Effects of Preferential Solvation and of Solvent–Solvent Interaction on the Rates of Nucleophilic Substitution involving Anions in Binary Mixed Solvents

Theoretical Approach

By Yasuhiko Kondo* and Shigekazu Kusabayashi

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Theoretical procedures for investigating rate constants and activation parameters measured in binary mixed solvents have been presented on the basis of the concept of ideal associated mixtures. In methanol + acetonitrile mixtures the behaviour of the rate constant and of activation parameters for the ethyl iodide plus bromide ion reaction were interpreted as resulting from the specific interaction of bromide ion with methanol. In methanol + *NN*-dimethylacetamide mixtures association complex formation between methanol and *NN*-dimethylacetamide makes a significant contribution to the activation parameters, and this factor must be taken into account in interpreting the observed rate behaviour.

Recently, the importance of a chemical interaction between an electrolyte and solvents has been stressed in interpreting the solution thermodynamic properties of electrolytes.[1-9] In favourable cases various kinds of solvates have been detected by n.m.r. techniques, which provides supporting evidence for the concept.[5]

In the previous work[9] and in the experimental part of this work,[10] various aspects of anion solvation and effects on the rates of nucleophilic substitution reactions have been investigated. One of the salient features of these studies is the fact that the transfer enthalpy of bromide ion and the rates of the nucleophilic substitution reaction respond characteristically to the thermodynamic properties of the solvent mixtures, depending on whether the pair of solvents shows an exothermic or an endothermic heat of mixing.[9, 10]

In this work we will be concerned with the theoretical approach to the effects of preferential solvation of anions and of solvent–solvent interactions on the rates of a nucleophilic substitution reaction in binary mixed solvents. The rates of the bromide ion plus ethyl iodide reaction in methanol + acetonitrile and in methanol + *NN*-dimethylacetamide mixtures will be analysed using this approach. Also, we will discuss how the information obtained through experimental observations is considered in the model treatment.

THEORETICAL

For the reaction type considered,

$$A + B \rightarrow M^{\neq} \rightarrow \text{products,}$$
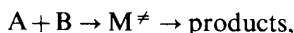
the rate constant in solvent j, k_j, is related to the rate constant in the gas phase, k_0, by the equation[11]

$$k_j = k_0 \left(\frac{\beta_{A,j} \beta_{B,j}}{\beta_{\neq,j}} \right) \tag{1}$$

where β_{ij} is the activity coefficient of the solute i in solvent j, and is defined by eqn (2)[11]

$$\beta_{ij} = (m_{gi}/m_{li})_j. \tag{2}$$

m_{gi} is the concentration of solute i in the vapour phase above the solution. m_{li} is the concentration of solute i in the solution.

The Henry's constant of solute i in solvent j, H_{ij}, is defined by eqn (3)[12]

$$H_{ij} = \lim_{x_i \to 0} (f_i/x_i)_j \tag{3}$$

where f_i and x_i are the fugacity and the mole fraction of solute i, respectively.

At extremely low concentrations of solute i the ideal gas law, eqn (4), holds and the solute concentration is related to the mole fraction of the solute and the molar volume of the solvent, V_j, by eqn (5):

$$f_i = p_i = (n_{gi}/V) RT = m_{gi} RT \tag{4}$$

$$m_{li} = n_{li}/(\sum_i n_{li} V_i) \approx x_i/V_j. \tag{5}$$

Thus the activity coefficient defined by eqn (2) can be found from the Henry's constant and the molar volume of the solvent

$$\beta_{ij} = (H_{ij} V_j/RT). \tag{6}$$

By following this procedure the original problem of solution kinetics can be transformed into that of non-electrolyte solution thermodynamics.

In ideal associated mixtures the fugacity of solute 2, f_2, is related to that of pure solute, f_2°, by eqn (7)[12]

$$f_2 = f_2^\circ y_2 \tag{7}$$

where y_2 is the mole fraction of solute defined using the number of moles actually existing in solution. On the other hand, Henry's constant is defined by using the stoichiometric mole fraction, x_i, by eqn (3). The combination of eqn (3), (6) and (7) reduces to the required equation for the activity coefficient of solute 2 in ideal associated mixtures

$$\beta_{2, \text{mix}} = \lim_{x_2 \to 0} (y_2/x_2)(f_2^\circ V_{\text{mix}}/RT). \tag{8}$$

The next step is to calculate the term

$$\lim_{x_2 \to 0} (y_2/x_2)$$

for a relevant model.

