desnoyers<sup>25</sup> have attempted to answer the question, whether alcohols interact primarily by direct hydrogen bonding or whether the observed effects are dominated by the alkyl groups. Pratt and Chandler postulated two distinctive modes of hy-

dration in terms of a model for methanol in water<sup>26</sup>. We think that the alkyl-alkyl correlations are affected by polar -OH groups in low concentration of alcohol, while at higher concentrations the alkyl-alkyl correlations dominate the solution behaviour. This can easily be seen by comparing the F values or  $N\langle(\Delta x)^2\rangle$  values for alcohols from methanol to *n*-propanol. The more number of alkyl residues in *n*-propanol seems to cause the extreme behaviour compared to that of methanol.

Franks and Desnoyers have drawn the conclusion from scattering data for  $x < x_c$  (where  $x_c$  is the actual concentration at which the derivative of thermodynamic properties shows extremas), the main effect of alcohol is to interfere destructively with the low density domains in water, whereas for  $x > x_c$  the predominant effect becomes one of the compositional microheterogeneities leading to alcohol clusterisation<sup>25</sup>. Our analysis of  $G_{ij}$ 's for alcohols supports this view strongly.

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