SOLVENT EFFECT ON THE IONISATION CONSTANT OF SOME AMINO SULPHONIC ACIDS

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ABSTRACT

*The ionization constant of 3 N-subs-
titutedamino-propane-1-sulphonic acids I
and II, are studied in an extensive series
ranging from pure water up to 60% by weight
acetone at 25°C. The results are indicative
of the fact that proton availability is co-
siderably changed throughout the additions
of organic solvent to water.*

INTRODUCTION

Amino sulphornic acids are the subject of various investigations, due to their applications in the biological as well as in the industrial fields[1-3]. Although these acids are readily formed in the environment as a consequence of sulphur-containing industrial waste. The present investigation deals with the study of the ionisation constant of some amino sulphonic in a wide range of the aqueous dipolar aprotic solvent, acetone. The solvent compositions represent an extensive ranging from pure water up to 60 % by weight of the organic solvent over which the dielectric constant, solvating power and proton availability of the medium changed widely.

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EXPERIMENTAL

Material :

3N-phenylamino-propane-1-sulphonic acid I and 3 N-butylamino-propane-1-sulphonic acid II were propared as previously described[4,5]

Contstant boiling hydrochloric acid was prepared from Carlo Erba concentrated acid and standarized against a standard solution of sodium carbonate. A saturated solution of reagent grade sodium hydroxide was allowed to stand for several days in a polyethylene bottle. The solution was filtered through a G 4 glass filter under nitrogen atmosphere and diluted with distilled water free from carbon dioxide. The solution was kept in a polyethylene bottle filled with nitrogn gas. Potassium chloride (GR) Merck was used after drying at 500°C. Acetone (Merck grade) was purified by refluxing with pure potassium permanganate, distilled and dried over potassium carbonate[6].

Procedure :

The following solutions were titrated with a standard carbonate free NaOH 0.1 M solution; i 5 ml 1 M KCl+3ml 0.1 M HCl + X ml acetone to attain the requisite percent + water up to 50 ml; and ii) 5 ml 1 M KCl + 3 ml 0.1 M HCl + 10 ml 0.001 I or II + X ml acetone + water up to 50 ml.

RESULTS AND DISCUSSION

For studying the solvent effect on the ionisation constant of some amino sulphonic acids, acetone was used as cos-solvent. To calculate the formation constant of ligand-proton system, the values of $\bar{n}_n$ ($\bar{n}_n$ = number of attached protons

to the ligand) at different pH values were calculated
using Irving and Rossotti[7,8] method:

$$\bar{n}_n = Y + \frac{(V' - V'')(N° + E°)}{(V° + V')T_L} \qquad (1)$$

Where V' and V'' denote the volume of alkali to reach
the same pH in the titration of acid and ligand; respec-
tively; $V°$, $E°$ and $N°$ are the total volume of titration
mixture, initial concentration of the free acid and nor-
mality of NaOH, respectively, Y is the total number of
dissociable protons attached to the ligand and T_L is the
total concentration of the ligand.

The formation curves at different solvent composition
are shown in fig. 1. The apparent K and pK values derived
from these plots for both, I and II, are compiled in the
table. It is readily seen that pK is increasing noticea-
bly with the progressive addition of the organic solvent.
The effect of the dielectric constant on the dissociation
constant may be taken as an indication for the role of the
solvent. The traditional quantitative theories
of the solvent effects[9] should give a linear relation
on plotting the logarithm of the dissociation constant
versus the electrostatic function according to the theory
applied by using equation 2.

$$pK = pK° + \frac{0.43\, Z_1 Z_2}{RT\; r_1\, r_2} \cdot \frac{1}{D} \qquad (2)$$

pK and pK° denote the acid dissociation constants in solvent

mixture and pure water, respectively, z_1 and z_2 are the charges on the ions at equilibrium and r_1 and r_2 the ionic radii. The linear relationship between pK and the reciprocal of dielectric constant of the medium mixture indicates that the change in pK values with solvent composition may be due to the electrostatic contribution. Moreover, the increase of the pK accompanying the additions of acetone may be due to the decrease of acidity of HCl accompanying the basicity increase of water. This has been attributed[10] to the progressive break down of the tetrahedral structure of water. Thus, instead of having the structure $(H_2O)_4 H^+$, one may have the species $(H_2O)_2 H^+$ besides; since the proton affinity in the open structure $(H_2O)_4 H^+$ is less than that in the compact structure, the latter will be holding the proton more firmly. Besides, the hydrocarbon group in acetone provides sites for the build-up of structure around the ketone molecule. In general, the variations of pK with solvent composition can be attributed to, (i) The breakdown of water structure as the cosolvent content is increased[11], (ii) the relative basicities of cosolvent and water molecules in a particular solvent mixture[12], (iii) the existence of different forms of solvated protons.[13,14]

It is clear from the table that the pK-values of acid I are relatively higher than that of acid II. This may be due to the presence of nitrogen atom near the aromatic ring enhances the delocalization of its lone pair of electrons. This delocalization probably facilitates drift of electrons from the suphonic group towards the aromatic ring results in weaking the SO_3-H bond.

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