MODEL

In the following treatment the subscripts 1 and 4 stand for solvent components and the subscript 2 for a solute. We consider the following ideal associated mixtures.

(1) Solvent 4 forms various association complexes with solvent 1, each of which

is composed of one molecule of solvent 4 and k molecules of solvent 1, *i.e.* $S_4 \cdot (S_1)_k$, and the equilibrium constants for the processes are given by the relations

$$S_4 + S_1 = S_4 \cdot S_1; \quad K_{c,1} = K$$

$$S_4 \cdot (S_1)_{k-1} + S_1 = S_4 \cdot (S_1)_k; \quad K_{c,k} = (1/k) K.$$

(2) A solute, M, is in equilibrium with clusters that contain $(z-j)$ molecules of solvent 4, and j molecules of solvent 1, *i.e.* $M \cdot (S_4)_{z-j} \cdot (S_1)_j$, and the equilibrium constants of the process are given as follows:

$$M + z S_4 \rightleftharpoons M \cdot (S_4)_z; \quad K_0$$

$$M \cdot (S_4)_{z-j+1} \cdot (S_1)_{j-1} + S_1 \rightleftharpoons M \cdot (S_4)_{z-j} \cdot (S_1)_j + S_4; \quad K_j.$$

(3) All the equilibrium constants are expressed using the mole fraction defined by the number of moles in solution as follows:

$$K_{c,k} = y_{c,k}/(y_1 y_{c,k-1})$$

$$K_j = y_{2,j} y_4/(y_{2,j-1} y_1)$$

where c refers to the complex.

The following material balances hold between the number of moles of component i before mixing, N_i, and the number of moles in solution, M_i, $M_{c,k}$ and $M_{2,j}$,

$$N_1 = M_1 + \sum_{k=1}^{\infty} k M_{c,k} + \sum_{j=0}^{z} j M_{2,j} \tag{9}$$

$$N_2 = M_2 + \sum_{j=0}^{z} M_{2,j} \tag{10}$$

$$N_4 = M_4 + \sum_{k=1}^{\infty} M_{c,k} + \sum_{j=0}^{z} (z-j) M_{2,j}. \tag{11}$$

where $M_{c,k}$ and $M_{2,j}$ stand, respectively, for the number of moles of the associated complex containing k molecules of solvent 1, and of the solute cluster composed of $(z-j)$ molecules of solvent 4 and of j molecules of solvent 1.

The stoichiometric mole fraction, x_i, and the mole fraction counted by the number of moles in solution, y_i and $y_{c,k}$, are defined by the equations

$$x_i = N_i/N_t \quad (i = 1, 2, 4) \tag{12}$$

where

$$N_t = N_1 + N_2 + N_4 \tag{13}$$

$$y_i = M_i/M_t \quad (i = 1, 2, 4) \tag{14}$$

$$y_{c,k} = M_{c,k}/M_t \quad (k = 1\text{-}\infty) \tag{15}$$

$$M_t = M_1 + M_2 + M_4 + \sum_{k=1}^{\infty} M_{c,k} + \sum_{j=0}^{z} M_{2,j}. \tag{16}$$

