

THERMOCHEMICAL STUDIES IN NON-AQUEOUS SOLVENTS*

RAM CHAND PAUL** *and* KULDIP SINGH DHINDSA***

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Thermochemical studies on the solutions of Lewis and protonic acids and organic tertiary bases have been carried out in formamide, acetone, n-butanol, n-hexane and solvent mixtures n-hexane-ethyl acetate with a view to understanding the nature of these solutions. Heats of solution have been determined at varying concentrations of the solutes and the factors affecting the enthalpy values discussed. Orders of strength of various Lewis and protonic acids as also of bases have been proposed. In the case of polar solvents, the neutralisation enthalpies have been considered to be mainly due to the combination of anions and cations characteristic of the solvent. In spite of different modes of reaction of Lewis and protonic acids in these solvents, the neutralisation enthalpies have been found to be very much comparable. Heats of neutralisation in n-hexane, a non-polar solvent, are much higher as compared to those in polar solvents suggesting thereby that in this solvent, the heat change corresponds to the direct combination of acids and bases. Studies in solvent mixtures of n-hexane-ethyl acetate indicate that n-hexane plays a significant role in desolvation of the acids from the polar constituent of mixtures.

Keywords : Thermochemical Studies; Non-aqueous Solvents

INTRODUCTION

WATER, because of its unique solvent properties, convenient working range, plentiful occurrence in nature, unusual dissolving power and ease of handling and purification, has hindered the development of chemistry in non-aqueous solvents. However, reactions of the compounds which are susceptible to hydrolytic attack can be studied only in non-aqueous solvents. More so, the inability of water to dissolve certain substances together with the need to get those in solution creates an interest in these solvents. For any fundamental understanding of the chemistry of these systems, data on solute-solvent interactions are needed. Acid-base neutralisation reactions and solvation studies have been mainly carried out with the help of conductometric, potentiometric, electrochemical and spectroscopic techniques and visual indicators. However, thermochemical investigations in these solvents have been scanty which may be due to one or more of the following reasons :

1. Most of the non-aqueous solvents are hygroscopic and readily absorb moisture even from atmosphere which, if not adequately avoided, can cause errors in the results.

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**Panjab University, Chandigarh, India.

***Central Quality Testing Laboratory, Haryana Agricultural University, Hissar, India.

2. Solubility of most of the substances in non-aqueous solvents is lower than that in water and the solubility data are not readily available.
3. Non-aqueous solvents which are low boiling are not the suitable media for such studies as their evaporation may cause errors.

Thermochemical measurements attracted attention as a result of suggestions by Pauling and Yost (1932) that heat of formation of a compound from its constituent atoms could be regarded as a fairly reliable measure of the strength of bonds. Differences in heats of reaction were made use of in interpreting relative strength of bonds.

For the present studies, different solvents covering a wide range of physical properties were selected. The solvents studied alongwith their physical constants are given in Table I. Heats of solution of acids and bases and their heats of neutralisation with organic tertiary bases have been determined in formamide, acetone, n-butanol, n-hexane and solvent mixtures of n-hexane-ethyl acetate with a view to studying the nature of solute-solvent interactions as also the role of solvent in these reactions.

TABLE I
Physical constants of the solvents studied

Solvent	B.P. °C	Density g/ml	Viscosity c.p.	Heat of vaporisation kcal/mole	Dielectric constant	Dipole moment (D)
Formamide	210.70 (dec)	1.3339	3.359	—	109.50	3.68
Acetone	56.24	0.78508	0.2954	—	29.70	2.72
n-Butanol	117.72	0.8021	2.271	11.081	17.10	1.68
Ethyl acetate	77.15	0.8946	1.088	—	6.40	1.84
n-Hexane	68.74	0.6548	0.2923	7.54	1.89	0.08

EXPERIMENTAL

Materials used in the present investigations were prepared/purified as reported earlier (Dhindsa, 1971). Thermochemical determinations were carried out in an isothermal phase change calorimeter designed after Dainton *et al.* (1957), using diphenyl ether (m.p. 26.9°) as dilatometric fluid. The details of the construction of calorimeter, its working and methods for determining the heat of solution and heat of neutralisation have already been described (Paul *et al.*, 1967) (see Fig. 1.).

