The RRS and fluorescence emission spectra of DABS-ASP and HDABS-ASP in solution were simultaneously observed at intervals of pH from 6.5 to 0.7. When HDABS-ASP was adsorbed on colloidal silver, its surface-enhanced RRS and fluorescence emission spectra were observed. Both its combined RRS-SERS spectrum in the region of large overlap between absorption spectra of dye and colloidal silver and its SERS-only spectrum in a region where the dye did not absorb strongly were obtained.

Absolute enhancements of RRS and fluorescence emission band intensities of HDABS-ASP on colloidal silver were obtained. Dependence of the surface enhancement of RRS and fluorescence emission varied nearly linearly with total silver concentration for HDABS-ASP on colloidal silver at pH \sim 4.5 and reached maximum values at 320 and 21, respectively. Surface enhancement of RRS and fluorescence band intensity reached a plateau near 0.20 and 0.30 g/L of silver for DABS-ASP on colloidal silver at pH \sim 6.0 with values of 66 and 4, respectively.

Absorption spectra of silver sols with adsorbed dye showed an intense band maximum at 400 nm and a very weak shoulder near 500 nm at pH 6.0. Spectra at pH 4.5 showed the 400-nm band and a distinct lower energy band between 450 and 550 nm. The lower-energy absorption band was assigned to small clusters or aggregates of silver particles.

The peak positions in SERRS excitation profiles for DABS-ASP or HDABS-ASP on colloidal silver matched the peaks in absorption band intensity for the aggregated silver particles.

The relative contributions of RRS and SERS to the SERRS enhancement of Raman bands of the dye on colloidal silver at any excitation wavelength could be distinguished by comparing the ratios of Raman band intensity in spectra taken in the blue (strong overlap of RRS-SERS) and red (SERS-only) regions, respectively.

The positions of fluorescence emission band maxima of HDABS-ASP with increasing silver concentration did not change. Single excitation profile peaks of DABS-ASP and HDABS-ASP on colloidal silver at 490 and 540 nm, respectively, showed that absorption bands of colloidal silver near 500 and 540 nm overlapped well with excitation profile peaks of the dyes, alone, in solution at 472, 510, and 505 nm. Little perturbation of the electronic levels of the adsorbed dye molecules from those of the dyes in solution was observed.

Acknowledgment. This work was supported in part by NIH Grant GM-30904, by NSF Grant CHE-801144, and by Army Research Office Grant DAAG-29-82-K-0062. We thank Professor M. Kerker for reading the manuscript and helpful discussions.

Registry No. DABS-ASP, 87667-33-2; Ag, 7440-22-4.

Hydrogen-Bonded Species of Pyridinium Halogenoacetates. 2. Thermometric Behavior in Aprotic Solvents

B. Chawla* and S. K. Mehta

Department of Chemistry, Indian Institute of Technology, New Delhi 110016, India (Received: July 7, 1983; In Final Form: November 8, 1983)

The enthalpies of reaction of a series of substituted pyridines and of triethylamine, quinoline, and isoquinoline (for the sake of comparison) with trifluoroacetic acid (TFA) in chloroform were measured at 25 °C at final solution concentrations ranging from 1×10^{-2} to 5×10^{-2} M. The enthalpies of reaction of 2,4,6-trimethylpyridine, pyridine, and 4-cyanopyridine with trichloroacetic acid (TCA), dichloroacetic acid (DCA), monochloroacetic acid (MCA), and acetic acid (AcOH) in chloroform were also measured at 25 °C. The concentration dependence of enthalpies of reaction was examined by measuring them for 2,4,6-trimethylpyridine-TFA, pyridine-TFA, and 4-cyanopyridine-TFA in chloroform over the entire possible solution concentration range at 25 °C. In order to study the energetic behavior of H-bonded species of the pyridine-TFA system in media of different dielectric constants, the enthalpy measurements were made in p-dioxane, o-xylene, and carbon tetrachloride. The thermometric results have been discussed in terms of interactions present in the H-bonded species of these systems in nonaqueous solutions.