From the basic assumptions (1) and (3) for the system, and making use of the relation

$$\exp(x) = 1 + x + (x^2/2!) + (x^3/3!) + \ldots$$

eqn (17)-(19) are derived:

$$y_{c,k} = (1/k!) (K y_1)^k y_4 \tag{17}$$

$$\sum_{k=1}^{\infty} k y_{c,k} = K y_1 y_4 \exp(K y_1) \tag{18}$$

$$y_4 + \sum_{k=1}^{\infty} y_{c,k} = y_4 \exp(K y_1). \tag{19}$$

In the case of no added solute, letting $M_2 = M_{2,j} = 0$ (for all values of j), eqn (16) reduces to eqn (20), making use of eqn (19):

$$y_1 + y_4 + \sum_{k=1}^{\infty} y_{c,k} = y_1 + y_4 \exp(Ky_1) = 1. \tag{20}$$

Similarly the stoichiometric mole fraction can be related to the mole fraction y_1 by combining eqn (9)-(16), (18) and (20):

$$x_4 = \frac{1 - y_1}{1 + \sum_{k=1}^{\infty} ky_{c,k}} = \frac{1 - y_1}{1 + Ky_1(1 - y_1)}. \tag{21}$$

On rearranging, the final formula for y_1 as a function of solvent composition x_4 is derived,

$$Kx_4 y_1^2 - (Kx_4 + 1) y_1 + 1 - x_4 = 0. \tag{22}$$

Limiting values of (y_2/x_2) can be expressed as a function of mole fraction y_i by combining eqn (9)-(16) and (18), which finally reduces to eqn (23)

$$\lim_{x_2 \to 0} (y_2/x_2) = \frac{1 + Ky_1(1 - y_1)}{1 + \sum_{j=0}^{z} (y_{2j}/y_2)} = \frac{1 + Ky_1(1 - y_1)}{1 + K_0\left[y_4^z + \sum_{j=1}^{z} \left(\prod_{l=1}^{j} K_l\right) y_4^{z-j} y_1^j\right]} \tag{23}$$

making use of assumption (3). Alternatively, for the system in which a solvent exchange process can be defined on each solvation site around the ion, the term which expresses the distribution of clusters, *i.e.*

$$\left\{ y_4^z + \sum_{j=1}^{z} \left(\prod_{l=1}^{j} K_l\right) y_4^{z-j} y_1^j \right\}$$

is rewritten as

$$\prod_{m=1}^{z} (y_4 + K_{se,m} y_1),$$

making use of the equilibrium constants defined for the solvent exchange process on the respective solvation site m around the ion, $K_{se,m}$.[9, 13]

Finally the activity coefficient of solute 2 in the mixed solvent is derived as

$$\beta_{2,mix} = \frac{f_2^\circ[1 + Ky_1(1 - y_1)]}{\left(1 + K_0 \prod_{m=1}^{z} (y_4 + K_{se,m} y_1)\right)} \left(\frac{V_{mix}}{RT}\right). \tag{24}$$

For an electrolyte the assumption $K_0 \gg 1$ would not be unreasonable; thus the activity coefficient in a mixed solvent as a relative value to that in the reference solvent 1 is given by eqn (25):

$$\log \beta_{2,mix} = \log \beta_{2,1} + \log [1 + Ky_1(1 - y_1)]$$
$$+ \log \prod_{m=1}^{z} K_{se,m} - \log \prod_{m=1}^{z} (y_4 + K_{se,m} y_1) + \log(V_{mix}/V_1). \tag{25}$$

For the system in which there is no association between components 4 and 1, substituting the relations $y_1 = x_1$ and $K = 0$ into eqn (25) gives eqn (26):

$$\log \beta_{2,mix} = \log \beta_{2,1} + \log \prod_{m=1}^{z} K_{se,m} - \log \prod_{m=1}^{z} (x_4 + K_{se,m} x_1) + \log(V_{mix}/V_1). \tag{26}$$

In this treatment the transfer free energy of a solute from solvent 1 to a mixed solvent is given by the relation

$$\Delta G_t^\circ = RT \ln \beta_{2,\mathrm{mix}} - RT \ln \beta_{2,1}.$$

Thus the transfer free energy derived in this work has essentially the same functional dependence on the solvent composition as derived on a different basis,[4,6] except for the extra term, $\log(V_{\mathrm{mix}}/V_1)$ contained in eqn (26) because of the different standard state adopted in previous treatments.[4,6]

