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THERMOMETRIC TITRATION OF SOME AMINES IN WATER–ACETONE MIXTURES

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ABSTRACT

The enthalpies of protonation of some N-bases in H_2O–acetone, 0, 0.25, 0.5, 0.75 and 0.95 mole fraction at 298 K have been determined by calorimetry. Solutions of amines in each solvent system were titrated enthalpimetrically with $HClO_4$ solution. The bases studied were piperidine, *n*-butylamine, 2-amino-2-methyl-1,3-propanediol, (AMP), tris(hydroxymethyl) aminomethane, tris, 2,2-bis-(hydroxymethyl-2,2′,2″-nitrilotriethanol, (bis-tris) and pyridine.

The results are discussed in terms of the preferential solvation of ions by two types of solvent molecules. The enthalpy of protonation of all the bases passes through a minimum at a solvent composition of 0.75 mole fraction of acetone.

INTRODUCTION

Thermometric titration of N-bases has been carried out in aqueous and non-aqueous media. Forman and Hume [1] estimated the isothermal heats of neutralization by hydrogen bromide in acetonitrile for a large group of aliphatic and aromatic amines by thermometric titration. Mead [2] performed analogous experiments with benzene as the solvent and trichloroacetic acid as the titrant. The enthalpies of the series in both solvents are close.

Aqueous acetone solutions are highly structured and there is reason to believe that water hydrogen bonds move more strongly to acetone than to itself. The extent of proton transfer equilibria (log K_f) in the hydrogen bonded complexes of p-FC_6H_4OH-acceptor in CCl_4: for acetone, 1.18; acetonitrile, 1.05; DMSO, 2.53; and NMe2Py, 2.38, has been shown for two groups of acceptors with similar basicities [3]. Several intensive studies of structure in H_2O–MeCN solution have been done. According to the model [4] H_2O–MeCN mixtures form two "microphases"; highly structured microphase "α", consisting predominantly of water in which all water molecules

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are coordinated, and a disordered microphase, "β", consisting mostly of MeCN. From proton NMR data and empirical solvation parameters Z and E_T [5], it has been suggested that when the MeCN content reaches $0.60 X_2$, microphase α virtually disappears. H_2O–MeCN mixtures are very similar to acetone–water solvents [6].

Absorption spectra of acetone in water have been measured by the low energy $n \rightarrow \pi^*$ transition sensitive carbonyl group. Spectroscopic effects ν_{max} and ϵ_{max} in H_2O–acetone mixtures show a broad maximum at 70–90 mole% acetone [7].

Mixtures of water and aprotic solvents are of special interest in our continuing investigation of solvent effects on acid–base behaviour [12]. Solvent effects in isoelectric reactions of the charge type

$$B + H^+ \rightleftharpoons BH^+$$

are useful in revealing selective solvation. In the present work some amines in water and in four solvent compositions for which the mole fractions (X_2) of acetone were 0.25, 0.50, 0.75 and 0.95 were titrated with perchloric acid.

EXPERIMENTAL

Reagent grade acetone was purified by common procedures. Deionized water was distilled in a glass still before use. The mixed solvents were prepared by weighing. Stock solutions of $HClO_4$ (from 60%) were prepared in H_2O–acetone solvents, and standardized by titration with an aqueous solution of sodium hydroxide which had, in turn, been standardized against potassium hydrogen phthalate (NBS standard reference material) just before use. Methods for the purification of the N-bases have been described previously [8]. Solutions of the amines in solvents mixture, 0.02 M, and solutions of the $HClO_4$ titrants in solvents, 0.2–0.4 M, were prepared by weight methods.

Heats of reaction were measured with a Tronac 450 titration calorimeter [9,10]. Techniques for the measurements followed closely the details described previously [11]. The reaction vessel contained an excess of the amine solution, and the titrant solution of the perchloric acid was added from the syringe burette of 2.00 ml capacity with a delivery rate of 0.006585 ml s^{-1}. Both solutions were at the same temperature, i.e., 298 K. The temperature changes in the reaction vessel resulting from the proton transfer between the reactants were detected by a thermistor and converted to voltage in a Wheatstone bridge circuit, and recorded. The heat of dilution of the titrant $HClO_4$ was determined separately and corrections were applied to the measured heats of reaction. The values found were (in kcal $mole^{-1}$): mole fraction of acetone, 0.25 (−3.58), 0.50, (−2.22), 0.75, (−1.91), and 0.95, (−3.65).