Introduction

Even though thermometric titration is a powerful tool for acid-base study,¹⁻⁴ only a few thermometric titrations of amines in nonaqueous media⁵⁻⁹ have been carried out. The only deliberate study of ion pairs by this method available in the literature is that of Goldshtein et al.¹⁰ The recent study of Arnett and Chawla¹¹ on the thermometric titration of a series of substituted pyridines with trifluoroacetic acid (TFA) in carbon tetrachloride is of direct relevance to the investigations presented in this paper. In their study, they have reported the enthalpies of reaction of pyridines with TFA at stoichiometries corresponding to formation of the 1:1 ($B^+H^--A^-$) complex, the 1:2 (B^+H^--AHA) complex, and the 2:1 ($B^+H^--BA^-$) complex.

In continuation of our systematic study on the hydrogen-bonded salts of a series of substituted pyridines and halogenoacetic acids in various nonaqueous solvents¹² (chloroform in particular), the enthalpies of reaction $(B + HA \rightarrow B^+H^- - A^-)$ for these systems

at stoichiometries corresponding to the formation of the 1:1 $(B^+H^--A^-)$ complex have been measured at 25 °C. the enthalpies of three of these systems over a wide range of final solution concentration have also been measured in order to study the effect of concentration on the behavior of hydrogen-bonded species present in solution. In order to study the effect of solvent on the

- (10) Goldshtein, I. P.; Guryanova, E. N.; Prepelkova, T. I. Zh. Obshch.
- Khim. 1972, 42, 2091. (11) Arnett, E. M.; Chawla, B. J. Am. Chem. Soc. 1978, 100, 217.
 - (12) Mehta, S. K.; Chawla, B. Electrochim. Acta 1982, 27, 9.

^{*} Address correspondence to this author at the Department of Chemistry, Duke University, Durham, NC 27706.

⁽¹⁾ Gyenes, I. "Titration in Nonaqueous Media"; Cohen, D., Millar, I. T., Eds.; Van Nostrand: Princeton, NJ, 1968.

⁽²⁾ Huber, W. "Titrations in Nonaqueous Solvents", translated by Express Translations Service, London; Academic Press: New York, 1968

⁽³⁾ Kucharsky, J.; Sajarik, L. "Titrations in Nonaqueous Solvents",

⁽³⁾ Kucharsky, J.; Sajarik, L. "Titrations in Nonaqueous Solvents, translated by K. Sumbera; Elsevier: Amsterdam, 1965.
(4) Fritz, J. S. "Acid-Base Titrations in Nonaqueous Solvents"; Allyn and Bacon: Boston, MA, 1973 and the references cited therein.
(5) Forman, E. J.; Hume, D. N. J. Phys. Chem. 1959, 63, 1949.
(6) Forman, E. J.; Hume, D. N. Talenta 1964, 11, 129.
(7) Keily, J.; Hume, D. N. Anal. Chem. 1956, 28, 1294.
(8) Keily, J.; Hume, D. N. Anal. Chem. 1956, 28, 1294.
(9) Mead, T. E. J. Phys. Chem. 1962, 66, 2149.
(10) Goldshtein J. P.; Guyranova, E. N. Prenelkova, T. J. Zh. Obshch.

TABLE I: Enthalpies of Reaction of Substituted Pyridines and Some Other Nitrogen-Containing Bases with Trifluoroacetic Acid in Chloroform and Their Aqueous pK_a Values at 25 °C

	base	pK _a	$-\Delta H$, kcal mol ⁻¹			
1	triethylamine	10.71	21.46 ± 0.43			
2	2,4,6-trimethylpyridine	7.60	15.91 ± 0.11			
3	2,6-dimethylpyridine	6.81	14.52 ± 0.11			
4	3,5-dimethylpyridine	6.23	13.96 ± 0.10			
5	4-methylpyridine	6.00	13.86 ± 0.06			
6	4-tert-butylpyridine	5.97	13.81 ± 0.18			
7	3-methylpyridine	5.79	13.44 ± 0.14			
8	pyridine	5.27	12.00 ± 0.04			
9	isoquinoline	5.07	12.03 ± 0.16			
10	quinoline	4.80	11.89 ± 0.07			
11	3-chloropyridine	2.40	7.79 ± 0.17			
12	4-cyanopyridine	1.48	6.61 ± 0.07			
13	3-cyanopyridine	1.17	6.38 ± 0.07			
14	2-bromopyridine	0.9	5.61 ± 0.10			
15	3,5-dichloropyridine	0.6	5.22 ± 0.28			

behavior of H-bonded species of the pyridine-trifluoroacetic acid system, four solvents have been employed for the enthalpy measurements at 25 °C.