APPLICATION TO REACTION RATES

As was discussed previously[9] and will be discussed in the experimental part of this work,[10] for the bromide ion plus ethyl iodide reaction the electrostatic contribution to the transfer activation parameters are largely cancelled out between the initial and the transition state, and as a result rates are mostly controlled by the specific solvation of bromide ion by methanol. Also, it was suggested that in amide + methanol mixtures only free methanol participates in specific solvation of bromide ion, and associated methanol acts as only neutral solvent; thus y_4 in eqn (25) should be replaced by $(1 - y_1)$.[9,10] Considering these suggestions and substituting eqn (25) into one of the activity coefficients of the reactants in the fundamental equation (1), the rate constant in mixed solvents is derived as eqn (27):

$$\log k_{\mathrm{mix}} = \log k_1 + \log \{1 + K y_1 (1 - y_1)\} + \log \prod_{m=1}^{z} K_{\mathrm{se},m}$$

$$- \log \prod_{m=1}^{z} [1 + y_1 (K_{\mathrm{se},m} - 1)] + \log (V_{\mathrm{mix}}/V_1). \tag{27}$$

Eqn (27) contains many parameters to be adjusted. To understand the general trends implied by the equation it is appropriate to start the analysis with a simplified formula. For the reaction in non-associated media, on letting $K = 0$, eqn (27) reduces to eqn (28), and on letting $x_4 = 1$ in eqn (28), eqn (29) is also derived:

$$\log k_{\mathrm{mix}} = \log k_1 + \log \prod_{m=1}^{z} K_{\mathrm{se},m} - \log \prod_{m=1}^{z} (x_4 + K_{\mathrm{se},m} x_1) + \log(V_{\mathrm{mix}}/V_1) \tag{28}$$

$$(k_4/k_1) = \prod_{m=1}^{z} K_{\mathrm{se},m}(V_4/V_1). \tag{29}$$

This equation, eqn (29), serves as the boundary condition for the value of $K_{\mathrm{se},m}$.

The activation enthalpy is defined as the temperature derivative of the rate constant by the equation

$$(\partial \ln k_{\mathrm{mix}}/\partial T) = (\Delta H_{\mathrm{mix}}^{\neq} + RT)/RT^2.$$

Performing the differentiations and making use of the relation

$$(\partial \ln K_{\mathrm{se},m}/\partial T) = \Delta H_{\mathrm{se},m}^\circ/RT^2,$$

the following equations are derived. [Throughout this work, temperature derivatives of the term (V_{mix}/V_1) will be neglected.]

$$\Delta H_{\mathrm{mix}}^{\neq} = \Delta H_1^{\neq} + \sum_{m=1}^{z} \frac{x_4 \Delta H_{\mathrm{se},m}^\circ}{(x_4 + K_{\mathrm{se},m} x_1)} \tag{30}$$

$$\Delta H_4^{\neq} - \Delta H_1^{\neq} = \sum_{m=1}^{z} \Delta H_{\mathrm{se},m}^\circ. \tag{31}$$

The reaction proceeds much faster in acetonitrile than in methanol. If we take acetonitrile as solvent 4 and methanol as solvent 1, this leads to the relation

$$\prod_{m=1}^{z} K_{\mathrm{se},m} \gg 1$$

on the basis of eqn (29). Substituting the activation enthalpies in acetonitrile and in methanol into eqn (31) the relation

$$\sum_{m=1}^{z} \Delta H^{\circ}_{\mathrm{se},m} < 0$$

is also derived. These relations confirm the view of specific solvation of bromide ion by methanol reached from transfer-enthalpy analysis.[9, 10]

Calculations of the rate constants have been repeated assuming various sets of $K_{\mathrm{se},m}$ values under the condition of eqn (29), and the optimum agreement was reached assuming three steps of solvent exchange processes.* Considering the success of the model calculation on the transfer enthalpy of bromide ion in mixed solvents,[9] and partly because of the brevity of the treatment, all three $\Delta H^{\circ}_{\mathrm{se},m}$ values were assumed to be equal. Under this condition, theoretical values of the activation enthalpy can be calculated from eqn (30) without recourse to any adjustable parameters, since the value $\Delta H^{\circ}_{\mathrm{se},m}$ can be determined uniquely by eqn (31), and $K_{\mathrm{se},m}$ values have already been determined in the rate-constant analysis. From the theoretical values of $\log k_{\mathrm{mix}}$ and of $\Delta H^{\neq}_{\mathrm{mix}}$ activation entropies have also been calculated. They are compared with the experimental values in fig. 1-3.