RESULTS AND DISCUSSION

With the objectives outlined under Introduction, the discussion has been divided into three parts. Work done in formamide has been discussed in detail whereas a comparative study has been presented in other solvents as well as solvent mixtures.

Thermochemical Studies in Formamide

Heat of Solution : Table II records heats of solutions of various Lewis acids in formamide. Antimony(V) chloride dissolves in formamide in an exothermic reac-

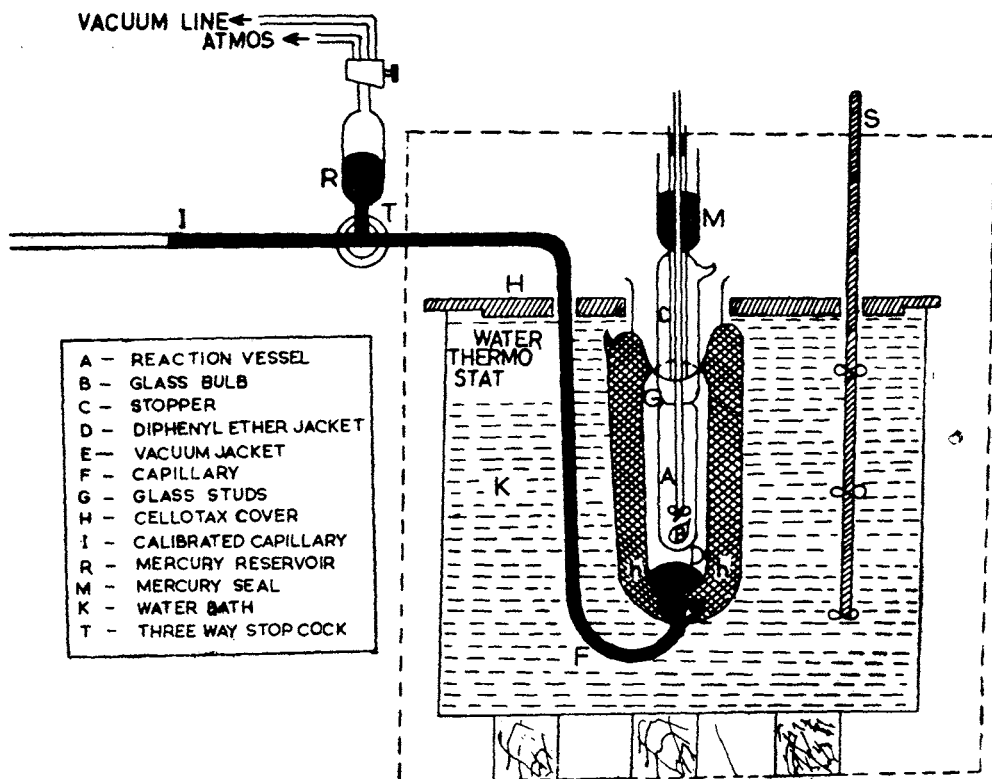


FIG. 1. Diagram of the calorimeter used.

tion, giving a light yellow solution. Its heat of solution in the concentration range $7.6\text{--}23.6 \times 10^{-3}$ moles/litre has been found to vary between 38.6–40.3 kcal/mole. Antimony(V) chloride has been reported to form a disolvate with formamide (Vaidya, 1967). However, it has been suggested that only one molecule of the solvent is directly attached to the Lewis acid and the second molecule is held by hydrogen bonding. This observation also finds support from a comparison of the heats of solution of the acid in formamide and dimethylformamide. Antimony(V) chloride, which is known to form 1 : 1 adduct with dimethylformamide, dissolves in it with the evolution of 43.3–44.1 kcal/mole (Paul *et al.*, 1965a). This value compares favourably with the heat of solution in formamide, on assuming 1:1 adduct formation. The overall enthalpy change may be attributed to the following reactions taking place in solution :