Experimental Section

The commercially available carbon tetrachloride, chloroform, p-dioxane, o-xylene, trifluoroacetic acid, trichloroacetic acid, dichloroacetic acid, monochloroacetic acid, acetic acid, 2,4,6trimethylpyridine, 2,6-dimethylpyridine, 3,5-dimethylpyridine, 4-methylpyridine, 3-methylpyridine, pyridine, triethylamine, quinoline, and isoquinoline were purified according to the standard established procedures^{13,14} before their use. 3,5-Dichloropyridine, 4-cyanopyridine, and 3-cyanopyridine were purified by sublimation. The high-purity samples of 4-*tert*-butylpyridine (Aldrich, England), 2-bromopyridine (Fluka, Switzerland), and 3-chloropyridine (Fluka, Switzerland) were used as such.

The water content of all the reagents was carefully checked before their use, with the automatic Karl Fischer titrator, Aquatest (IV) (Photovolt Corp. New York), and was found to be less than 0.003% in most cases. The reagents found wet were dried again over activated 4A molecular sieves for about 24 h.

Heats of reaction of substituted pyridines and some other bases (for the sake of comparison) with various halogenoacetic acids in aprotic solvents at 25 °C were measured with a Tronac 450 titration calorimeter described elsewhere.¹¹

The solutions of acids and bases in nonaqueous solvents were prepared under dry nitrogen environment.

The performance of the calorimeter was checked by a chemical calibration made by measuring the heat of protonation of an aqueous solution of THAM [tris(hydroxymethyl)aminomethane] with aqueous hydrochloride solution at 25 °C. The resulting ΔH value of 11.35 ± 0.05 kcal mol⁻¹ (from five measurements) agreed well with the accepted literature value of 11.33 kcal mol⁻¹. The value of 11.35 ± 0.04 kcal mol⁻¹ has also been reported very recently by Arnett and Chawla.¹¹

Results

The enthalpies of reaction, ΔH , of a series of substituted pyridines and of triethylamine, isoquinoline, and quinoline (for the sake of comparison) with trifluoroacetic acid (TFA) in chloroform were measured at 25 °C at low final solution concentrations ranging from 1×10^{-2} to 5×10^{-2} M.

The final enthalpy values were obtained by averaging the values of ΔH obtained from several measurements. Since the ΔH values were measured in very dilute solutions, the concentration effect, if any, was masked by the experimental error. The final ΔH values along with their standard deviations and aqueous pK_a 's of the bases are given in Table I.



Figure 1. Enthalpies of reaction of pyridines-halogenoacetic acids in chloroform vs. aqueous pK_a 's of pyridines.

The enthalpies of reaction of 2,4,6-trimethylpyridine, pyridine, and 4-cyanopyridine with trichloroacetic acid (TCA), dichloroacetic acid (DCA), monochloroacetic acid (MCA), and acetic acid (AcOH) in chloroform were also measured at 25 °C at low final solution concentrations and are given along with the aqueous pK_a values of the acids in Table II. The enthalpy values for these systems and for the systems presented in Table I are plotted in Figures 1 and 2.

The concentration dependence of enthalpies of reaction was examined by measuring them for 2,4,6-trimethylpyridine-TFA, pyridine-TFA, and 4-cyanopyridine-TFA in chloroform over the entire possible final solution concentration range at 25 °C. The enthalpy values for these systems are given in Table III.

The energetic behavior of H-bonded species of the pyridine-TFA system was also studied at low concentrations in different solvents at 25 °C. The solvents, other than chloroform ($\epsilon = 4.8$), used are the following: *p*-dioxane ($\epsilon = 2.2$), *o*-xylene ($\epsilon = 2.6$), and carbon tetrachloride ($\epsilon = 2.2$). *o*-Dichlorobenzene could not be used because of very low solubility of TFA in it. The ΔH values are given in Table IV.

Discussion

1. Energetics of Substituted Pyridines-Trifluoroacetic Acid in Their Dilute Chloroform Solutions. The enthalpy measurements were made at low solution concentrations in order to maintain the presence of mainly hydrogen-bonded ion pairs in systems where the proton transfer occurs as suggested by our recent conductance and ¹³C magnetic resonance studies^{12,15} and also by IR and NMR studies made by Dega-Szafram et al.^{16,17} Therefore, the results presented in Table I were examined in the

⁽¹³⁾ Perrin, D. D.; Armarego, W. L. E.; Perrin, D. R. "Purification of Chemicals"; Pergamon Press: London, 1966.