For the sake of the consistency of the treatment in the various series and of the brevity of the analysis, the rate behaviour in NN-dimethylacetamide+methanol mixtures has been analysed under the presumption of a binominal distribution of clusters with three steps of solvent exchange equilibria. Under this condition, eqn (27) reduces to eqn (32) and (33), and eqn (33) then gives the boundary condition for $K_{\mathrm{se},m}$:

$$\log k_{\mathrm{mix}} = \log k_1 + \log[1 + K y_1 (1 - y_1)]$$
$$+ 3 \log K_{\mathrm{se},m} - 3 \log[1 + y_1 (K_{\mathrm{se},m} - 1)] + \log (V_{\mathrm{mix}}/V_1) \quad (32)$$

$$(k_4/k_1) = K^3_{\mathrm{se},m} (V_4/V_1). \quad (33)$$

Again, differentiating eqn (32), (33) and (22) with respect to temperature and making use of the relation

$$(\partial \ln K/\partial T) = \Delta H^{\circ}/RT^2,$$

theoretical equations for the activation enthalpy were derived as follows:

$$\Delta H^{\neq}_{\mathrm{mix}} = \Delta H^{\neq}_1 - \left(\frac{1}{1-y_1}\right) RT^2 \left(\frac{\partial y_1}{\partial T}\right) + \frac{3}{[1 + (K_{\mathrm{se},m} - 1) y_1]}$$
$$\times \left[(1 - y_1) \Delta H^{\circ}_{\mathrm{se},m} - (K_{\mathrm{se},m} - 1) RT^2 \left(\frac{\partial y_1}{\partial T}\right) \right] \quad (34)$$

$$\Delta H^{\neq}_4 - \Delta H^{\neq}_1 = 3 \Delta H^{\circ}_{\mathrm{se},m} \quad (35)$$

$$RT^2 \left(\frac{\partial y_1}{\partial T}\right) = \frac{K x_4 y_1 (1 - y_1) \Delta H^{\circ}}{K x_4 (2y_1 - 1) - 1}. \quad (36)$$

* Throughout the work the density of the mixed solvent has been calculated from those of pure solvents from the equation
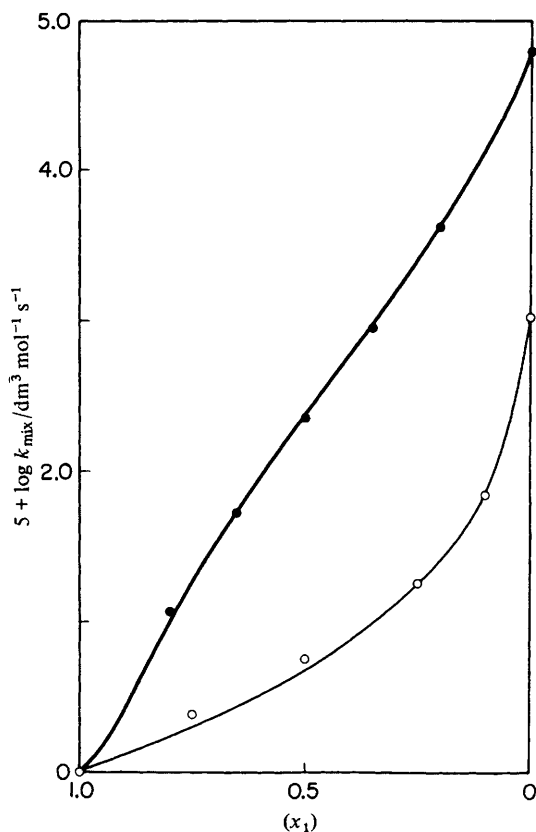$$d_{\mathrm{mix}} = x_1 d_1 + x_4 d_4.$$

Fig. 1.—Plots of $\log k_{mix}$ against mole fraction of methanol for the reaction of ethyl iodide with bromide ion (30 °C): $\bigcirc$, experimental results in methanol+acetonitrile mixtures; $\bullet$, experimental results in methanol+NN-dimethylacetamide mixtures; (——) calculated by eqn (28) with $K_{se,1} = 75.0$, $K_{se,2} = 7.16$ and $K_{se,3} = 1.53$; (——) calculated by eqn (32) with $K_{se,m} = 30.1$ and $K = 3.8$.