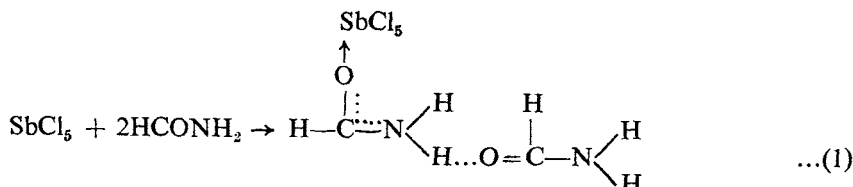
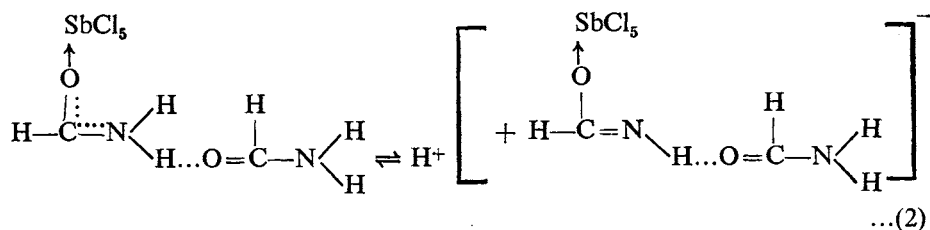


TABLE II

Heats of solution of Lewis acids in formamide at varying concentrations of the solutes

Acid (mole/litre) $\times 10^3$	$-\Delta H$ kcal/mole	Acid (mole/litre) $\times 10^3$	$-\Delta H$ kcal/mole
	SbCl₅		ZrCl₄
7.6	40.3	4.4	30.4
11.2	39.5	6.8	30.2
15.6	39.3	9.2	29.7
19.2	38.7	11.2	30.3
23.6	38.6		
	SnCl₄		SnBr₄
10.8	32.2	6.4	21.8
13.6	32.1	9.6	21.4
18.0	31.7	13.2	21.7
21.6	31.9	18.8	21.3
25.2	31.5	20.4	21.1
	TiCl₄		SnI₄
		5.2	18.1
13.6	38.5	7.2	17.9
16.8	37.3	9.6	17.9
22.0	35.9	10.0	18.1
30.0	34.9	11.6	17.7
	SbCl₃		
9.2	8.9		
12.8	8.6		
17.2	8.7		
22.0	8.4		
25.6	8.4		

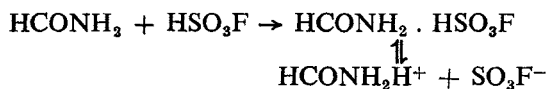


As the adduct indicated in eqn. (1) remains in solution, the net enthalpy change may arise due to the formation of (1) the solvate, (2) its ionisation and (3) solvation of the ions produced. The first step involves bond formation between oxygen and antimony and is highly exothermic. The second step involves the ionisation of the solvate and is endothermic. The solvation of the ions is again exothermic. In addition, some heat is also absorbed in breaking the hydrogen bonding in the solvent. It is,

TABLE III

Heats of solution of various protonic acids in formamide at different acid concentrations

Acid (mole/litre) $\times 10^3$	$-\Delta H$ kcal/mole	Acid (mole/litre) $\times 10^3$	$-\Delta H$ kcal/mole
HSO ₃ F		CH ₂ ClCOOH	
16.0	27.6	21.2	1.5
24.8	27.6	36.0	1.5
28.8	27.2	43.6	1.4
32.8	27.2	57.6	1.5
48.8	27.2	60.4	1.5
CCl ₃ COOH		CH ₃ COOH	
9.6	3.2	42.0	0.9
18.8	3.1	56.4	0.9
23.6	3.1	70.4	0.9
28.0	2.9	82.8	0.9
37.2	2.7	119.2	0.9
CHCl ₂ COOH		HCOOH	
20.4	2.3	40.0	1.9
27.2	2.3	60.8	1.8
36.0	2.1	80.0	1.9
43.2	2.1	122.4	1.9
50.0	2.1	182.4	1.8



The heat of solution of fluorosulphuric acid in formamide, thus, is the net result of solvate formation, ionisation of the solvate in excess of the solvent and subsequent solvation of the proton. N.M.R. studies of amides in fluorosulphuric acid have indicated that the amides are protonated at carbonyl oxygen (Gillespie & Birchall, 1963).