⁽¹⁴⁾ Riddick, J. A., Bunger, W. B., Eds. "Techniques of Organic Chemistry"; Wiley-Interscience: New York, 1970; Vol. 2.

⁽¹⁵⁾ Chawla, B.; Mehta, S. K. Spectrochim. Acta, Part A 1981, 37, 853.
(16) Dega-Szafran, Z.; Szafran, M. J. Chem. Soc., Perkin Trans 2 1982, 195.

⁽¹⁷⁾ Dega-Szafran, Z.; Dulewicz, E. J. Chem. Soc., Perkin Trans. 2 1983, 345.

TABLE II: Enthalpies of Reaction of Three Substituted Pyridines with Five Halogenoacetic Acids in Chloroform and the pK_a 's of Acids at 25 °C

	$-\Delta H$, kcal mol ⁻¹			
acid	pK _a	2,4,6-trimethylpyridine	pyridine	4-cyanopyridine
trifluoroacetic acid	0.2	15.91 ± 0.11	12.00 ± 0.04	6.62 ± 0.07
trichloroacetic acid	0.7	15.37 ± 0.16	12.18 ± 0.11	6.17 ± 0.09
dichloroacetic acid	1.48	12.66 ± 0.07	9.60 ± 0.23	4.54 ± 0.09
monochloroacetic acid	2.84	8.75 ± 0.08	6.20 ± 0.04	3.56 ± 0.05
acetic acid	4.75	3.36 ± 0.23	3.03 ± 0.19	1.13 ± 0.08

TABLE III: Enthalpies of Reaction of Three Substituted Pyridines with Trifluoroacetic Acid over a Wide Range of Concentrations in Chloroform at 25 °C

soln	$-\Delta H$,	soln	$-\Delta H$,				
concn, M	kcal mol ⁻¹	concn, M	kcal mol ⁻¹				
2,4,6-Trimethylpyridine							
0.0063	15.75	0.2241	15.02				
0.0101	15.95	0.2567	14.66				
0.0166	15.97	0.3576	14.00				
0.0172	15.97	0.6315	11.51				
0.0522	15.87	0.8089	10.66				
0.1502	15.42	0.9379	9.53				
0.1995	15.23						
Pyridine							
0.0310	11.98	0.3022	11.95				
0.0761	12.01	0.4601	11.16				
0.1175	12.08	0.5239	10.75				
0.1192	11.99	0.5331	10.73				
0.1962	11.97	0.6926	9.59				
0.2501	11.99	0.7401	9.25				
0.2654	12.03	0.8115	9.01				
0.2654	12.04						
4-Cvanopvridine							
0.0191	6.70	0.3324	6.51				
0.0191	6.53	0.3674	6.42				
0.0284	6.59	0.4596	6.26				
0.1517	6.66	0.5634	5.94				
0.2251	6.60	0.6732	5.78				

TABLE IV: Enthalpies of Reaction of Pyridine with Trifluoroacetic Acid in Four Aprotic Solvents at 25 °C

solvent	$-\Delta H$, kcal mol ⁻¹	
<i>p</i> -dioxane carbon tetrachloride <i>o</i> -xylene chloroform	$8.13 \pm 0.22 9.00 \pm 0.05, 8.97 \pm 0.10^{a} 9.96 \pm 0.01 12.00 \pm 0.04$	

^aReference 11.

light of the limiting behavior of H-bonded ion pairs expected to be present.

The effect of substitution of electron-donating and electronwithdrawing groups on the pyridine ring on the enthalpy of the reaction

$$R = \frac{\Delta H}{R} R + HO_2CCF_3 \xrightarrow{\Delta H} R = \frac{1}{R} R + HO_2CCF_3 = (1)$$

can be observed by inspecting the data presented in Table I and Figure 1. The sensitivity of ΔH with the change in substitution on the pyridine ring is considerable as compared to that of the most negligible effect on equivalent conductance of the pyridinium salts in their dilute solutions of chloroform.¹² The substitution of one or more electron-donating groups in the pyridine ring increases the enthalpy of reaction in the following order:

pyridine < 3-methylpyridine < 4-*tert*-butylpyridine < 4-methylpyridine < 3,5-dimethylpyridine < 2,6-dimethylpyridine < 2,4,6-trimethylpyridine

The reverse is true for the substitution of groups with varying electron-withdrawing power. The increase in electron-withdrawing



