Menschutkin Reaction of Triethylamine and of Pyridine with Methyl Iodide. Activation Enthalpy *versus* Activation Entropy Correlations and Extended Brönsted Treatments in Acetonitrile–Methanol Mixtures

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The rate constants and activation parameters for the reaction of triethylamine with methyl iodide and for pyridine with methyl iodide have been determined in acetonitrile–methanol mixtures. Enthalpies of solution have also been determined for triethylamine, pyridine, triethylmethylammonium iodide, and methylpyridinium iodide in the same solvent mixtures. Transfer enthalpies of amines and of quaternary ammonium iodide have been split into constituent terms, *i.e.*, 'more physical' interaction and specific interaction enthalpies. Correlations involving activation enthalpy *versus* activation entropy plots, and extended Brönsted plots, yielded straight lines only when corrected for the specific interaction term.

In linear free energy correlations of solvent effects on reaction rates and equilibria, and also in structure–reactivity correlations, protic and aprotic solvents often constitute separate groups.[1–4] These phenomena have been incorporated into π^*, α, and β correlations on a quantitative, though empirical basis.[5,6] The direct measurement and analysis of thermodynamic quantities for appropriate species under experimental conditions would be desirable for further sophisticated analysis of reactions in solution, as well as for the critical analysis of empirical solvent parameter methods.

In the present work activation parameters for the quaternization reaction of triethylamine, and of pyridine, with methyl iodide and the enthalpy of solution of relevant species measured in acetonitrile–methanol mixtures are reported. After the physical meaning of the transfer enthalpies of these species has been made clear in terms of the 'more physical' and specific interaction enthalpies, the applicability of the treatment is tested in the form of empirical energy correlations, *i.e.*, activation enthalpy *versus* activation entropy plots and extended Brönsted plots.

Experimental

Materials.—Triethylamine, after refluxing with acetic anhydride, was distilled, passed through an alumina column, and distilled after storage over potassium hydroxide. Pyridine was successively distilled from barium oxide, calcium hydride, then under an atmosphere of nitrogen. Methyl iodide, acetonitrile, and methanol were treated as described elsewhere.[3]

Kinetic Measurements.—Rate constants were determined at four of the following temperatures, 0.0, 20.0, 30.0, 40.0, and 50.0 °C, as described elsewhere,[7,8] and experimental errors were estimated to be *ca.* ± 2%.

Heat of Solution Measurements.—Heats of solution were measured with a Tokyo Riko twin isothermal calorimeter (TIC-2D) at 25.0 ± 0.05 °C;[8,9] the final concentration ranges were 0.9—1.3 × 10^{-2} mol dm^{-3} for salts and 3—6 × 10^{-2} mol dm^{-3} for neutral bases. Experimental errors were estimated to be *ca.* ± 2%.

Results and Discussion

Rate Constants and Activation Parameters.—Rate constants and activation parameters for the reaction of both triethylamine and pyridine with methyl iodide are given in Table 1. For both reactions, the logarithmic rate changes almost linearly with solvent composition. Thus, no convincing evidence could be drawn from the rate constant studies alone about the presence of specific interactions of reactants and/or of the activated complex with either component of the mixed solvent. This is in sharp contrast to the reaction of bromide ion with ethyl iodide in the same solvent mixtures.[9]

For the triethylamine with methyl iodide reaction, both activation enthalpies and activation entropies indicate sharp changes at low methanol concentrations and a maximum was observed at $x_{MeOH} = 0.5$ for the activation entropies. These features suggest a specific interaction of triethylamine with

Table 1. Rate constants and activation parameters in acetonitrile–methanol mixtures at 30 °C

	Triethylamine + MeI			Pyridine + MeI		
x_{MeOH}[a]	$10^4 k_{mix}$ / dm^3 mol^{-1} s^{-1}	$\Delta H_{mix}^{\ddagger}$ / kJ mol^{-1}	$\Delta S_{mix}^{\ddagger}$ / J K^{-1} mol^{-1}	$10^5 k_{mix}$ / dm^3 mol^{-1} s^{-1}	$\Delta H_{mix}^{\ddagger}$ / kJ mol^{-1}	$\Delta S_{mix}^{\ddagger}$ / J K^{-1} mol^{-1}
0	517	36.6	−149.0	55.8	52.9 (54.2[b])	−132.9
0.1	278	48.4	−115.3	41.2	56.3	−124.1
0.25	139	54.2	−101.8	28.4	58.8	−119.0
0.5	61.5	57.7	−97.1	16.3	63.5	−108.1
0.75	27.7	59.0	−99.5	8.70	67.4	−100.4
1.0	8.43	64.2	−92.1	2.97	70.9	−97.8

[a] x_{MeOH}, mole fraction of methanol. [b] From reference 10.