Fluorosulphuric acid is a very strong acid and its ionisation has been proposed as :

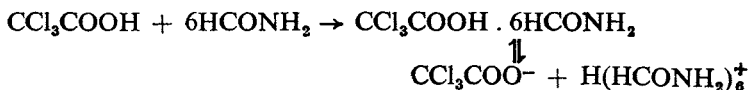


Since formamide is basic in nature, the solvated proton in the cation HSO_3FH^+ is likely to be exchanged with formamide. The enthalpy change on dissolution may therefore, represent the difference in the energy of desolvation of the proton from the acid and its solvation by formamide molecule. The reaction may be written as :



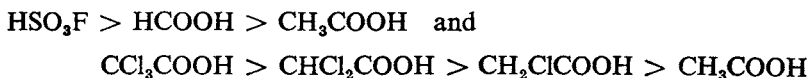
Trichloroacetic acid is freely miscible with formamide and its solution at different concentrations are fairly stable and ionic. Its heat of solution has been found to

be 2.7–3.2 kcal/mole and the values decrease slightly with increasing concentrations of the acid. The plots of specific conductance versus acid/formamide molar ratio show the formation of solvates with the composition 1:1, 1:2 and 1:6 (Paul & Vaidya, 1968). Since the heat of solution has been measured at relatively low concentrations, formation of the solvate with molar ratio 1:6 is more likely. Heat of solution of the acid may be due to following reactions :



Formamide has an association factor of six and it is likely, therefore, that an associated solvent cluster gets attached as a unit. The internal structure of the solvent is, therefore, not likely to affect the heat of solution in this case.

Dichloroacetic, monochloroacetic, acetic and formic acids are weak acids and behave in the same way as trichloroacetic acid. The molar heats of solution of the acids given in Table III indicate that the acids may be arranged in the following orders of decreasing strengths :



A comparison of the strengths of Lewis and protonic acids is not possible due to differences in the nature of the reactions involved. The heat of solution of Lewis acids is primarily due to solvate formation resulting in oxygen-metal bond whereas in protonic acids, it is due to the protonation of the solvent.

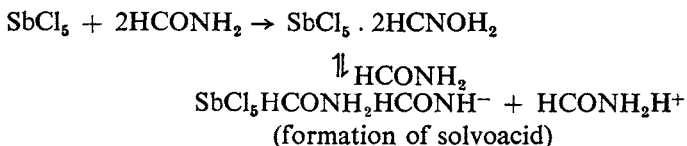
The solutions of organic tertiary bases (B) have been proposed to ionise as (Vaidya, 1967) :



Heats of solution of the bases could not be accurately measured due to very small enthalpy changes which is quite expected in view of the basic nature of the solvent.

Heat of Neutralisation : Heats of neutralisation of triethylamine, α -picoline, pyridine and dimethylaniline against excess of antimony(V), tin(IV) and titanium(IV) chlorides have been measured in formamide and given in Table IV.

Neutralisation of the solutions of the bases with the solution of antimony(V) chloride in formamide results in the evolution of 11.0–14.5 kcal/mole. Since antimony(V) chloride acts as a monobasic acid, the heat of neutralisation may be due to the formation of solvoacid, formation of solvobase and the neutralisation reaction :



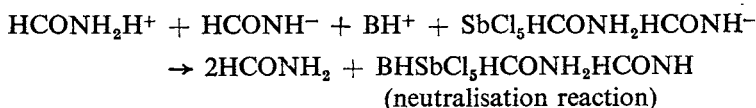
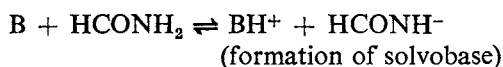


TABLE IV

Heats of neutralisation of Lewis acids with organic tertiary bases in formamide

Base	Moles of acid/mole of base. (Range)	$-\Delta H$ kcal/mole*
<i>Antimony(V) Chloride</i>		
Triethylamine	2.5-4.5	14.5
α -picoline	2.7-4.5	12.9
Pyridine	2.3-3.7	12.1
Dimethylaniline	2.2-4.1	11.0
<i>Tin(IV) Chloride</i>		
Triethylamine	2.3-4.8	14.1
α -picoline	2.4-4.3	11.2
Pyridine	2.1-3.9	12.5
Dimethylaniline	2.2-3.9	9.4
<i>Titanium(IV) Chloride</i>		
Triethylamine	2.2-3.7	14.5
Pyridine	2.5-4.3	14.3**
Dimethylaniline	1.9-4.1	9.0

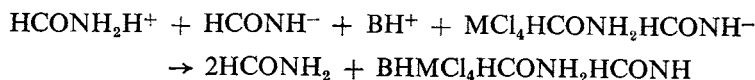
*The values are average of 4-5 experiments.