Figure 2. Enthalpies of reaction of pyridines with halogenoacetic acids vs. aqueous pK_a 's of acids.

power of the group decreases the enthalpy of the reaction. The observed decreasing order in ΔH is as follows:

pyridine > 3-chloropyridine > 4-cyanopyridine >

3-cyanopyridine > 2-bromopyridine > 3,5-dichloropyridine

It is interesting to see that the increased gas-phase proton affinity¹⁸ of aromatic heterocyclics with the addition of an extra fused benzene ring to the original aromatic moiety diminishes in nonaqueous solution. It has been observed that the addition of a benzene ring to the pyridine ring at two adjacent positions does not alter ΔH significantly. The ΔH values for pyridine, quinoline,



and isoquinoline with TFA in chloroform are approximately the same (see Table I for ΔH values). Since the measurements have been made in dilute solutions and we expect mainly the H-bonded ion pairs to be present, the ΔH values should reflect the hydrogen-bond-donating power of the pyridinium, quinolinium, and isoquinolinium ions to the trifluoroacetate ion in solution. Therefore, the ΔH values are indicative of the fact that the hydrogen-bond-donating power of these ions toward trifluoroacetate ion is to be approximately the same. Their pK_a 's in water at 25 °C (see Table I) also suggest their similar behavior toward water molecules. The same is also true for the other pyridinium ions.

⁽¹⁸⁾ Meot-Ner (Mautner), M. J. Am. Chem. Soc. 1979, 101, 2396.

The substituted pyridines of similar pK_a values have approximately the same ΔH values for reaction 1. The comparisons of ΔH and pK_a values of 3,5-dimethylpyridine with those of 4-methylpyridine and 4-tert-butylpyridine, of 4-cyanopyridine with those of 3cyanopyridine, and of 2-bromopyridine with those of 3,5-dichloropyridine prove the validity of the statement.

A proportionality between the enthalpies of reaction in a nonaqueous medium and the pK_a 's of the corresponding pyridinium ions in water at 25 °C is shown in Figure 1. The observed linear relationships imply that even if some of the reactions to form stoichiometric complex are imcomplete, the corresponding free energies of formation are probably proportional to ΔH for that process; i.e., the driving force for the completion is enthalpy controlled. This could be due to very little effect from ring substitution on the relative entropy for the process. Similar behavior has also been observed by Arnett and Chawla¹¹ in their thermometric titrations of only a few substituted pyridines with trifluoroacetic acid in carbon tetrachloride at 25 °C. The ΔH values for the systems compared are higher in CHCl₃ than those in CCl₄. This would be expected because of the higher dielectric constant of CHCl₃ than that of CCl₄ (see section 4, eq 7).

Finally, it is noted that the highly exothermic enthalpy value for triethylamine also falls on the straight line in Figure 1 of ΔH vs. pK_a . This is in conformity with its well-established higher basicity in aqueous solution.

2. H-Bonded Ion Pairs of Pyridinium Ion with Different Anions in Chloroform. Figure 2 and Table II give at a glance the effect of different anions on the enthalpies of reaction of three pyridines, namely, 2,4,6-trimethylpyridine (substituted with electron-donating groups), pyridine (unsubstituted), and 4-cyanopyridine (substituted with an electron-withdrawing group) in dilute solutions of chloroform at 25 °C. The ΔH values of these systems were plotted against pK_a 's of the acids, which resulted in three separate straight lines. The ΔH increases with the increase of proton-donating power of the halogenoacetic acid or with decrease in H-bondaccepting ability of the anion in the following order:

$$CH_{3}CO_{2}^{-} < ClCH_{2}CO_{2}^{-} < Cl_{2}CHCO_{2}^{-} < Cl_{3}CCO_{2}^{-} < F_{3}CCO_{2}^{-}$$

Though this order is retained qualitatively for the three pyridines studied, however, the magnitude of the effect for the change of acetic acid by trifluoroacetic acid increases with the decrease of H-bond-donating power of the corresponding pyridinium ions in the following order:

4-cyanopyridinium ion < pyridinium ion < 2,4,6-trimethylpyridinium ion

For the sake of comparison, the ΔH values of various pyridines with five acids in CHCl₃ at 25 °C have also been plotted against the pK_a 's of the corresponding pyridinium ions in Figure 1. Five separate straight lines with different slopes are obtained. The slope of the line increases with the increase in proton-donating power of the acid.