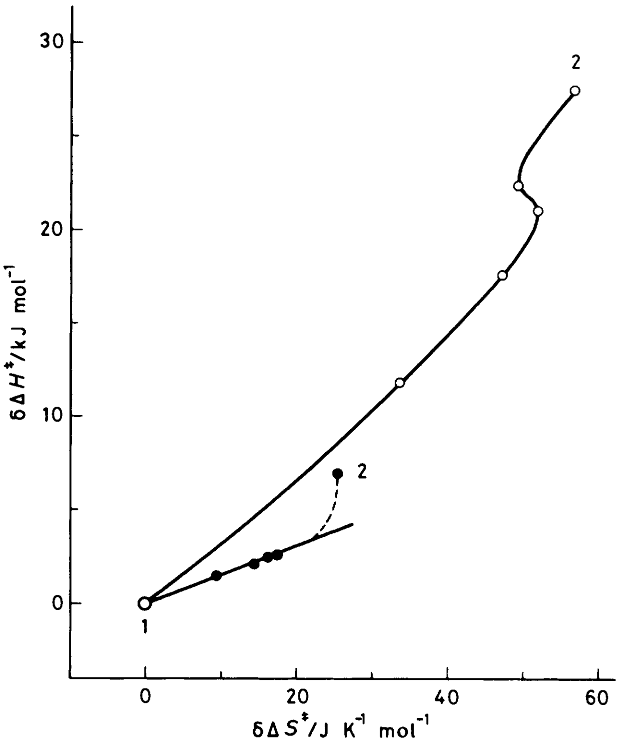

Figure 1. Correlation between activation enthalpy and activation entropy for the reaction of triethylamine with methyl iodide in acetonitrile–methanol mixtures. ○, Overall quantities; ●, quantities due to physical interaction. 1, Acetonitrile; 2, methanol

methanol. For the pyridine with methyl iodide reaction, both activation parameters indicate only moderate changes over the entire region and thus neither the temperature derivatives nor the activation free energy itself measured in mixed solvents provide sufficient criteria for the contribution to the kinetic behaviour of a specific interaction, although the hydrogen-bonding interaction between pyridine and methanol has been detected by various means.[11-13]

These characteristic features of activation parameters for the two reactions are clearly indicated by activation enthalpy *versus* activation entropy correlations, *i.e.*, the skewed S shape on the one hand and the almost linear plot on the other (see open circles in Figures 1 and 2), when acetonitrile was chosen as the reference solvent.

Enthalpies of Solution and Extended Brönsted Treatments.—Enthalpies of solution are summarized in Table 2. These values all show sharp decreases in the low methanol content region, followed by quite minor changes for neutral bases, and then by steady increases with increasing methanol content for the reaction products, *i.e.*, quaternary ammonium iodide. This suggests that the transfer enthalpies consist of at least two terms that have different responses to changing solvent composition, *i.e.*, a 'more physical' interaction and a specific interaction with methanol. The 'more physical' interaction includes electrostatic interactions, van der Waals forces, solvent–structure modifying interactions, and cavity terms, which are generally observed for every solute–solvent pair.[8,9] The specific interaction includes hydrogen-bonding and charge-transfer interactions, which are met only for specific solute–solvent pairs.[8,9] For neutral bases the specific interaction term is predominant, whilst for the salts produced both terms are significant. For pyridine the transfer enthalpies in mixed solvents yield the first evidence for the presence of a specific interaction with methanol.

