# Nucleophilic Substitution in Binary Mixed Solvents

Kinetics and Transfer Enthalpies of Anions in the Mixed Solvents Methanol+ Propylene Carbonate and Methanol+N-methyl-2-pyrrolidone

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Rate constants and activation enthalpies for the reaction of ethyl iodide with bromide ion have been determined in two solvent mixtures, *i.e.*, methanol+propylene carbonate and methanol+Nmethyl-2-pyrrolidone mixtures. Heats of solution have also been determined for ethyl iodide, tetra-n-butylammonium-bromide, -perchlorate and -tetra-n-butylborate in the two solvent mixtures. Judging from these transfer enthalpies, perchlorate ion seems to be a pertinent model compound for the activated complex of the reaction. Single ion transfer enthalpies have been evaluated on the basis of the  $(n-Bu)_4NB(n-Bu)_4$  assumption in the two solvent mixtures. Transfer enthalpy against composition profiles for perchlorate ion are similar in the two solvent mixtures, whereas for bromide ion the corresponding profiles are quite different in the two solvent mixtures, *i.e.*, a sharp minimum was observed for the profile in MeOH+PC mixtures. From these observations and from other evidence, it is concluded that bromide ion solvation involves both electrostatic interactions and specific interactions between solute and solvents. Model calculations performed on the basis of the above views reproduce the bromide ion profile in MeOH+PC mixtures well.

Nucleophilic substitution at a saturated carbon atom is one of the most widely studied reactions in organic chemistry <sup>1-4</sup> and is of renewed interest from various aspects.<sup>5-7</sup>

Dipolar aprotic and protic solvent effects on rates have been the key phenomena which led Parker to the concept of solvent activity coefficients of an ionic solute.<sup>8,9</sup> The next step in understanding solvation phenomena of ionic solutes would be to dissect and evaluate the constituent terms from physical or chemical aspects.<sup>10-14</sup>

Sometimes chemical phenomena behave differently in mixed solvents than would be expected from their behaviour in pure solvents : more direct information on the solvation of a solute can be deduced from the analysis of the phenomena observed in mixed solvents.<sup>15, 16</sup> As a continuing study of solution phenomena in mixed solvents,<sup>17, 18</sup> in this work we measure the rates of the substitution reaction of ethyl iodide with bromide ion and then measure the enthalpy of solution of the respective solutes in order to evaluate the single ion transfer enthalpies in two types of mixed solvent. Finally, we discuss the factors affecting anion solvation and how these quantities are connected with the thermodynamic quantities of the solvent mixtures.

## EXPERIMENTAL

## MATERIALS

After storage over freshly activated 4A molecular sieves for over a week, propylene carbonate was distilled twice under reduced pressure. After storage over calcium hydrid-for a few days *N*-methyl-2-pyrrolidone was distilled three times under reduced pressure, stored under a nitrogen atmosphere and used within a few days after distillation. Tetrae

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n-butyltin was distilled three times under reduced pressure. Tetra-n-butylammonium perchlorate, precipitated by mixing hot aqueous solutions of tetra-n-butylammonium bromide and sodium perchlorate, was recrystallized three times from water and dried over phosphorus pentoxide at 65°C under reduced pressure for over a week. Tetra-n-butylammonium tetra-n-butylborate was synthesized by essentially the same procedure as described by Fuchs et al.<sup>19</sup> The compound thus prepared contains impurities which, although a small amount, seriously affect the heat of solution measurements in N-methyl-2-pyrrolidone. It was therefore carefully purified by recrystallization successively from isopropyl ether, isopropyl ether+acetone (50: 1), isopropyl ether+ethanol (50: 1) after refluxing for  $\approx 10$  h, isopropyl ether+methanol (50:1) after refluxing for  $\approx 1$  h and finally from isopropyl ether+acetone. The treatments by isopropyl ether+ethanol and isopropyl ether+methanol were crucial for purifying the compound (elementary analysis, calculated : C, 79.78; H, 15.06; N, 2.91; B, 2.25 %; found: C, 79.78; H, 15.10; N, 2.95; B; 2.17 %). The compound was dried over phosphorus pentoxide at 65°C under reduced pressure for over a week before use. Tetra-n-butylammonium bromide, ethyl iodide and methanol were purified as described elsewhere.18