If the proton-transfer process

$$R$$
 (CO_2H) (L) (CO_2H) (L) (L) (CO_2H) $(CO_$

is accompanied by a change in either R or R', it follows, as shown in eq 2, that the logarithm of the constant for the proton-transfer

$$R^{\prime}CO_{2}H + \underset{R}{\swarrow} \underset{}{\swarrow} \underset{N}{\swarrow} \underset{N}{\longrightarrow} \underset{R}{\twoheadrightarrow} \underset{R}{\swarrow} \underset{R}{\swarrow} \underset{N}{\swarrow} \underset{R}{\twoheadrightarrow} \underset{R}{\longrightarrow} \underset{R}{\twoheadrightarrow} \underset{R}{\swarrow} \underset{R}{\swarrow} \underset{R}{\swarrow} \underset{R}{\swarrow} \underset{R}{\twoheadrightarrow} \underset{R}{\rightthreetimes} \underset{R}{\r} \underset{R}{\r$$

process is linearly related to the heat evolved in the process (log $K = m\Delta H + b$) and is the logarithm of the ratio of association constants of the acid and the base ($K = K_a^{HA}/K_a^{B+H}$). Therefore, $-\log K = \Delta p K_a = m\Delta H + b$, where $\Delta p K_a = p K_a^{HA} - p K_a^{B+H}$. This relationship holds good for trifluoroacetic acid and tri-



Figure 3. Enthalpies of reaction of pyridines-halogenoacetic acids in chloroform vs. their $\Delta p K_a$'s.

chloroacetic systems (Figure 3), where proton transfer is maximum and has the form

$$\Delta p K_a = 0.638 \Delta H + 2.93 \tag{3}$$

Deviation from eq 3 has been observed for dichloroacetic acid, monochloroacetic acid, and acetic acid systems and the equations for these systems are

$$\Delta p K_a = 0.753 \Delta H + 3.43$$
 (4)

$$\Delta p K_a = 1.18 \Delta H + 5.34 \tag{5}$$

$$\Delta p K_a = 2.49 \Delta H + 6.20 \tag{6}$$

This is contrary to the observations of Mashkovskii and Odinokov,¹⁹ whose ΔH values of various acid-base systems in carbon tetrachloride (obtained by infrared spectroscopy) fit in a unique form, $\Delta p K_a = -2.86 \Delta H + 27.6$.

3. Concentration Effect on H-Bonded Ion Pairs. The concentration dependence of ΔH of 2,4,6-trimethylpyridine, pyridine, and 4-cyanopyridine with trifluoroacetic acid in chloroform at 25 °C is shown in Figure 4. It is observed that in all three cases ΔH remains unchanged up to a certain concentration, and thereafter decreases sharply with the increase in final solution concentration. The concentration at which the decrease in ΔH starts is characteristic of the nature of the ring substitution. However, Arnett and Chawla¹¹ have reported that the enthalpy of reaction of pyridine-TFA in CCl4 increases with the increase in concentration after remaining unchanged up to a certain concentration (see Figure 2 of ref 11). Their system has been repeated and ΔH values were found to be reproducible. However, during critical examination, it was observed that the final solutions at higher concentrations were milky, which indicates the precipitation of pyridinium trifluoroacetate in the concentrated carbon

⁽¹⁹⁾ Mashkovskii, A. A.; Odinokov, S. E. Dokl. Acad. Nauk. SSSR 1972, 204, 1165.





Figure 4. Variation of enthalpies of pyridine-trifluoroacetic acid systems as a function of solution concentrations.

tetrachloride solutions and hence the increase in the ΔH values. This was further supported by the negligible conducting power of these concentrated CCl₄ solutions. On the other hand, the concentrated solutions of 2,4,6-trimethylpyridine–, pyridine–, and 4-cyanopyridine–trifluoroacetic acid in chloroform were comparatively highly conducting¹² (the conductance measurements were made immediately after the completion of the calorimetric run).