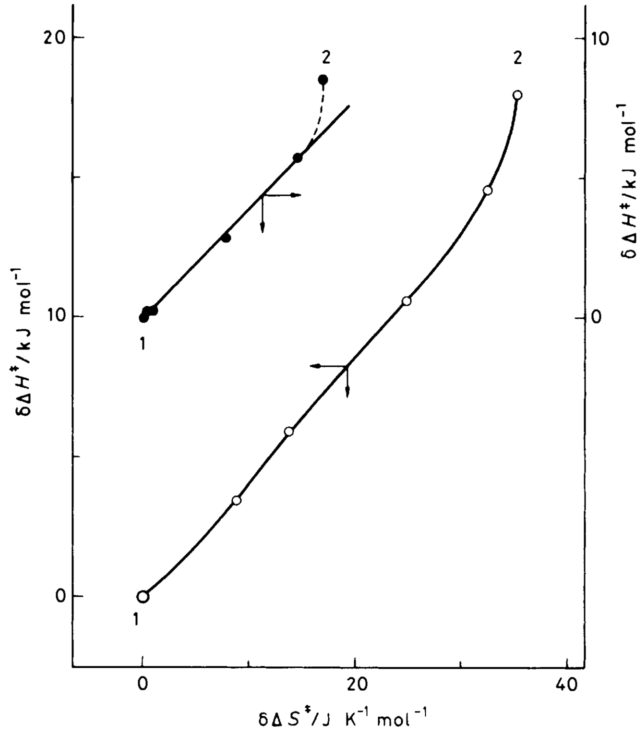

Figure 2. Correlation between activation enthalpy and activation entropy for the reaction of pyridine with methyl iodide in acetonitrile–methanol mixtures. ○, Overall quantities; ●, quantities due to physical interaction. 1, Acetonitrile; 2, methanol

Table 2. Enthalpies of solution in acetonitrile–methanol mixtures at 25 °C (kJ mol^{-1})

x_{MeOH}	Et_3N	$Et_3MeN^+I^-$	Pyridine	$MePyr^+I^-$	MeI[d]
0	5.30	9.14	1.64	10.5	3.62
	(5.50[a])				
0.1	−4.38	5.71	−1.17	7.11	
0.25	−9.46	6.99	−3.18	9.06	3.59
0.5	−11.7	11.0	−4.27	13.1	3.41
0.75	−12.4	16.2	−4.38	18.75	3.08
1.0	−12.4	24.9	−4.06	28.6	2.58
	(−12.4[a])		(−3.96[b])		
			(−4.1[c])		

[a] From reference 14. [b] From reference 15. [c] From reference 13. [d] From reference 16.

The combination of activation enthalpies and enthalpies of solution for neutral bases and methyl iodide lead to the transfer enthalpies of the activated complexes (Table 3). For the two reactions given these values increase monotonically with increasing methanol content; similar trends were previously observed for the reaction of two thione derivatives with methyl iodide.[16]

The extended Brönsted plots with respect to solvent variation give curves, as could partly be anticipated from the individual pattern of transfer enthalpy *versus* solvent composition profiles (see open circles in Figures 3 and 4).

Theoretical Analysis of Transfer Quantities.—Transfer enthalpies of the neutral compounds ethyl iodide, methyl iodide, and *NN'*-dimethylimidazolidine-2-thione, for which the

Table 3. Transfer enthalpies of the activated complexes in acetonitrile–methanol mixtures at 30 °C (kJ mol⁻¹)

x_{MeOH}	Et_3N + MeI	Pyridine + MeI
0	0	0
0.1	2.1	0.6
0.25	2.8	1.05
0.5	3.9	4.5
0.75	4.2	7.9
1.0	8.9	11.3