#### HEAT OF SOLUTION MEASUREMENTS

Heats of solution at 298.15 $\pm$ 0.02 K were measured with a LKB-8700-1 precision calorimetry system and with a Tokyo Riko TIC-2D twin isothermal calorimeter. The LKB-8700-1 calorimetry system was tested according to the standard procedure. The Tokyo Riko TIC-2D calorimeter was tested by measuring the heat of solution of KCl at a concentration of 1 mol per 5500 mol H<sub>2</sub>O. From nine independent measurements we obtained an enthalpy of solution of 4139 $\pm$ 11 cal mol<sup>-1</sup>. This value is in fair agreement with the literature value, 4146 cal mol<sup>-1,20</sup> The final concentration ranges of the solutes used for the measurements were  $\approx 5 \times 10^{-3}$  mol dm<sup>-3</sup> for (n-Bu)<sub>4</sub>NB(n-Bu)<sub>4</sub>, (0.8–2.0)  $\times 10^{-2}$  mol dm<sup>-3</sup> for (n-Bu)<sub>4</sub>NBr and (n-Bu)<sub>4</sub>NClO<sub>4</sub>, (0.4–2.0)  $\times 10^{-1}$  mol dm<sup>-3</sup> for EtI and (1.0–1.5)  $\times 10^{-2}$  mol dm<sup>-3</sup> for (n-Bu)<sub>4</sub>NB(n-Bu)<sub>4</sub> decomposed moderately rapidly, so that the uncertainty should be larger, and was estimated to be  $\pm 0.3$  kcal mol<sup>-1</sup>.

## PARTIAL MOLAR ENTHALPY OF MIXING, $\bar{h}_{i,mix}^{M}$

These have been calculated from the enthalpy change accompanying the dissolution of pure component, *i*, sealed in an ampoule, into a mixture of given composition. The measurements were performed at least twice and uncertainties were estimated to be within 2 %.

#### KINETIC PROCEDURE

Rates were followed by potentiometric titration using a silver nitrate solution and the results were treated assuming reversible second-order kinetics as described elsewhere.<sup>18</sup> All measurements were performed at least twice and the uncertainties were estimated to be within 2 %. The measurements were performed at three or four of the following temperatures, *i.e.*, 0.0, 20.0, 30.0, 40.0, 50.0 and 60.0°C. Enthalpies are given in terms of the "defined calorie" (4.184 J).

## **RESULTS AND DISCUSSION**

## REACTION RATES IN SOLVENT MIXTURES

Rate constants and activation enthalpies for the reaction of ethyl iodide with bromide ion are summarized in table 1. Logarithmic relative rates in pure solvents follow the pattern expected on the basis of solvent activity coefficients for the bromide ion, *i.e.*, the values for log  $(k_{\rm NMeFy}/k_{\rm MeOH})$  and log  $(k_{\rm PC}/k_{\rm MeOH})$  are 5.11 and 3.34, while the corresponding differences of the solvent activity coefficients of bromide ion,  $-\Delta \log \circ_{\gamma Br^{-}}$ , are 3.8 [(-1) (-2.3 -1.5)]<sup>9</sup> for the former and 2.8 [(-1) (-2.3 -0.5)]<sup>9</sup> for the latter.

In propylene carbonate + methanol mixtures both logarithmic rates and activation enthalpies show marked changes in the region of small methanol content (fig. 1 and 2), as also observed to some extent in acetonitrile + methanol mixtures.<sup>18</sup> The effects suggest the existence of specific bromide ion solvation by methanol in these solvent mixtures.

In contrast to the above, in N-methyl-2-pyrrolidone+methanol mixtures both values change linearly over the entire region of solvent composition. In both systems

MeOH+PC mixtures			MeOH+NMePy mixtures		
XMeOH <sup>a</sup>	$k_{\rm mix}/10^{-5}$ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	$\frac{\Delta H_{\min}^{*}}{\text{kcal mol}^{-1}}$	ХМеОН	$k_{\rm mix}/10^{-5}$ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	$\Delta H_{\rm mix}^{\pm}/{ m kcalmol^{-1}}$
0.0	2210.0	17.0	0.0	1.30×10 <sup>5</sup>	14.7
0.10	174.0	1 <b>9.9</b>	0.20	7880.0	16.0
0.25	41.5	20.7	0.30	2540.0	16.5
0.50	10.9	21.1	0.35	1540.0	16.4
0.75	3.92	21.9	0.50	371.0	17.6
1.0	1.01	22.7	0.65	78.7	18.7
			0.80	16.4	18.8
			1.0	1.01	22.7

Table 1.—Rate constants and activation enthalpies for the reaction of ethyl iodide with bromide ion  $(30^{\circ}C)$ 

<sup>*a*</sup>  $x_{MeOH}$ ; mole fraction of MeOH.



