

## Thermodynamics of molecular interactions of 1,4-dioxane with formamides or N,N-dimethylformamide at 308.15 K

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### Introduction

In view of the two well known resonance structures [1] of the amide group, the lower amides in pure state may exist like alkanols [2,3], dimers and higher r-mers, though Davies [4] favor dimeric state for them in solution. The addition of 1,4-dioxane (A) to formamide (B) thus provide an ideal situation of H-bonded interaction resulting in the formation of various molecular entities. Since A+B mixture is formed by the replacement of like contacts in the pure state by unlike contact in the mixture and as the formations of molecular entities in the present (A+B) mixtures may be visualized to be due to the changes in the topology of A brought on by B, it appears that a recent graph theoretical approach [5,6] should not only provide valuable information about the state of A and/or B in an (A+B) mixture but should also be in a position to explain as to why only certain characteristic infra red absorptions in A and/or B are influenced in the process of mixture formation. This prompted us to perform molar excess volume and molar excess enthalpies studies at 308.15 K on 1,4-dioxane (A) + formamide or N,N-dimethylformamide (B) mixtures.

### Experimental

Formamide, N,N-dimethylformamide, 1,4-dioxane (Merch or Sigma) were purified by standard procedures. Molar excess volumes (VE) for the various binaries were determined in a V-shaped dilatometer in the manner explained elsewhere [14]. The molar excess enthalpy of mixing (HE) data at 308.15 K for the various (A+B) mixtures were determined using flow isothermal micro calorimeter (LKB-2107, Bromma, Sweden),.

### Results

The measured  $X^E$  (where  $X = V$  or  $H$ ) data at 308.15 K were fitted to the following Redlick and Kister equation  $X^E = x_A x_B \left[ \sum_{n=1}^3 X^{(n)} (x_A - x_B)^n \right]$ , where  $X^{(n)}$  are the adjustable parameters, and  $x_A$  and  $x_B$  are the mole fractions of A and B.

## Discussion

The  $V^E$  data of formamide suggest that if formamide is associated then the addition of dioxane causes not only structural changes in formamide but also i) the depolymerization of formamide and ii) the interaction of monomer of formamide with dioxane, the later effect making significant contribution to the measured equilibrium properties. If this be true then  $V^E$  of dioxane + DMF should be comparatively more positive. The  $V^E$  data of dioxane + dimethylformamide mixture do lend further credence to this view point.

In spite of this qualitative description of the present  $V^E$  data, the degree of association of B and influence dioxane on it remains to be investigated. For this purpose we analyzed the present  $V^E$  data in terms of an approach that employs the graph theoretical concept of molecular connectivity parameter of the third degree,  ${}^3\xi$ , of the constituents of these mixtures.  $V^E$  according to this approach is given by

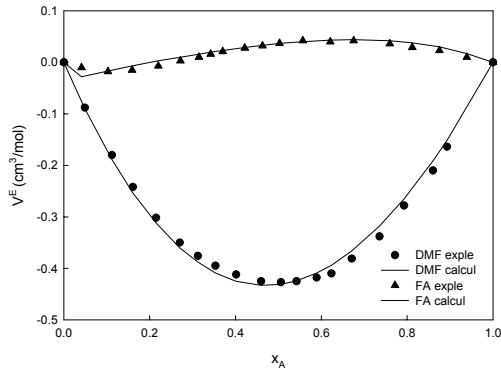
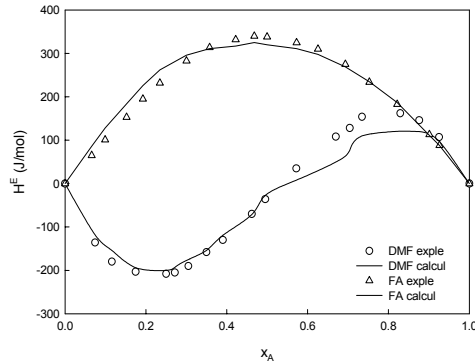
$$V^E = \alpha_{ij} \left[ \left\{ \sum x_i ({}^3\xi_i)_m \right\}^{-1} - \sum \frac{x_i}{{}^3\xi_i} \right] \quad (1)$$

where  $\alpha_{ij}$  is the constant characteristic of the (i+j) mixture and can be evaluated using equimolar experimental  $V^E$  value.  $x_A$ ,  $({}^3\xi_i)_m$  and  $({}^3\xi_i)$  ( $i=A$  or  $B$ ) denote mole fraction, and connectivity parameter of third degree of  $i$  in the mixture and in the pure state, respectively.