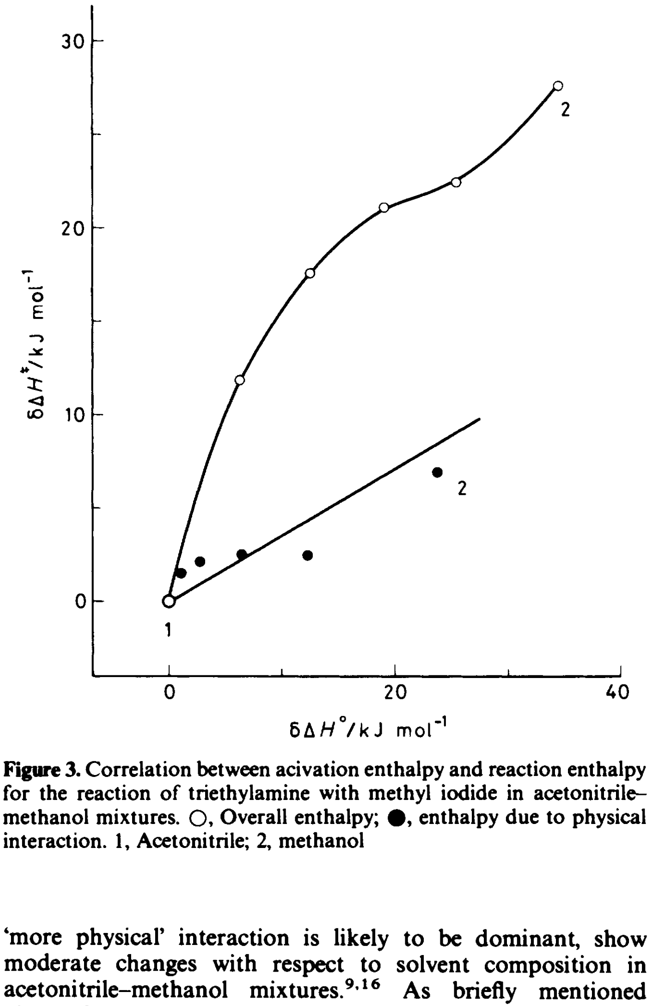

Figure 3. Correlation between acivation enthalpy and reaction enthalpy for the reaction of triethylamine with methyl iodide in acetonitrile–methanol mixtures. ○, Overall enthalpy; ●, enthalpy due to physical interaction. 1, Acetonitrile; 2, methanol

'more physical' interaction is likely to be dominant, show moderate changes with respect to solvent composition in acetonitrile–methanol mixtures.[9,16] As briefly mentioned above, the 'more physical' enthalpy seems to make only a minor contribution to the overall transfer enthalpies of neutral bases. Thus, to simplify the treatment, the 'more physical' enthalpy can reasonably be assumed to change linearly with solvent composition, equation (1), where AN stands for acetonitrile and x_1 stands for the mole fraction of methanol.

$$\Delta H_{t,phys}^{AN\to mix} = \Delta H_{t,phys}^{AN\to MeOH}\, x_1 \qquad (1)$$

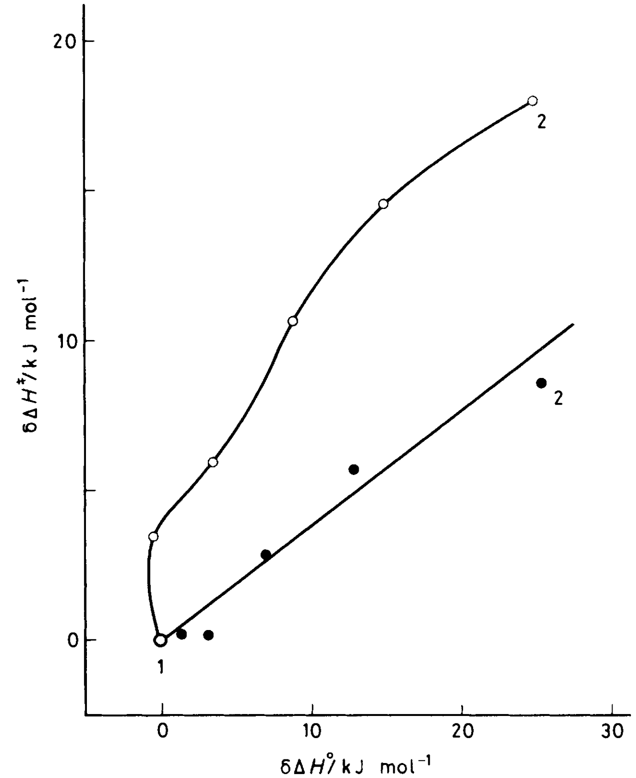

Figure 4. Correlation between activation enthalpy and reaction enthalpy for the reaction of pyridine with methyl iodide in acetonitrile–methanol mixtures. ○, Overall enthalpy; ●, enthalpy due to physical interaction. 1, Acetonitrile; 2, methanol

Assuming a solvent exchange (se) equilibrium (2), for the solvation site around a solute, and on the assumption of a binominal distribution of clusters, a theoretical equation, equation (3), for the transfer enthalpy due to a specific interaction (SI) has been derived, where $\Delta H_{t,SI}^{AN\to MeOH} = z\Delta H_{se}$.[8,16]

$$M\cdot(S_4)_{z-i+1}\cdot(S_1)_{i-1} + S_1 \underset{\Delta H_{se}}{\overset{K_{se}}{\rightleftharpoons}} M\cdot(S_4)_{z-i}\cdot(S_1)_i + S_4 \qquad (2)$$

$$\Delta H_{t,SI}^{AN\to mix} = \Delta H_{t,SI}^{AN\to MeOH}\, K_{se}x_1/(x_4 + K_{se}x_1) \qquad (3)$$