RESULTS AND DISCUSSION

The experimental heat of protonation, $-\Delta H_p$, of amines by perchloric acid in H_2O–acetone mixtures is given by the equation

$$-\Delta H_{exp} = -\Delta H_p - \Delta H_{dil}$$

Results from measurements of heat of dilution, $-\Delta H_{dil}$, 0.25–0.45 M $HClO_4$ in each solvent mixture, are summarized in the Experimental Section. Enthalpy of protonation, $-\Delta H_p$, presented in Table 1 for the dilution corrections of titrant, and the corresponding standard deviation (S.D.) are listed.

The solvent effect of acetone on the protonation of amines is evident in Fig. 1, where enthalpy of protonation is plotted as a function of acetone mole fraction (X_2). The observed changes of enthalpy are the result of specific solvation interactions of H_2O and acetone with the proton, the acid BH^+, and the conjugate base B. The enthalpy of protonation is lowest in H_2O–acetone mixtures for solvent composition $X_2 = 0.75$. The curves for the enthalpy of protonation in H_2O–acetone are qualitatively similar to those for protonated bases, $pK^S_{BH^+} = f\ (X_2)$, in mixtures of water with *N*-methyl-

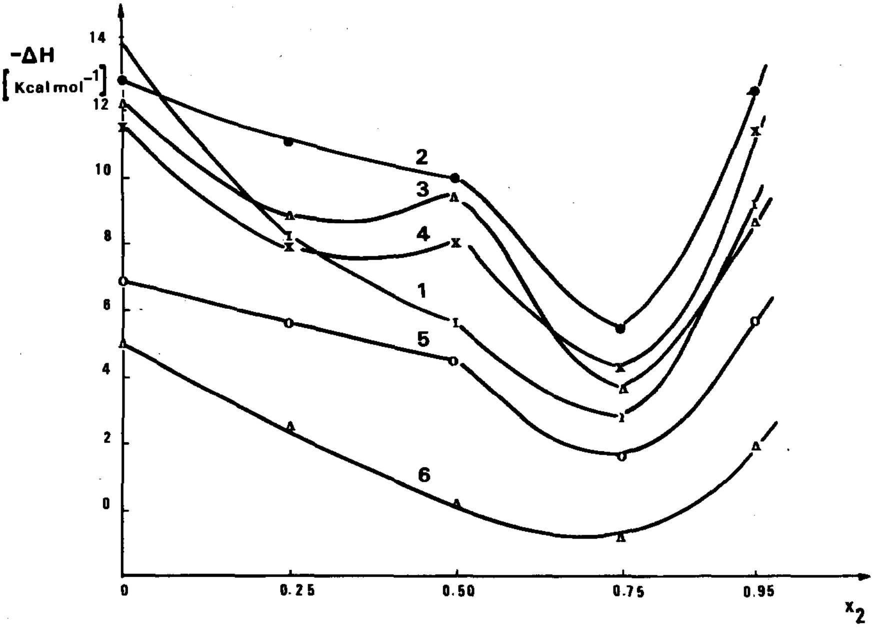

Fig. 1. Enthalpy of protonation, $-\Delta H$ in kcal mole^{-1}, for N-bases + $HClO_4$ in acetone $-H_2O$ mixture in 0.25, 0.50, 0.75 and 0.95 mole fraction of Acetone (X_2). N-Bases: piperidine (1), *n*-Butylamine (2), 2-amino-2-methyl-1,3-propanediol, "AMP" (3), tris (hydroxymethyl) aminomethane, "tris" (4), 2,2-bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol, "bis-tris" (5), and pyridine (6).

TABLE 1

Molar enthalpies for reactions $B+H^+ \rightleftharpoons BH^+$ in water–acetone mixtures at 298 K

X_2 = mole fraction of acetone.