FIG. 1.—Plots of log k<sub>mix</sub> against mole fraction of methanol (x<sub>MeOH</sub>) for the reaction of ethyl iodide with bromide ion (30°C). □, NMePy + MeOH mixtures; ○, PC + MeOH mixtures.

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FIG. 2.—Plots of  $\Sigma \Delta H_t^{AS \to mix}$  and  $\Delta H_{mix}^{\ddagger}$  against  $x_{MeOH}$ .  $\bigcirc$  and  $\Box$ , activation enthalpies in PC+ MeOH and in NMePy+MeOH mixtures;  $\bigcirc$  and  $\blacksquare$ ,  $\Sigma \Delta H_t^{AS \to mix}$  in PC+MeOH and in NMePy+ MeOH mixtures.

the behaviour on a logarithmic scale is reflected in the activation enthalpy against solvent composition profiles. Thus these systems deserve analysis in terms of solute enthalpy of transfer against solvent composition profiles.

# HEAT OF SOLUTION OF THE SOLUTE

From thermodynamic considerations the following relation can be derived between the activation enthalpies and the transfer enthalpies of the respective solutes of the reaction,

$$\Delta H_{\rm B}^{*} - \Delta H_{\rm A}^{*} = \Delta H_{\rm t}^{\rm A \to B}({\rm TS}^{-}) - \Delta H_{\rm t}^{\rm A \to B}({\rm EtI}) - \Delta H_{\rm t}^{\rm A \to B}({\rm Br}^{-})$$
(1)

where A and B are two given solvents or solvent systems.

The terms on the left hand side are pseudo-thermodynamic quantities as defined by transition state theory, whereas those on the right hand side are pure thermodynamic

quantities. Usually the experimental uncertainties in the activation parameters are large compared with those for the thermodynamic quantities. There are also theoretical difficulties with respect to the activation parameters. If we can find suitable model compounds for the activated complex and carry out thermodynamic measurements for these compounds, we can replace the pseudo-thermodynamic quantities by purely thermodynamic quantities and thus more detailed and theoretically more reliable discussions will be possible.

Perchlorate ion should be a pertinent model compound since it satisfies the prerequisites for a model compound, *i.e.*, its molecular size and charge distribution should be similar and the compound should be stable enough for thermodynamic measurements. Heats of solution of various solutes are summarized in tables 2 and 3.

Heats of solution of these solutes are combined so as to simulate the activation enthalpy against composition profile for the reaction, on the basis that the perchlorate ion serves as a model compound for the activated complex of the reaction, *i.e.*, eqn (2),

$$\Sigma \Delta H_t^{\text{AS} \to \text{mix}} \equiv \Delta H_{\text{AS}}^{\ddagger} + \Delta H_t^{\text{AS} \to \text{mix}} [(n-\text{Bu})_4 \text{NClO}_4] - \Delta H_t^{\text{AS} \to \text{mix}} [\text{(EtI)} - \Delta H_t^{\text{AS} \to \text{mix}} [(n-\text{Bu})_4 \text{NBr}]$$
(2)

TABLE 2.--ENTHALPY OF SOLUTION IN PC+MeOH MIXTURES AT 25°C (kcal mol<sup>-1</sup>)

х <sub>МеОН</sub>	EtI	(n-Bu) <sub>4</sub> NBr	(n-Bu)4NClO4	(n-Bu) <sub>4</sub> NB(n-Bu) <sub>4</sub>
0.0	0.978	5.92	3.12	10.21
		(5.70 <sup>21</sup> )	(3.03 <sup>21</sup> )	
0.10		2.82	3.09	10.26
0.25	0.967	2.47	3.31	10.04
0.50	0.910	2.74	3.64	9.54
0.75	0.804	2.96	4.10	8.65
0.90	<u> </u>	3.23	4.68	8.12
1.0	0.662	4.17	6.66	8.31
		$(5.0^{19})$ (4.19 <sup>23</sup> )	(6.86 <sup>23</sup> )	(14.1 19)