The boundary condition for the transfer enthalpies is given by equation (4).

$$\Delta H_t^{AN\to MeOH} = \Delta H_{t,phys}^{AN\to MeOH} + \Delta H_{t,SI}^{AN\to MeOH} \qquad (4)$$

Transfer enthalpies of the neutral bases could be reproduced quite successfully by combination of equations (1) and (3), and the constituent terms are summarized in Table 4. The specific interaction enthalpies for neutral compounds could be reproduced by equation (3), in which mole fraction is used as a variable (see also reference 16). In contrast, for anionic nucleophiles, including iodide ion, an activity instead of mole fraction had to be used to reproduce the contribution of specific interaction enthalpies.[8,9] Thus, a specific interaction, which implicitly implies 'hydrogen-bonding' interactions in these cases, works in different ways in reactant- and product-solvation in the reactions discussed here. As partly inferred from previous work,[9,16] the specific interaction energy of quaternary ammonium iodide is largely ascribed to that of iodide ion with methanol. Thus by subtracting the specific interaction energy of iodide ion, $\Delta H_{t,SI}^{AN\to mix}$ (I^-), at relevant solvent compositions,[16] from the transfer enthalpies of quaternary ammonium salts in Table 4, the physical interaction enthalpies could be deduced and are summarized in Table 4.

The transfer enthalpy of the activated complex shows neither a sharp change nor a minimum at any of the solvent com-

Table 4. Dissection of transfer enthalpies into constituent terms and the parameters used in the analysis at 25 °C (kJ mol^{-1})

	Et$_3$N		Et$_3$MeN$^+$I$^-$ [a]	Pyridine		MePyr$^+$I$^-$ [a]
x_{MeOH}	$\Delta H_{t,phys}$	$\Delta H_{t,SI}$	$\Delta H_{t,phys}$	$\Delta H_{t,phys}$	$\Delta H_{t,SI}$	$\Delta H_{t,phys}$
0	0	0	0	0	0	0
0.1	0.6	−10.3	1.7	0.4	−3.2	1.7
0.25	0.7	−15.5	3.4	0.9	−5.75	4.1
0.5	1.6	−18.6	7.8	1.9	−7.8	8.5
0.75	2.2	−19.9	14.0	2.8	−8.8	15.15
1.0	2.9	−20.6	25.8	3.75	−9.45	28.1
	$z\Delta H_{se}$ = 20.6, K_{se} = 9.04			$z\Delta H_{se}$ = −9.45, K_{se} = 4.67		

[a] Calculated as $\Delta H_t^{AN\to mix}$ (salt) − $\Delta H_{t,SI}^{AN\to mix}$ (I$^-$).

positions, leading to the conclusion that the transfer enthalpy of the activated complex consists mostly of the 'more physical' interaction enthalpies.

Usually, empirical energy correlations, such as an extended Brönsted treatment and an activation enthalpy *versus* activation entropy plot, are intended to lead to deductions about the various characteristics of an activated complex in relation to those of the reactants and of the products of the respective reactions. For physically sound deductions to be made, these correlations have to be carried out in energy terms that are common throughout the reactants, activated complex, and products. The specific interaction enthalpy, although significant for the reactants, is largely lost in the transition state, and reappears for the products, with a different type of interaction from that of the reactants. Thus, at least, the specific interaction terms have to be eliminated in these correlations.

The extended Brönsted plots with respect to solvent variation in terms of 'more physical' enthalpies are shown in Figures 3 and 4 as filled circles. The plots still seem to be sigmoidal. The maximum deviation from the correlation line is *ca.* 1 kJ mol^{-1}, which corresponds to the estimated uncertainties of the treatment. At this stage further analysis of the profile is impossible. The values of the slopes of the correlation line, *i.e.*, 0.35 and 0.38 for the triethylamine and pyridine reaction, respectively, lie within the normal range expected for these correlations, *i.e.*, within zero and unity.[9,16] The importance of the constituent analysis in transfer quantities, especially in protic solvents, is clear from an inspection of the Figures.