It is clear from eqn (33) that the value $K_{se,m}$ is uniquely determined from the rate constants in pure solvents. Thus, in rate-constant analysis only one parameter, K, remains to be adjusted. For an assumed value of K, y_1 values have been calculated from eqn (22), and then theoretical values of $\log k_{mix}$ have been calculated from eqn (32) as a function of solvent composition. Similarly, the $\Delta H^{\circ}_{se,m}$ value was uniquely determined from eqn (35). The values of K, $K_{se,m}$ and of y_1 have already been determined. For an assumed value of ΔH°, the values of $RT^2 (\partial y_1/\partial T)$ have been calculated from eqn (36). On substituting all these values into eqn (34), theoretical values of $\Delta H^{\neq}_{mix}$ have been obtained. Activation entropies have also been calculated from these theoretical values. In these analyses NN-dimethylacetamide was taken as solvent 4 and methanol as solvent 1. The relations, $K_{se,m} > 1$ and $\Delta H^{\circ}_{se,m} < 0$, derived from the substitution of the experimental results into eqn (33) and (35) under the above notation, also agree with the views attained from the transfer-enthalpy analysis.[9, 10] All the optimum values are given in fig. 1-3.
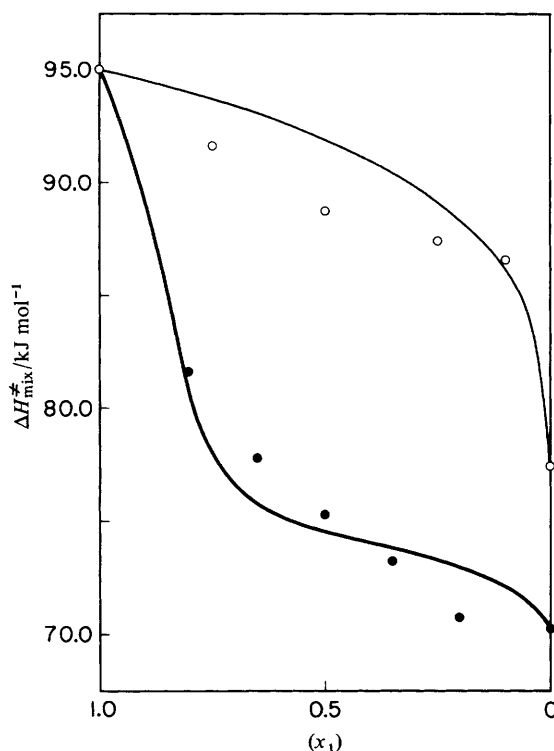
FIG. 2.—Plots of $\Delta H_{mix}^{\neq}$ against mole fraction of methanol: $\bigcirc$, experimental results in methanol + aceto-nitrile mixtures; $\bullet$, experimental results in methanol + NN-dimethylacetamide mixtures; (———) calculated by eqn (30) with $\Delta H_{se,m}^{\circ} = -5.9$ kJ mol^{-1} and the set of $K_{se,m}$ values determined above; (———) calculated by eqn (34) with $\Delta H_{se,m}^{\circ} = -8.2$ kJ mol^{-1}, $\Delta H^{\circ} = -8.8$ kJ mol^{-1}, and the set of $K_{se,m}$ and of K values determined above.

DISCUSSION

In the analysis of the rate behaviour in methanol + acetonitrile mixtures, three steps of solvent exchange processes and also strong preferential solvation of bromide ion by methanol have been suggested. Transfer-enthalpy analysis also supports the view of preferential solvation of bromide ion by methanol.[9] However, as is partly inferred from measurements of the partial molal heat of mixing,[9, 10] the activity coefficient of methanol is significant in the region of low methanol content, and this might possibly bring about phenomena which would be taken as originating from the preferential solvation of bromide ion. A detailed analysis of the preferential solvation will have to be postponed until exact activity coefficients are available.