TABLE 3.—ENTHALPY OF SOLUTION IN NMePy+MeOH MIXTURES AT 25°C (kcal mol<sup>-1</sup>)

x <sub>MeOH</sub>	EtI	(n-Bu) <sub>4</sub> NBr	(n-Bu) <sub>4</sub> NC1O <sub>4</sub>	(n-Bu) <sub>4</sub> NB(n-Bu) <sub>4</sub>	(n-Bu) <sub>4</sub> Sn
0.0	0.125	5.00 (3.9 <sup>19</sup> )	1.05	4.46 (4.8 <sup>19</sup> )	3.47
0.20		4.28	1.48	4.52	3.45
0.25	0.184				—
0.35		4.20	1.84	4.63	3.35
0.50	0.270	4.03	2.31	4.86	3.23
0.65		3.94	2.95	4.91	3.13
0.75	0.388				
0.80		3.90	3.78	5.23	2.88
0.90			4.75	5.86	
1.0	0.662	4.17	6.66	8.31	2.56
		(5.0 <sup>19</sup> ) (4.19 <sup>23</sup> )	(6.86 23)	(14.1 <sup>19</sup> )	

where AS and mix denote the dipolar aprotic solvents, *i.e.*, propylene carbonate and *N*-methyl-2-pyrrolidone, and solvent mixtures. The above quantities are plotted together with activation enthalpies in fig. 2.

The combined enthalpy changes, *i.e.*,  $\Sigma \Delta H_t^{AS \to mix}$ , reproduce fairly well the activation enthalpy against composition profiles for the two solvent mixtures. Thus in the following discussions we will take the perchlorate ion as a model compound for the activated complex of the reaction.

х <sub>МеОН</sub>	Br⁻	C1O4-	B(n-Bu) <sub>4</sub> -	
 0.0	0.0	0.0	0.0	
0.1	-3.13	-0.06	0.02	
0.25	-3.37	0.27	-0.08	
0.50	-2.85	0.85	-0.34	
0.75	-2.18	1.76	-0.78	
0.90	-1.65	2.60	-1.04	
1.0	-0.80	4.48	-0.95	

Table 4.—Single ion enthalpy of transfer from PC to solvent mixtures,  $\Delta H_t^{PC \rightarrow mix}$ , at 25°C (kcal mol<sup>-1</sup>)

Table 5.—Single ion enthalpy of transfer from NMePy to solvent mixtures,  $\Delta H_t^{\text{NMePy} \rightarrow \text{mix}}$ , at 25°C (kcal mol<sup>-1</sup>)

х <sub>МеОН</sub>	Br-	C104-	B(n-Bu) <sub>4</sub> -
0.0	0.0	0.0	0.0
0.20	-0.75	0.40	0.03
0.35	-0.89	0.70	0.08
0.50	-1.17	1.06	0.20
0.65	-1.29	1.68	0.22
0.80	-1.49	2.34	0.38
0.90	-1.70	3.00	0.70
1.0	-2.75	3.68	1.92

## SINGLE ION ENTHALPIES OF TRANSFER

For a more detailed discussion of ionic solvation it is necessary to evaluate single ion enthalpies of transfer from solvent to solvent. For this purpose, heats of solution of TBATBB  $[(n-Bu)_4NB(n-Bu)_4]$  have been determined in two solvent mixtures (tables 2 and 3). To check the extra-thermodynamic assumption, heats of solution of tetra-n-butyl tin  $[(n-Bu)_4Sn]$  have also been determined (table 3). The single ion enthalpies of transfer thus determined, *i.e.*, using the TBATBB assumption, are summarized in tables 4 and 5.

The transfer enthalpy of tetra-n-butyl borate ion from N-methyl-2-pyrrolidone to MeOH as estimated according to Kim's procedure,<sup>22</sup> 1.37 kcal mol<sup>-1</sup>,\* is in

\*  $\Delta H_t^{\text{NMePy} \rightarrow \text{MeOH}}$  {(n-Bu)<sub>4</sub>Sn} combined with the transfer energy due to ion-dipole interaction of 2.28 kcal mol<sup>-1</sup> estimated for tetraphenyl-borate ion in ref. (22) gives  $\Delta H_t^{\text{NMePy} \rightarrow \text{MeOH}}$  {(n-Bu)<sub>4</sub>B<sup>-</sup>} = 1.37 kcal mol<sup>-1</sup>.

reasonable agreement with the observed value,  $1.92 \text{ kcal mol}^{-1}$ . Krishnan and Friedmann evaluated the enthalpy of transfer of bromide ion from propylene carbonate to methanol as  $-2.14 \text{ kcal mol}^{-1}$  from the Ph<sub>4</sub>AsBPh<sub>4</sub> assumption and 1.66 kcal mol<sup>-1</sup> from the hydrocarbon assumption.<sup>23</sup> Our value,  $-0.8 \text{ kcal mol}^{-1}$ , is between the two extremes. With respect to the reliability of the Ph<sub>4</sub>AsBPh<sub>4</sub> assumption, various criticisms have been made,<sup>23-27</sup> indicating that the TBATBB assumption might be more reliable.