The subtraction of the transfer enthalpy of iodide ion due to physical interaction, 23.7 kJ mol^{-1},[9] from those of the quaternary ammonium iodides gives the transfer enthalpy of the quaternary ammonium cations due to physical interaction, *i.e.*, 2.1 and 4.4 kJ mol^{-1} for triethylmethylammonium and methylpyridinium ions (all values refer to the transfer from acetonitrile to methanol). The comparison of these values indicates that the cationic part contributes only slightly to transfer enthalpies, and leads to the supposition that the slope values in the extended Brönsted treatments are largely determined by the charge develpment on the leaving iodine atom.

The analysis of the enthalpies thus successfully evaluates the contribution of specific interaction to activation as well as to reaction enthalpies for both reactions. Activation entropy *versus* solvent composition profiles show a maximum for the triethylamine reaction, and much smaller changes for the pyridine reaction. These seemingly inconsistent observations can be brought into line, if the relevant procedures are developed for evaluating the transfer entropy due to specific interaction.

Thermodynamically, enthalpy and Gibbs energy are related by equation (5).[17] The integration of equation (3) with respect

$$d(\Delta G^\circ/T)/dT = -\Delta H^\circ/T^2 \qquad (5)$$

to temperature, after substituting equation (6) into equation (3), leads to equation (7).

$$d\ln K_{se}/dT = \Delta H_{se}/RT^2 \qquad (6)$$

$$\Delta G_{t,SI}^{AN\to mix} = -RT\ln(x_4 + K_{se}x_1)^z \qquad (7)$$

Thus, the theoretical equations of enthalpy change and of Gibbs energy change, both due to specific interaction, can now be derived, *i.e.*, equations (3) and (7). The entropy change due to specific interaction can be given by equation (8).

$$\begin{aligned}\Delta S_{t,SI}^{AN\to mix} &= (\Delta H_{t,SI}^{AN\to mix} - \Delta G_{t,SI}^{AN\to mix})/T \\ &= (z\Delta H_{se}/T)(K_{se}x_1)/(x_4 + K_{se}x_1) \\ &\quad + R\ln(x_4 + K_{se}x_1)^z \end{aligned} \qquad (8)$$

In the transfer enthalpy analysis on the basis of equation (3), two parameters, *i.e.*, $z\Delta H_{se}$ and K_{se}, could be deduced. If the parameter $z\Delta H_{se}$ could be separated into its constituents, z and ΔH_{se}, by independent means, three thermodynamic quantities, $\Delta H_{t,SI}^{AN\to mix}$, $\Delta G_{t,SI}^{AN\to mix}$, and $\Delta S_{t,SI}^{AN\to mix}$, could be evaluated on the basis of one special model from equations (3), (7), and (8).

The presence of an extreme value in the specific interaction entropy *versus* solvent composition plot is given by condition (9) and substitution of equation (8) into equation (9) leads to

$$d\Delta S_{t,SI}^{AN\to mix}/dx_1 = 0 \qquad (9)$$

equation (10). For an assumed value of z, the value ΔH_{se} can be calculated from the parameter previously determined, $z\Delta H_{se}$.

$$x_1 = \frac{(-1)}{(K_{se}-1)}\left[\left(\frac{\Delta H_{se}}{RT}\right)\frac{K_{se}}{(K_{se}-1)} + 1\right] \qquad (10)$$

The substitution of the set of values z, ΔH_{se}, and K_{se} into equation (10) gives the desired solvent composition. In the present reaction a transfer entropy minimum leads to a maximum in the activation entropy *versus* solvent composition profile, arising from the specific interaction of a nucleophile with methanol. Thus the calculated value of x_1 using equation (10) is designated as $x_{max.,calc.}$ and is summarized in Table 5, together with the observed composition of the activation entropy maximum, $x_{max.,obs.}$.

For the triethylamine with methyl iodide reaction, good agreement was reached at $z = 2$, and for the DTTT with methyl iodide reaction, there was better agreement at $z = 0.8$ rather than at $z = 1$; the relevant values are indicated in parentheses.

Table 5. Constituents of transfer enthalpies for the different nucleophiles: solvent composition at maximum activation entropy, solvation number, and isokinetic temperatures in acetonitrile–methanol mixtures

Nucleophile[a]	Constituents of ΔH_t	$x_{\text{max.,obs.}}$	$x_{\text{max.,calc.}}$	z	β_{phys}/K
DMIT[16]	Phys				496
DTTT[16]	Phys + SI	0.3	0.17	1	400
			(0.24)	(0.8)	(700)
Pyridine	Phys + SI		1.03	1	393
Et_3N	Phys + SI	0.5	0.45	2	150

[a] DMIT, *NN'*-dimethylimidazolidine-2-thione; DTTT, 2,3-dihydro-1,2,5-trimethyl-1,2,4-triazole-3-thione.