	$B(pK_a^{H_2O})$	[8,15]	$-\Delta H$(kcal mole^{-1})				
			$X_2=0$	$X_2=0.25$	$X_2=0.50$	$X_2=0.75$	$X_2=0.95$
1	Piperidine	(11.12)	12.93±0.04	11.00±0.11	9.96±0.10	5.43±0.08	12.49±0.13
2	*n*-Butylamine	(10.64)	14.13±0.01	8.24±0.07	5.59±0.11	2.76±0.17	9.11±0.02
3	AMP	(8.80)	12.18±0.07	8.82±0.09	9.31±0.02	3.61±0.07	8.64±0.10
4	Tris	(8.07)	11.47±0.09	7.89±0.09	7.98±0.09	4.30±0.08	11.28±0.01
5	Bis-tris	(6.48)	6.91±0.02	5.63±0.02	4.43±0.12	1.64±0.05	5.70±0.12
6	Pyridine	(5.29)	4.94±0.09	2.46±0.11	0.12±0.07	−0.87±0.03	1.84±0.06

propionamide (NMP, $\epsilon = 176$) [13], or with methanol ($\epsilon = 22.4$) [14,15]. They also compare favourably with earlier works on pK_a^S, with cationic acids in H_2O–NMe2Py, [8] and H_2O–DMSO [12], where the mixtures were found to pass through a minimum in the vicinity of $X_2 \cong 0.5$.

The less exothermic behaviour of tris, AMP and bis-tris systems have been observed in the 0.5 mole fraction solvent (Fig. 1). It is possible that interaction of the –OH groups of tris, AMP and bis-tris with the solvent may be involved, with or without compensating endothermic processes related to structural reorganization of the unit. The difficulty of preparing a stable anhydrous acetone solution of the strong acid, $HClO_4$, is a drawback in the determination of enthalpies of protonation in acetone.

The heat of neutralization in acetonitrile [1] has been shown to be a good measure of the relative strengths of aromatic amines, and aliphatic primary and straight chain secondary amines. It is reasonable to conclude that in CH_3CN and $(CH_3)_2CO$, there is little solvation of amines or ammonium ions compared with that in water. The heat of neutralization of *n*-butylamine in acetonitrile is 25.8 kcal mole^{-1}, and that of pyridine is 14.4 kcal mole^{-1}. The values are 14.1 and 4.94 kcal mole^{-1} in water. The heats of reaction of substituted benzoic and acetic acids with 1,3-diphenylguanidine in CH_3CN ($-\Delta H$, kcal mole^{-1}) are 12.4, 13.4, 17.4 and 19.2 for benzoic, *p*-nitrobenzoic, perchloric and trichloroacetic acids, respectively [16]. In recent work Arnet and Chwala [18] show a good correlation between the enthalpies of formation and basicities for the 1:1 hydrogen bonded complexes formed from substituted pyridines (Py) and trifluoroacetic acid (HA) in CCl_4.

A compilation of enthalpy data for families of complexes (amines + phenols, pyridines + phenols) in benzene, toluene and CCl_4 has been made [17] and the values correlated with dipole moments ($\Delta\mu$). Three types of complex (–OHN–) are distinguished: one group of low polarity (7 kcal mole^{-1}), one of the medium polarity (7–18), and one of higher polarity (more than 18 kcal mole^{-1}). The majority of the systems belong to the proton transfer type.

Studies of monoprotic [19] and diprotic carboxylic acids [20] $pK_a^{H_2O}$ [5–10] in water with aqueous sodium hydroxide showed that the ΔH^0 value for neutralization of a single carboxylic group does not differ appreciably from the value for "strong acid–base" neutralization (-13.5 kcal mole^{-1}) and is not greatly affected by the dissociation constant of the carboxylic group. This means that the enthalpy change of ionization (ΔH_i^0) is low for –COOH groups. However, for cationic acids, BH^+, we observed an influence of pK_a on the enthalpy of protonation in aqueous solutions and mixtures with acetone. The enthalpy of ionization (ΔH_p^0) is related to the dissociation constant of the acid by the relationship

$$\Delta H_i^0 = T\Delta S_p^0 - RT \ln K_a$$

In a study of carboxylic acids, the values for K_a were small, with the ΔS_p^0 being correspondingly larger.

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