**A thick yellow precipitate separated out.

Heats of reaction of titanium(IV) chloride with triethylamine, pyridine and dimethylaniline in formamide have been found to be 14.5, 14.3 and 9.0 kcal/mole of the base neutralised. Relatively higher value for enthalpy of neutralisation in the case of pyridine may be due to the formation of a solid salt which separated out during the reaction. Thus the overall heat change includes the heat of precipitation also.

Since the Lewis acids were taken in excess in these measurements, they are expected to behave as monobasic acids. It has been observed that an increase in the amount of the acid from 1.9 to 4.8 moles/mole of the base, had no effect on the enthalpy values.

The neutralisation reaction in case of tin(IV)⁻ and titanium(IV)⁻ chloride may be written as :

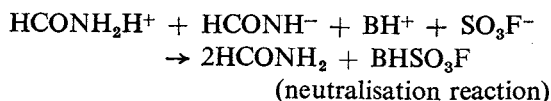
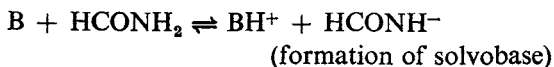
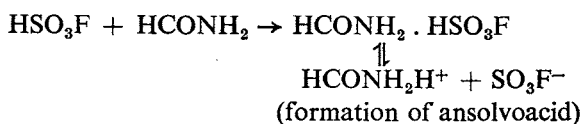


Heats of neutralisation of triethylamine, α -picoline, pyridine and dimethylaniline with excess of fluorosulphuric, trichloroacetic and formic acids have been measured in formamide and recorded in Table V.

TABLE V
Heats of neutralisation of protonic acids with organic tertiary bases in formamide

Base	Moles of acid/mole of base (Range)	$-\Delta H$ kcal/mole
<i>HSO₃F</i>		
Triethylamine	2.3-3.0	11.4
α -picoline	2.1-3.0	7.7
Pyridine	2.2-4.0	6.4
Dimethylaniline	2.2-3.6	6.3
<i>CCl₃COOH</i>		
Triethylamine	2.1-4.2	6.2
α -picoline	2.5-4.4	5.1
Pyridine	2.1-4.4	3.5
Dimethylaniline	2.4-3.9	3.5
<i>HCOOH</i>		
Triethylamine	2.0-4.5	8.3
α -picoline	2.2-4.2	4.8
Pyridine	1.9-3.4	3.2
Dimethylaniline	2.0-5.1	3.5

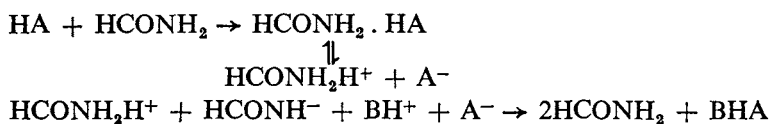
Neutralisation of the solutions of the bases with solution of fluorosulphuric acid in formamide medium results in the evolution of 6.3-11.4 kcal/mole. The neutralisation may be represented by the following reactions :



Since the neutralisation product remained in solution, the enthalpy change is mainly due to the following reaction which results in the formation of feebly ionised solvent molecules :

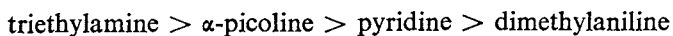


Heats of reaction of the bases with trichloroacetic and formic acids have been found to be relatively low and vary in the range 3.2–8.3 kcal/mole. The neutralisation reaction may be written as :



Since these are weak acids and do not protonate the solvent to the same extent as does fluorosulphuric acid, some heat is absorbed when the unreacted acid ionises as the reaction proceeds in the forward direction, thus absorbing heat of ionisation which consequently results in low heat of neutralisation.