Recently Cox and Waghorne noticed the sharp minimum which appeared in the transfer entropy against composition profile for alkali metal ions, and ascribed the phenomenon to the preferential solvation of these ions by one of the component solvents.[14] The activation entropy maximum observed in methanol + acetonitrile mixtures in this work corresponds to their observations and would be interpreted on the basis of their theory as preferential solvation of bromide ion by methanol. In our treatment, however, the main features in the three activation parameters could be
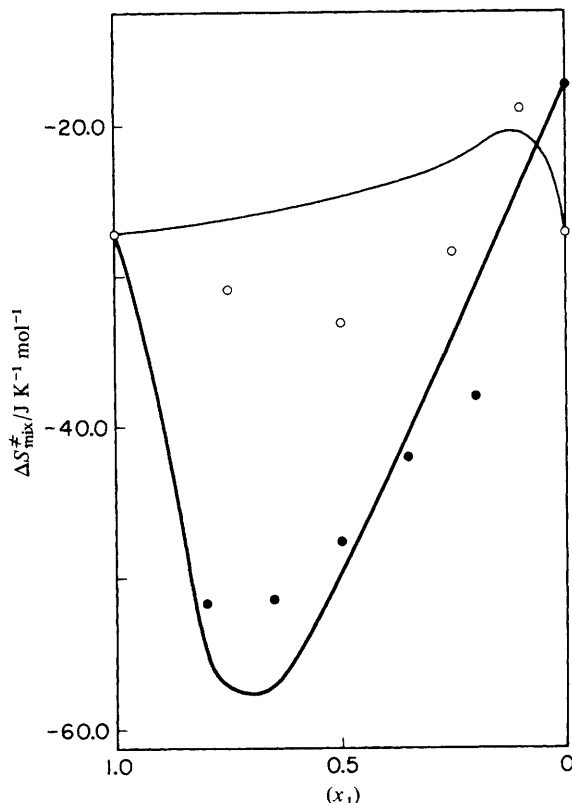
FIG. 3.—Plots of $\Delta S^{\neq}_{mix}$ against mole fraction of methanol: $\bigcirc$, experimental results in methanol + aceto-nitrile mixtures; $\bullet$, experimental results in methanol + NN-dimethylacetamide mixtures; (——) calculated in methanol + acetonitrile mixtures; (——) calculated in methanol + NN-dimethylacetamide mixtures.

reproduced consistently without recourse to an *ad hoc* expression for the respective activation parameters.

Comparative studies in two thermodynamically contrasted systems clearly indicate the contrasting behaviour in the activation parameters; especially, maximum and minimum values in the activation entropy against composition profiles are very pronounced. Solvent–solvent interactions seem to play a significant role in associated mixtures.

An amide molecule could interact with methanol at least at three sites, *i.e.* the carbonyl π-electron, the oxygen lone pair and the nitrogen lone pair. In addition, on dissolving into methanol there would be formed new structures around each amide molecule. This phenomenon would be non-stoichiometric in origin and could not be simulated by any stoichiometric means. In this work the interaction has been taken into account as infinite-chain association with attenuation in calculating equilibrium constants. According to the model, the interaction manifests itself in the activation parameters through various forms, *i.e.* y_1, K, ΔH°, and $(\partial y_1/\partial T)$. The calculation clearly simulates the interactions in the region of high methanol content, as partly inferred from the minimum in the activation entropy against composition profile.

Grunwald and Effio warned against the conventional use of the constant-composition condition in analysing the solution phenomena observed in mixed

solvents.[15] They put forward a method of avoiding the complexity originating from the non-ideal nature of thermodynamic quantites of the solvent mixtures, although their procedures were criticized later.[16] In contrast, the model approach as performed in this work can provide a way of investigating the origin of such complexities in solution kinetics and thermodynamics, and in favourable cases can give information that is not otherwise obtainable. This suggests that the experimental analysis should proceed in conjunction with theoretical approaches.

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