Since the degree of association of pure  $B$  in the present (A+B) mixtures is not known with certainty and it is also difficult to comprehend as to how the addition of A would modify it further, we regarded  $({}^3\xi_i)$  and  $({}^3\xi_i)_m$  ( $i=A$  or  $B$ ) as adjustable parameters and evaluated them by fitting the experimental  $V^E$  data to Eq. (1) by hit and trial method. Examination of Fig. 1 reveals that  $V^E$  values agree well with their corresponding experimental values and thus  $({}^3\xi_i)$  or  $({}^3\xi_i)_m$  values can be relied upon to utilized to investigate the state of association of B.

For this purpose we assumed formamide and DMF to exist exist in various configurations (ranging from dimmers and r-mers (both cyclic as well as open for formamide and DMF) and then calculated  $({}^3\xi'_i)$  values (from equation ()) in the manner explained elsewhere[5] for these configurations. These  $({}^3\xi'_i)$  values when compared with the corresponding  ${}^3\xi$  values of pure components.

The present treatment suggests that while formamide ( ${}^3\xi = 0.6$ ) exists as an equilibrium mixture of monomer ( ${}^3\xi' = 0.312$ ) and cyclic dimer ( ${}^3\xi' = 0.94$ ) or an equilibrium mixture monomer and an open chain trimer ( ${}^3\xi' = 0.856$ ), DMF ( ${}^3\xi = 2.0$ ) exists as cyclic dimer ( ${}^3\xi' = 2.12$ ). This is consistent with the available information about formamide and DMF [1-4]. Again the  ${}^3\xi$  value of 0.76 for dioxane in all A+ B mixtures compare well with the  ${}^3\xi'$  value of 0.74 dioxane. This suggests that the present approach can be relied upon to yield meaningful information about the state of aggregation of the component of binary mixtures.

Fig. 1. Excess volume versus  $x_A$ Fig. 2. Excess enthalpy versus  $x_A$ 

The process of present (A+B) mixtures formation requires

- a mixing of (A) with (B) to establish (A)-(B) contacts with an interaction energy  $\chi_{AB}$  per mole of (A)-(B) contacts
- These (A)-(B) contacts between A and B would then cause rupture of intermolecular association in B to yield monomers of B with an interactional energy  $\chi_{BB}$  per mole
- The monomers of B then undergo solvation in A to give A-B molecular entity with an interactional energy  $\chi_{12}$  per mole .

The total enthalpy change due to processes (a), (b) and (c) is given by:

$$H^E = [x_A x_B V_B / \sum x_A V_A] [\chi_{AB} + x_A \chi_{BB} + x_B \chi_{12}] \quad (2)$$

Since  $V_B/V_A = (\xi_A^3/\xi_B^3)$ , and if for these mixtures, if it is assumed that  $\chi_{AB} = \chi_{12} = \chi_{AB}^*$  then Eq. (2) reduces to:

$$H^E = [x_A x_B (\xi_A^3/\xi_B^3) / \{x_A + x_B (\xi_A^3/\xi_B^3)\}] [(1 + x_B) \chi_{AB}^* + x_A \chi_{BB}] \quad (3)$$

Calculation of  $H^E$  from above equation requires the knowledge of two unknown interaction parameters  $\chi_{AB}^*$  and  $\chi_{BB}$  which were calculated using  $H^E$  data at two compositions  $x_A = 0.4$  and  $0.5$  for various (A+B) mixtures and were subsequently used to evaluate  $H^E$  at other  $x_A$  and calculated  $H^E$  found to compare well with their corresponding experimental values Fig.2 .

## References

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