On the basis of heats of neutralisation of different bases with any one acid, these may be arranged in the following order of decreasing donor strength :



The values of the heat of neutralisation clearly indicate that neutralisation essentially involves the combination of the solvoacids and the solvobases and is not a simple acid-base reaction as in carbon tetrachloride or n-hexane where the solvent acts only as diluent and the enthalpy values vary between 30 to 45 kcal/mole (Paul *et al.*, 1964*b*, 1973). As the bases have been taken in solution and the neutralisation products remain completely dissociated, it may be suggested that heats of neutralisation are mainly due to the formation of feebly ionised formamide molecules from its ions. The results discussed above support the auto-ionisation of the solvent as :



Comparative Study

It has been considered appropriate to make a comparative study of the work carried out in various solvents and correlate it with similar data reported in literature. Table VI records the heats of solution of antimony(V) chloride and tin(IV) chloride in various solvents. A perusal of the table reveals that the values vary appreciably from one solvent to another. It has been suggested that the heat change is mainly due to the formation of a donor-acceptor complex between oxygen of the solvent and the metal atom in the Lewis acids. The variations in the heats of solution may be due to the differences in basicity of the solvent and steric and inductive effects. Ionising and solvating power of the medium and its internal structure also effect heat of solution. Reorganisation energies of the Lewis acids when their hybrid state changes on complex formation also effect the enthalpy change.

Since in the bonding of donor-acceptor molecules, electron transfer is of primary importance, ionisation potential of the donor and electron affinity of the metal atom in the Lewis acid can considerably influence the strength of oxygen-metal bond. As electron affinity is likely to remain the same for a given acceptor,

TABLE VI
Heats of solution of SbCl₅ and SnCl₄ in different solvents

Solvent	Heat of solution ($-\Delta H$ kcal/mole) of		
	SbCl ₅	SnCl ₄	Reference
Formamide	38.6-40.3	31.5-32.2	
Acetone	30.4-38.2	25.9-36.1	
n-Butanol	33.9	30.6	
Dimethylformamide	43.3-44.1	41.1-41.7	(Paul <i>et al.</i> , 1965a)
Ethyl acetate	37.1-38.4	30.0-32.1	(Paul <i>et al.</i> , 1969a)
Acetic acid	20.5-37.7	11.0-26.4	(Ahluwalia, 1966)

its heat of reaction with different solvents may give quantitative information about the charge density of the donor. The donor strength of the solvents employed in the present study may thus decrease in the order :



Protonic acids act as ansolvoacids in polar solvents and behave in a different way than the Lewis acids. Heat of solution of fluorosulphuric acid in various solvents has been presented in Table VII. As discussed earlier, the heat of solution of fluorosulphuric acid is due to solvate formation, ionisation of the solvate and subsequent solvation of the ions produced. However, strong protonic acids exhibit high degree of auto-ionisation and the proton is solvated by the acid itself. On addition of the acid to the solvent, the protonated acid donates its proton to the solvent. Heat of solution of the acid may, therefore, be considered to be due to the desolvation of the proton from the acid and its solvation by the solvent. The proton accepting power of these solvents decreases in the order :



These solvents protonate the bases and a comparison of the heats of solution of α -picoline and pyridine reveals that the protonating capacity falls rapidly from the acidic to the basic solvent as is evident from Table VIII.

The order of the relative acid character of the solvents remains unchanged.

Heat of neutralisation of a strong acid and a strong base in water always results in the release of nearly the same amount of heat if the reactants and the products remain completely soluble and ionised. It has been suggested that the heat of reaction is due to the combination of H⁺ and OH⁻ ions. By analogy, it has been assumed that for all neutralisation reactions in polar solvents, the enthalpy values are determined by their mode of ionisation. The strength of an acid or base depends upon its ability to promote the ionisation of the solvent or conversely, it is the ability of the solvent to form solvates with the reacting species and induce ionisation of the adducts. It is interesting to note that for a given solvent, heats of neutralisation of the bases with both the Lewis and protonic acids are nearly the same in all the cases as is evident from Table IX.