As far as the transfer enthalpy is concerned, dipolar aprotic and protic solvent effects on bromide ion solvation are not as significant as would be expected on the basis of solvent activity coefficients.<sup>9</sup> This indicates the importance of the transfer entropy term as one of the constituent terms of the free energy of transfer, especially for the transfer between the dipolar aprotic and protic solvents.<sup>28-31</sup>

Of the ions studied, the bulky  $(n-Bu)_4B^-$  ion shows the smallest variation of transfer enthalpy with solvent composition; this is as expected and is in accord with the theoretical suppositions on which the  $(n-Bu)_4B^-/(n-Bu)_4N^+$  assumption is based. The transfer enthalpy of the perchlorate ion steadily increases with increasing methanol content of the solvent mixtures, but the behaviour of the bromide ion is quite different in the PC+MeOH solvent system where its transfer enthalpy passes through a sharp minimum.

In organic chemistry, the perchlorate ion has been taken as non-reactive. In fact, spectroscopically there is little evidence for specific solute-solvent interactions with perchlorate ion; <sup>25, 27, 32</sup> at most only quite weak interactions have been detected.<sup>33, 34</sup> However, a model calculation performed according to Kim's procedure,<sup>22</sup> on the basis of Buckingham theory <sup>35</sup> and assuming tetrahedral coordination,<sup>22, 25</sup> suggests that the contribution to transfer enthalpy from ion-dipole interaction energy should amount to 15.0 and 29.7 kcal mol<sup>-1</sup> for transfer from NMePy to MeOH and from PC to MeOH. Thus, the solute-solvent interaction as observed for perchlorate ion must be more "physical", presumably mainly electrostatic in nature.

Several spectroscopic studies have been performed and quantitative data have been obtained on methanol-bromide ion interactions.<sup>34, 36-39</sup> Similarly performed model calculations as mentioned above suggest a contribution to transfer enthalpy from the ion-dipole interaction energy of 16.4 and 34.2 kcal mol<sup>-1</sup> for transfer from NMePy to MeOH and from PC to MeOH. Considering both these facts and the characteristic features observed in  $\Delta H_t^{AS \to mix}$  against composition profiles, the transfer enthalpy of bromide ion should be taken as a composite quantity of more "physical" and specific solute-solvent interaction energies.

## PARTIAL MOLAR ENTHALPY OF MIXING

As partly inferred from the transfer enthalpy against composition profile and as discussed elsewhere, 40-42 the thermodynamic properties of the solvent mixtures would significantly affect the solvation energy of a solute in these solvent mixtures. Any characteristic features of the solvent mixtures should be reflected in the behaviour of an ionic solute in the case where specific solute-solvent interactions play an important role. For this purpose, the partial molar enthalpy of mixing of a component, *i*, is defined by eqn (3),

$$\bar{h}_i^{\rm M} = \bar{h}_i - h_i^{\circ} \, \cdot \tag{3}$$

 $h_i^{M}$  has been determined for both mixtures. These values (tables 6 and 7) satisfy the Gibbs-Duhem relation as is required by thermodynamics<sup>43</sup> with a relative uncertainty of  $\pm 2\%$ , which corresponds to an estimated experimental error.

xpc	$\bar{h}_{\mathrm{PC}}^{\mathrm{M}}$	$x_{\rm PC}$	$h_{\rm MeOH}^{\rm M}$
1.0	0	0.99472	1.56
		0.895	1.16
0,752	0.113	0.745	0.723
0.652	0.193	0.647	0.526
0.502	0.342	0.496	0.328
0.352	0.515	0.348	0.184
0.251	0.705	0.248	0.115
0.101	1.13		
$1.25 \times 10^{-3}$	1.77	0.0	0
For $\overline{h_{m}^{M}}$	A = 2.9528, B =	= -5.3960 C = 6	4.1754

TABLE 6.—PARTIAL MOLAR ENTHALPY OF MIXING,  $\overline{h}_{i}^{M}$ , at 25°C PC+MeOH MIXTURES (kcal  $mol^{-1}$ )

For h<sub>MeOH</sub> A = 2.7065, B = -4.3720, C = 3.2875.