For the pyridine with methyl iodide reaction the calculated value of the solvent composition, $x_{\text{max.,calc.}} = 1.03$ means that the maximum lies beyond the experimentally accessible range of solvent composition, $0 \leqslant x_1 \leqslant 1$. This feature is consistent with the fact that no maximum was observed for the reaction. However, if we also assume $z = 2$ for this reaction, equation (10) predicts the presence of a maximum at a solvent composition of $x_{\text{max.,calc.}} = 0.38$; this contradicts the experimental observation.

Since the three parameters, *i.e.*, z, ΔH_{se}, and K_{se}, could be determined separately, it is now possible to calculate the remaining two thermodynamic quantities, *i.e.*, $\Delta G_{\text{t,SI}}{}^{\text{AN}\rightarrow\text{mix}}$ and $\Delta S_{\text{t,SI}}{}^{\text{AN}\rightarrow\text{mix}}$, from equations (7) and (8).

The solvent effect on the activation entropy due to physical interaction, $\delta\Delta S_{\text{phys}}{}^{\ddagger}$, can be calculated from the relationship in equation (11), which was derived from the thermodynamic cycle;

$$\delta\Delta S^{\ddagger} = \delta\Delta S_{\text{phys}}{}^{\ddagger} - \Delta S_{\text{t,SI}}{}^{\text{AN}\rightarrow\text{mix}} \qquad (11)$$

the same situation holds for $\delta\Delta G_{\text{phys}}{}^{\ddagger}$. Thus, the activation enthalpy *versus* activation entropy correlation can also be made using physical interaction terms. These are indicated in Figures 1 and 2 as filled circles. Except for the values in pure methanol, where other contributions such as those due to the ordered structure of the solvent could be involved, correlations for both reactions are reasonable and show the same pattern of behaviour. In contrast, the original correlations for the two reactions show different patterns. Isokinetic temperatures deduced above, β_{phys}, are in reasonable agreement with those derived from $\delta\Delta H_{\text{phys}}{}^{\ddagger}$ *versus* $\delta\Delta G_{\text{phys}}{}^{\ddagger}$ plots by Krug's procedure,[18] and the average values are summarized in Table 5.

It is noteworthy that the isokinetic temperatures of two reactions, *i.e.*, pyridine with methyl iodide and DMIT with methyl iodide, lie above room temperature, whilst that of triethylamine with methyl iodide lies below it. Structural factors, *i.e.*, whether the developing positive charge during the reaction is exposed to solvent or not, might be the reason for this difference. This difference in the isokinetic temperature seems to have some direct effect on $\Delta V^{\ddagger}$ *versus* ΔV° correlations, as will be discussed in future work.

Cox and Waghorne originally proposed that the presence of minima in transfer entropy *versus* solvent composition profiles is direct evidence for the preferential solvation of a solute in a mixed solvent.[19] This proposal is supported for one particular model in the present work. Furthermore, the absence of minima in the profile does not indicate that a specific interaction between the solute and one component of the solvent mixtures does not have any contribution to the transfer entropies. The present work provides a method of evaluating the transfer Gibbs energy and transfer entropy due to specific interactions, even in a case where an extreme value is not observed in the transfer entropy *versus* solvent composition profile.

Abraham and Nasehzadeh have developed an empirical method for evaluating the standard entropy of specific triethylamine–solvent interactions.[14] The combination of these values leads to the entropy change due to specific interaction for transferring triethylamine from acetonitrile to methanol, −21 J K^{-1} mol^{-1}.[14] The substitution of the three parameters, *i.e.*, z, ΔH_{se}, and K_{se}, into equation (8), after setting x_1 equal to unity, leads to −31.3 J K^{-1} mol^{-1} for this entropy change. Both methods indicate that a specific interaction plays a significant role in the overall entropy change of transfer, −40 J K^{-1} mol^{-1}.[14]

In systems that involve protic solvent–base and protic solvent–nucleophile pairs, thermodynamic quantities due to a specific interaction occupies a significant part in the overall quantities. Sometimes the effects are prohibitingly large to allow the characteristic features of an activated complex to be interpreted from conventionally treated empirical energy correlations. The possibilities are suggested above in various examples.

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