TABLE VII

Heat of solution of fluorosulphuric acid in different solvents

<i>Solvent</i>	Heat of solution of HSO_3F ($-\Delta H$ kcal/mole)	Reference
Formamide	27.4	
Acetone	20.6-26.9	
n-Butanol	25.0	
Methanol	24.8-25.6	(Paul <i>et al.</i> , 1968 <i>b</i>)
Ethanol	29.7-31.3	(Ahluwalia, 1966)
Dimethyl formamide	31.8	(Paul <i>et al.</i> , 1965 <i>b</i>)
Ethyl acetate	23.3-24.3	(Paul <i>et al.</i> , 1969 <i>b</i>)
Acetic acid	24.3-25.1	(Ahluwalia, 1966)

TABLE VIII

Heats of solution of α -picoline and pyridine in different solvents

<i>Solvent</i>	Heat of solution ($-\Delta H$ kcal/mole) of			Reference
	α -picoline	pyridine		
Acetic acid	8.2	7.0		(Ahluwalia, 1966)
Methanol	1.5	0.9		(Paul <i>et al.</i> , 1968 <i>b</i>)
Ethanol	1.1	0.8		(Ahluwalia, 1966)
n-Butanol	0.8	no heat		
Acetone	0.2	—		
Formamide	no heat	no heat		

TABLE IX

Heats of neutralisation of α -picoline with SnCl_4 and HSO_3F in different solvents

<i>Solvent</i>	Heat of neutralisation ($-\Delta H$ kcal/mole) of α -picoline with		Reference
	SnCl_4	HSO_3F	
Formamide	11.2	7.7	
Acetone	10.8	11.3	
n-Butanol	7.4	8.4	
Dimethyl formamide	4.2	7.2	(Paul <i>et al.</i> , 1965 <i>a, b</i>)
Ethyl acetate	19.9	19.3	(Paul <i>et al.</i> , 1969 <i>a, b</i>)
n-hexane	33.5	29.3	

The suggestion that both the Lewis and protonic acids induce same type of ionisation in the solvent is, therefore, supported. The values for heat of neutralisation are much higher in n-hexane as compared to those in polar solvents indicating a

different mode of neutralisation reactions in this solvent. It has been proposed that in n-hexane, an inert solvent, acids and bases combine directly to give neutralisation products which are generally solid and the solvent plays no role other than acting as a diluent. In polar solvents acids & bases behave as solvo acids and solvobase whereas in n-hexane these are free to exercise intrinsic strengths.

Solvent Mixtures

Mixing of solvents has often been used to modify the acidic or basic properties of the solvents. Thermochemical studies in non-polar solvent mixtures are of interest as by mixing the solvents in different proportions it is possible to get a medium of desired dielectric constant and sometimes hydrogen bonding and solubility characteristics can also be altered (Laitinen 1960; and Padova, 1968). In the present work, heats of solution of Lewis and protonic acids and their heats of neutralisation with organic bases have been determined in n-hexane-ethyl acetate mixtures at different compositions with a view to understanding the nature of these solutions. Table X records heats of solution of some acids in n-hexane-ethyl acetate mixtures.

TABLE X

Heats of solution of Lewis and protonic acids in n-hexane-ethyl acetate mixtures

Volume % of n-hexane	Heat of solution ($-\Delta H$ kcal/mole) of				
	SnCl ₄	TiCl ₄	SnBr ₄	HSO ₃ F	H ₂ SO ₄
0*	31.1	27.9	12.5-14.4	23.8	10.2
20	28.7	26.1	7.4 - 9.2	19.4	7.1
50	20.0**	19.4**	4.5 - 6.4	9.5	5.4
100	†	†	†	††	††

*Data from Paul *et al.* (1969a, b).

**Precipitation occurs.

†Heat of change is practically immeasurable and falls within experimental error.

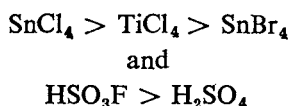
††Immiscible.

A perusal of Table X reveals that the values of the heat of solution are highest in pure ethyl acetate and show a marked decrease as the amount of n-hexane is increased. Heats of transfer from ethyl acetate to 20 per cent n-hexane-ethyl acetate mixture show a positive variation for all the acids. A further decrease in the values occurs in 50 per cent n-hexane-ethyl acetate mixture.