TABLE 7.—PARTIAL MOLAR ENTHALPY OF MIXING,  $h_i^M$ , at 25°C NMePy+MeOH MIXTURES (kcal mol<sup>-1</sup>)

x <sub>NMePy</sub>	$ar{h}^{ m M}_{ m NMePy}$	XNMePy	$h_{\rm MeOH}^{\rm M}$	
1.0	0	0,9895	-0.506	
		0.895	-0.448	
0.802	-0.0129	0.796	-0.386	
0.653	-0.0552	0.644	-0.277	
0.501	-0.130	0.494	-0.160	
0.352	-0.262	0.346	-0.0710	
0.202	-0.390	0.198	-0.0240	
0.101	-0.478			
$1.08 \times 10^{-3}$	-0.696	0.0	0	
For $\bar{h}_{NMePy}^{M}$	A = -0.18893,	B = -0.86833,	C = 0.39850.	
For hMach	A = -0.48090,	B = -0.68657,	C = 0.65655.	

Propylene carbonate and methanol mix endothermically. This suggests that the self-association of methanol is partially broken and, as a result, methanol molecules move more freely in the mixture. In contrast, the NMePy+MeOH system shows an exothermic heat of mixing. This indicates that methanol molecules are associated with NMePy molecules more strongly than they are self-associated. Thus a methanol molecule in PC+MeOH mixtures will have a greater ability to form a hydrogenbonded complex with bromide ion than would expected from pure methanol, whereas a methanol molecule in NMePy+MeOH mixtures will have a lower ability; these features should be reflected in the transfer enthalpy against composition profiles of the bromide ion.

For mixtures in which the entropy of mixing is approximately ideal, the activity coefficient of a component, *i*, can be estimated from the relation,

$$\mu_i - (\mu_i^\circ + RT \ln x_i) = RT \ln \gamma_i \approx \overline{h_i^M}.$$
(4)

In the following discussions, the activity coefficient will be estimated on the basis of eqn (5), in which the coefficients, A, B and C have been determined by a least-squares treatment of the experimental data

$$RT \ln \gamma_i = \bar{h}_i^{\rm M} = A(1-x_i)^2 + B(1-x_i)^3 + C(1-x_i)^4.$$
(5)

The activity coefficients thus estimated will not be thermodynamically very reliable. However, in comparing thermodynamic properties of mixtures having such significantly different natures as endothermic on one hand and exothermic on the other, the activity coefficients will at least reflect the true nature of the mixtures.

## THEORETICAL TREATMENT OF ANION SOLVATION

As discussed in part above and described elsewhere, 10-14, 33 the solute-solvent interaction energy seems to be a quantity composed of various terms. For the present systems it is convenient to classify these terms as (i) generally observable terms throughout all solute-solvent combinations and (ii) uniquely observable terms for a particular solute-solvent system. For the former an example is a more "physical" interaction, *i.e.*, the electrostatic interaction as ascribed to perchlorate ion solvation. For the latter, the hydrogen-bonding interaction between methanol and bromide ion would serve as an example.

The transfer enthalpy against composition profile for perchlorate ion can be fairly well reproduced by the analytical formulae,

$$\Delta H_t^{\text{AS} \to \text{mix}}(\text{ClO}_4^-) = \Delta H_t^{\text{AS} \to \text{MeOH}}(\text{ClO}_4^-)x[1-2x(1-x)]$$
$$\equiv \Delta H_{t,\text{PHYS}}^{\text{AS} \to \text{mix}}$$
(6)

where x is the mole fraction of methanol. Thus we take this equation to express the contribution to the transfer enthalpy against composition profile of the more "physical" interaction.

Specific solute-solvent interactions can be expressed as solvent exchange equilibria on the solvation sites around the ion, as carried out previously <sup>17, 42, 44</sup>

$$M(S_1)_{i-1}(S_4)_{z-i+1} + S_1 \underset{\Delta H_{se}}{\overset{K_{se}}{\rightleftharpoons}} M(S_1)_i(S_4)_{z-i} + S_4.$$

For the system in which the solvent exchange process can be expressed as a chemical equilibrium, the probability ratio of the clusters in solution is given by the equation

$$\frac{[M(S_1)_i(S_4)_{z-i}]}{[M(S_1)_{i-1}(S_4)_{z-i+1}]} = \frac{K_{se}a_1}{a_4}$$
(7)

where z and  $a_i$  are the number of solvation sites and the activity of the solvent, *i*, respectively. For the ionic solute having z independent solvation sites, the cluster distribution will be given by the binominal form,  $(K_{se} a_1 + a_4)^z$ .