Since in dilute solutions ΔH values for the three systems investigated (see Table III) remain unchanged with the change in concentration, formation of mainly H-bonded ion pairs has been suggested. Our conductance measurements¹² on these systems strongly support this observation. According to the conductance studies,¹² there exists a mixture having varying composition of free ions, H-bonded ion pairs, and H-bonded higher ionic aggregates depending upon the concentration of the solution. This is conveniently described in the following manner:



Since ΔH values decrease with the increase of concentration ($\Delta H_2 < \Delta H_1$) and the transformation of H-bonded ion pairs (I) to higher aggregates (II) does occur at higher concentrations,¹² the process (conversion of I to II) is entropy driven. Therefore, ΔS must be positive and large enough so that $T\Delta S$ exceeds ΔH in magnitude to result in negative ΔG . When the concentration is increased, the H-bonded ion pairs combine to form a structured network (higher aggregates) with the simultaneous release of the bound solvent molecules. This release of bound solvent provides the increase in entropy necessary to drive the structure-forming process.



Figure 5. Variation of enthalpy of pyridine-trifluoroacetic acid system as a function of inverse of dielectric constant of the solvent: (1) p-dioxane, (2) carbon tetrachloride, (3) o-xylene, (4) chloroform.

In our earlier conductance observations, we have proposed the formation of triple ions for these systems at higher solution concentrations.¹² If it is so, the release of solvent molecules on aggregation of H-bonded ion pairs can be demonstrated schematically with the help of Scheme I.

The decrease in ΔH of the 2,4,6-trimethylpyridine (with electron-donating substituent)-F₃CCO₂H system with the increase in solution concentration is much sharper than the decrease in ΔH 's of pyridine (unsubstituted)-F₃CCO₂H and 4-cyanopyridine (electron-withdrawing substituent)-F₃CCO₂H and 4-cyanopyridine (electron-withdrawing substituent)-F₃CCO₂H systems. The weak H-bonding interaction between the 2,4,6-trimethylpyridinium and trifluoroacetate ions will facilitate the formation of higher aggregates more easily in this system as compared to the other two. For the same reason, the formation of higher aggregates starts at lower concentration in the case of the 2,4,6-trimethylpyridine-F₃CCO₂H system. The concentrations at which the formation of higher aggregates starts were obtained by extrapo

2655

lating the two straight-line portions as shown in Figure 4. The values of concentration 1.00×10^{-1} , 3.15×10^{-1} , and 3.70×10^{-1} M are almost the same as those obtained from conductance measurements.12

4. Solvent Effect on H-Bonded Ion Pairs. The effect of the dielectric constant coupled with solvating power of the solvents on ΔH is illustrated in Table IV and Figure 5. At a particular constant temperature, the strengthening, weakening, and breaking of the hydrogen bond of the H-bonded ion pair

in dilute solutions will mainly depend on the dielectric constant of the solvent used. Since strengthening and weakening do not produce significant change in the entropy of solvation of an H-bonded ion pair, the free energy of transfer of the H-bonded ion pair from one solvent to another will approximately be equal to the enthalpy change of the process. Therefore, ΔH in low dielectric constant media where the dissociation of H-bonded ion pairs is negligible¹² may be represented with the help of the Born equation as follows:

$$\Delta H = \Delta G + \text{constant} = (-NZe^2/2r)(1 - 1/\epsilon) + \text{constant}$$
(7)

 $\Delta G = -(NZe^2/2r)(1-1/\epsilon)$ Born equation

Accordingly, ΔH of pyridine-F₃CCO₂H in *p*-dioxane, carbon

tetrachloride, o-xylene, and chloroform is linearly related to the inverse of permittivity (ϵ) of the solvent (see Figure 5). The increase in the ΔH with the increase of dielecric constant (or decrease of $1/\epsilon$ is due to weakening of H-bonding in B⁺H--A⁻.

Acknowledgment. We are thankful to the Department of Science and Technology, New Delhi, India, for providing the financial support for purchasing a Tronac 450 titration calorimeter.