Basicity of the medium relative to ethyl acetate decreases on addition of n-hexane. Since heats of solution are mainly due to the reaction between ethyl acetate and acids, these are therefore, expected to decrease in the mixtures. Addition of n-hexane to ethyl acetate also results in lowering of the dielectric constant, thereby decreasing the solubility and hence the ionisation of the solvate leading to decrease in heats of solution. However, such a lowering in dielectric constant is

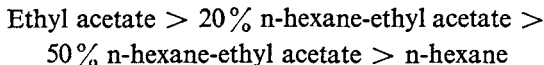
expected to be small and, therefore, may not account for large differences in heat of solution values obtained in present study. In spite of the fact that the bulk properties of the mixtures are mainly determined by the polar constituent, as n-hexane plays no part in the chemical reaction, the short range ion-dipole interactions are considerably reduced which affect the heats of solvation, resulting in lowering the heats of solution.

The extent of ion-pair formation increases as the concentration of n-hexane is increased in the mixture. This is evident from the heats of solution of tin(IV) and titanium(IV) chlorides in the 50 : 50 mixture where solid addition compounds of the Lewis acids with ethyl acetate separate out. The heats of solution in these cases also include heats of precipitation of adducts. The reactions responsible for the heats of solution in the mixtures are the same as reported in ethyl acetate (Paul *et al.*, 1969*a,b*). On the basis of heats of solution, the acids studied may be given the following orders of decreasing acid strengths :



which are the same as reported in ethyl acetate by Paul *et al.* (1969*a, b*).

From the heat of solution of a particular acid in the pure and mixed solvents, the following order of decreasing base strength of the solvents emerges :



Heats of neutralisation of organic tertiary bases like α -picoline, pyridine and dimethylaniline with tin(IV) and titanium(IV) chlorides, and fluorosulphuric and sulphuric acids have been measured in 20 volume per cent of n-hexane in ethyl acetate and recorded in Table XI alongwith the heat of neutralisation values of these acid-base pairs in the constituents of the mixture for comparison.

It is evident from the table that the heats of neutralisation increase from pure ethyl acetate to pure n-hexane. It has already been stated that the mode of the neutralisation reaction is considerably altered by the nature of the solvents. In polar solvents, the enthalpy changes are due to the reaction between solvoacids and solvobases, whereas in non-polar solvents the acids and bases combine directly. Large difference in the heats of neutralisation in the two solvents are thus expected. In the 20 per cent n-hexane-ethyl acetate mixture, although the mode of reaction is the same as in pure ethyl acetate (Paul *et al.*, 1969*a, b*), the increase in the heats of neutralisation may be due to the relative ease with which the acids and the bases can react, being less solvated in mixture than in pure ethyl acetate. Pifer and coworkers (1953) have reported striking changes in the sensitivity of reactions on addition of solvents with low dielectric constants. Wooten and Hammett (1935) have also reported that a change in solvent resulting in a decrease in dielectric constant of the medium should result in a change in relative strength, the direction of which is determined by the influence of the solvent on the ionisation of the acid.

TABLE XI

Heats of neutralisation of Lewis and protonic acids with bases in n-hexane-ethyl acetate mixtures

Volume % of n-hexane	Base	Heat of neutralisation ($-\Delta H$ kcal/mole) of the base with			
		SnCl ₄	TiCl ₄	HSO ₃ F	H ₂ SO ₄
0*	α -picoline	19.9	15.9	19.3	16.6
	pyridine	11.9	14.0	14.7	15.1
	dimethylaniline	14.5	10.7	13.8	—
20	α -picoline	23.4	23.2	21.9	20.7
	pyridine	19.2	18.5	22.7	16.3
	dimethylaniline	19.2	19.7	18.9	16.1
100	α -picoline	33.5	39.1	29.3**	25.8**
	pyridine	30.2	32.5	28.2**	23.5**
	dimethylaniline	27.1	28.9	26.9**	20.2**

Precipitation occurs in almost all the cases.

*Values from Paul *et al.* (1969a, b).

**Values reported are per mole of the acid.

It is clear from the above discussion that whereas there is a lowering in heats of solution of the acids with the addition of n-hexane to ethyl acetate, the heats of neutralisation show an increase which indicates that n-hexane plays a significant role in desolvation of the acids from the polar constituent of the mixtures.

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