In the simplest case, each solvent exchange process will have the same enthalpy change for all solvent exchange processes,  $\Delta H_{se}$ . In such a case, the total energy of the solute system,  $\Delta H_{T}$ , will be given by eqn (8), when the cluster distribution is given by the binominal form, using the binominal form as a normalizing factor. This is essentially the same procedure as applied to n.m.r. shift treatments <sup>45</sup>

$$\Delta H_{\rm T} = \sum_{i=0}^{z} \frac{z!}{i!(z-i)!} \left\{ \frac{(K_{\rm se}a_1)^i(a_4)^{z-i}i\Delta H_{\rm se}}{(K_{\rm se}a_1+a_4)^z} \right\}.$$
(8)

Since  $z\Delta H_{se}$  in the model corresponds to the transfer enthalpy of the solute due to a specific interaction from pure solvent,  $S_4$ , to pure solvent,  $S_1$ , *i.e.*,  $\Delta H_{t,SI}^{AS \to MeOH}$ , and  $\Delta H_T$  is equal to zero and to  $z\Delta H_{se}$  in pure solvents,  $S_4$  and  $S_1$ , thus the transfer enthalpy due to a specific interaction,  $\Delta H_{t,SI}^{AS \to mix}$ , should be equal to  $\Delta H_T$  and is given, after rearrangement, by

$$\Delta H_{t,SI}^{AS \to mix} = \Delta H_{t,SI}^{AS \to MeOH} K_{se} a_1 / (K_{se} a_1 + a_4).$$
<sup>(9)</sup>

The experimentally observable transfer enthalpy of bromide ion can be expressed as the sum of two terms

$$\Delta H_{t}^{AS \to mix}(Br^{-}) = \Delta H_{t,PHYS}^{AS \to mix} + \Delta H_{t,SI}^{AS \to mix}.$$
 (10)

The equilibrium constant for bromide ion-methanol interaction has been determined as  $4 \text{ dm}^3 \text{ mol}^{-1}$  in propylene carbonate.<sup>34</sup> For consistency this equilibrium constant must be transformed into  $K_{se}$ , as defined above. According to the procedure described below,\*  $K_{se}$  for bromide ion-MeOH is  $\approx 1.6$ .



 $x_{MeOH}$ 

FIG. 3.—Single ion enthalpies of transfer from PC to solvent mixtures for bromide ion.  $\bigcirc$ , experimental; —, calculated by eqn (10) with  $\Delta H_{t, PHYS}^{PC \rightarrow MeOH} = 6.2 \text{ kcal mol}^{-1}$ ,  $\Delta H_{t, SI}^{PC \rightarrow MeOH} = -7.0 \text{ kcal mol}^{-1}$  and  $K_{se} = 2.0$ .

Recently Arnett *et al.*<sup>13</sup> estimated the solvation enthalpy of pyridine in water due to hydrogen-bonding interaction,  $-\Delta H_s$ , as 4.3 kcal mol<sup>-1</sup>. Spectroscopic studies on bromide ion-methanol and pyridine-methanol interaction gave the enthalpy change of hydrogen-bonding interaction as  $-6^{38}$  and  $-3.2^{45}$  kcal mol<sup>-1</sup> in carbon tetrachloride. A linear enthalpy relationship between these quantities, *i.e.*,  $4.3 \times (6/3.2)$ , leads to  $-\Delta H_s = 8.1$  kcal mol<sup>-1</sup> for the bromide ion solvation enthalpy due to hydrogen bonding in water; a similar value will also apply in methanol.

\* The equilibrium constant of  $4 \text{ dm}^3 \text{ mol}^{-1}$  should first be transformed into thermodynamic quantity,  $K_{\text{th}}$ , after being multiplied by the number of moles of PC in 1 dm<sup>3</sup> and by the activity coefficient ratio estimated for  $x_{\text{PC}} = 0.9$  on the basis of eqn (5), thus giving  $K_{\text{th}} = 4 \times 11.7 \times (1.0/7.1) = 6.6$ . Judging from the experimental conditions, the observed equilibrium process would correspond to the first solvent exchange process in the model and, assuming a tetrahedral coordination for the bromide ion,  $K_{\text{th}}$  will be equal to  $4K_{\text{se}}$ , thus giving  $K_{\text{se}} = 1.65$ .