Registry No. TFA, 76-05-1; TCA, 76-03-9; DCA, 79-43-6; MCA, 79-11-8; AcOH, 64-19-7; triethylamine, 121-44-8; 2,4,6-trimethylpyridine, 108-75-8; 2,6-dimethylpyridine, 108-48-5; 3,5-dimethylpyridine, 591-22-0; 4-methylpyridine, 108-89-4; 4-tert-butylpyridine, 3978-81-2; 3-methylpyridine, 108-99-6; pyridine, 110-86-1; isoquinoline, 119-65-3; quinoline, 91-22-5; 3-chloropyridine, 626-60-8; 4-cyanopyridine, 100-48-1; 3-cyanopyridine, 100-54-9; 2-bromopyridine, 109-04-6; 3,5-dichloropyridine, 2457-47-8; triethylamine-TFA, 454-49-9; 2,4,6-trimethylpyridine-TFA, 57313-93-6; 2,6-dimethylpyridine-TFA, 70320-26-2; 3,5-dimethylpyridine-TFA, 81675-57-2; 4-methylpyridine-TFA, 29885-74-3; 4-tert-butylpyridine-TFA, 30254-33-2; 3-methylpyridine-TFA, 81675-56-1; pyridine-TFA, 464-05-1; isoquinoline-TFA, 4215-41-2; quinoline-TFA, 89937-06-4; 3-chloropyridine-TFA, 89937-07-5; 4-cyanopyridine-TFA, 29885-70-9; 3-cyanopyridine-TFA, 81675-55-0; 2-bromopyridine-TFA, 89937-08-6; 3,5-dichloropyridine-TFA, 89937-09-7; 2,4,6-trimethylpyridine-TCA, 53088-80-5; 2,4,6-trimethylpyridine-DCA, 57313-89-0; 2,4,6-trimethylpyridine-MCA, 24145-70-8; 2,4,6-trimethylpyridine-AcOH, 89937-10-0; pyridine-TCA, 3486-54-2; pyridine-DCA, 16983-41-8; pyridine-MCA, 933-24-4; pyridine-AcOH, 5153-63-9; 4-cyanopyridine-TCA, 89937-11-1; 4-cyanopyridine-DCA, 89958-45-2; 4-cyanopyridine-MCA, 89937-12-2; 4-cyanopyridine-AcOH, 89937-13-3.

Phase Diagram of a Ternary Fluid Mixture in the Vicinity of Its Critical Line in the Presence of Isotope-Exchange Reactions

P. Gansen and D. Woermann*

Institut für Physikalische Chemie, Universität Köln, Federal Republic of Germany (Received: July 26, 1983; In Final Form: November 22, 1983)

The coexistence surface of the ternary system isobutyric $acid/H_2O$, D_2O in which two independent isotope-exchange reactions take place is determined by chemical analysis of the two fluid phases coexisting at temperatures below the upper critical solution temperature. The acid is generated by hydrolysis of isobutyric acid anhydride in H_2O , D_2O mixtures of known composition. The form of the coexistence surface practically does not change with the equivalent fraction Y of exchangeable protons. The critical composition determined on the basis of the equal volume criterion decreases slightly with increasing values of Y (about 3%). The critical temperature is a linear function of Y. It increases by about 20 K. In the systems isobutyric acid (COOH)/D₂O and isobutyric (COOD)/H₂O the composition of the mixture with maximal phase separation temperature is not identical with the critical composition. This can be understood on the basis of the form of the coexistence surface of the system isobutyric acid/H₂O, D₂O, confirming predictions of Knobler and Scott. The properties of the coexistence surface of the system isobutyric acid/ H_2O , D_2O appear to be typical for critical systems in which isotope-exchange reactions take place. This is shown by studies of the temperature of phase separation vs. composition of the systems phenol (OH)/D₂O and 2-butoxyethanol $(OH)/D_2O$ near the upper and lower critical point, respectively.

Introduction

The systems isobutyric acid (COOH)/H₂O (HA/H₂O), isobutyric acid $(COOD)/D_2O$ (DA/D_2O) , isobutyric acid $(COOH)/D_2O$ (HA/D₂O), and isobutyric acid (COOD)/H₂O (DA/H_2O) have upper consolute points. The critical composition of all four systems has approximately the same value. However, they differ in one respect, in the systems HA/D_2O and DA/H_2O , isotope-exchange reactions take place. In each of these systems the composition with the maximal phase separation temperature is different from the critical composition determined by the equal volume criterion.¹⁻³ The critical temperature is about 0.1 K lower than the maximal temperature of phase separation (Figures 1 and 2). Knobler and Scott have proposed an explanation of this phenomenon.⁴ For further study of the influence of isotope-exchange reactions on the composition dependence of the temperature of phase separation, the coexistence surface of the ternary

(4) Ch. H. Knobler and R. L. Scott, J. Chem. Phys., 76, 2606 (1982).

⁽¹⁾ E. Gulari, B. Chu, and D. Woermann, J. Chem. Phys., 73, 2480 (1980).

⁽²⁾ P. Gansen, T. Jansen, W. Schön, and D. Woermann, Ber. Bunsenges. (3) I. Schäfke, Master Thesis, Universität Köln, 1983.