In applying eqn (10) to the analysis of the transfer enthalpy of bromide ion in solvent mixtures, three conditions must be satisfied. First, the equality must be satisfied among three transfer enthalpies,

$$\Delta H_{t}^{AS \rightarrow MeOH} = \Delta H_{t,PHYS}^{AS \rightarrow MeOH} + \Delta H_{t,SI}^{AS \rightarrow MeOH}$$

and then  $\Delta H_{4,SI}^{AS \to MeOH}$  and  $K_{se}$  should be close to -8 kcal mol<sup>-1</sup> and 1.6, respectively. Under these boundary conditions, with the use of activity coefficients estimated from eqn (5), curve fitting procedures were carried out and the final results are shown in fig. 3 and 4.



FIG. 4.—Single ion enthalpies of transfer from NMePy to solvent mixtures for bromide ion. O, experimental; ---, calculated by eqn(10) with  $\Delta H_{1,MPHYS}^{MePy \rightarrow MeOH} = 4.25$  kcal mol<sup>-1</sup>,  $\Delta H_{1,M}^{MePy \rightarrow MeOH} = -7.0$  kcal mol<sup>-1</sup> and  $K_{se} = 2.0$ ; -----; calculated by eqn (6) and (11) with the same parameters used above; ----, calculated by eqn (6) and (11) after replacing  $a_4$  by  $(1-a_1)$ .

In PC+MeOH mixtures, the transfer enthalpy against composition profile was fairly well reproduced by the equation, with reasonable values for the parameters, *i.e.*,  $\Delta H_{t, \text{PHYS}}^{PC \to MeOH} = 6.2 \text{ kcal mol}^{-1}$  and  $\Delta H_{t, \text{SI}}^{AS \to MeOH} = -7.0 \text{ kcal mol}^{-1}$ , and  $K_{se} = 2.0$  (fig. 3). The model calculation indicates that each system should follow its own transfer enthalpy against composition profile according to its thermodynamic properties, even though the model could not reproduce well the profile in NMePy+MeOH mixtures.

From the exothermic heat of mixing, methanol molecules are suggested to form a hydrogen-bonded complex with pyrrolidone molecules. As in the bulk phase, hydrogen bonding interactions would take place between methanol and pyrrolidone molecules on solvation sites around the ionic solute. In such a case only methanol molecules which exist in excess over pyrrolidone molecules should contribute to the specific solvation of bromide ion. The same line of treatment as described above, except that only the clusters Br<sup>-</sup> (NMePy)(MeOH)<sub>3</sub> and Br<sup>-</sup> (MeOH)<sub>4</sub> contribute to the total enthalpy with a statistical weight of  $2\Delta H_{se}$  and  $4\Delta H_{se}$ , leads to the following equation, assuming a tetrahedral coordination of bromide ion.<sup>26</sup> The calculated results are shown in fig. 4 as a partially dotted curve

$$\Delta H_{t,S1}^{\text{AS} \to \text{mix}} = \Delta H_{t,S1}^{\text{AS} \to \text{MeOH}} (K_{se}a_1)^3 (2a_4 + K_{se}a_1) / \{ (a_4 + K_{se}a_1)^4 \}.$$
(11)

In NMePy+MeOH mixtures, the sum of the activities of the components, *i.e.*,  $a_1+a_4$ , is always < 1. If the mixture is taken as an ideal associated mixture, the term  $1-(a_1+a_4)$  should indicate the fraction of the associated component, *i.e.*, in this case hydrogen-bonded methanol with pyrrolidone. In the third model, we assume that all components other than free methanol behave as neutral components, *i.e.*,  $a_4$  in eqn (11) should be replaced by  $(1-a_1)$ . The calculated values are shown as a full line in fig. 4. The agreement with experimental results becomes better. In any case, in NMePy+MeOH mixtures a more sophisticated treatment of ion solvation is required to reproduce experimental results.

## CONCLUSIONS

Sometimes solution phenomena reveal their individualities more vividly in solvent mixtures than in pure solvents. At first sight, the dissection of the activation parameters into initial state and transition state contributions suggests that the solvent effects on the rates are controlled mainly by transition state solvation; this contradicts the accepted views of organic chemistry. Detailed discussion on anion solvation in terms of more "physical" and specific solvation leads to the conclusion that most of the contribution from the more "physical" interaction cancels out between the initial state and the transition state. As a result, a specific interaction of bromide ion with methanol controls the dipolar aprotic–protic solvent effects on the substitution reaction. Thus, further dissections into constituent terms, *i.e.*, physical or chemical interactions, are required for a detailed discussion on ion solvation and for an analysis of solvation-related solution phenomena.

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