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A Potentiometric Study of the Cationic Homoconjugation Equilibria in Substituted Pyridine N-Oxide Systems in Binary Polar Solvents, Acetonitrile – Nitromethane

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The equilibria of dissociation of cationic acids:

$$BH^+ \rightleftarrows B + H^+ \tag{1}$$

and of cationic homoconjugation of the acids with conjugate bases:

$$BH^+ + B \rightleftarrows (BHB)^+ \tag{2}$$

(where B is the base molecule and BH^+ is a cation of protonated base B) in mixed polar solvents have been systematically studied in our laboratory [1–4]. Measurements carried out in acid-base systems have shown that the pK_a are mostly non-linearly related to the composition of the solvent mixtures, the non-linearity prevailing at low pK_a values of the cationic acids [1]. Furthermore, a study [4] with potentiometric standards (picric acid and 2,6-dinitrophenol) has shown that also with molecular acids and phenols the pK_a's vary in a non-linear manner.

These studies [1–3] afforded also preliminary information on the influence of composition of mixed solvents on cationic homoconjugation equilibria. These also revealed a non-linear nature of these variations [1–3]. However, the measurements were conducted in mixtures, in which one of the components was unfavourable for homoconjugation, in particular the amphiprotic methanol and water. For this reason, the purpose of this contribution was to explore the tendency toward cationic homoconjugation in systems involving substituted pyridine *N*-oxides in mixed solvents, in which both components are highly favourable for cationic homoconjugation equilibria. Consequently, two polar aprotic protophobic solvents of low basicity, acetonitrile and nitromethane, have been chosen, differing in acidities. Consequently, to perform

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the purpose of this contribution, the cationic homoconjugation constants in systems involving substituted pyridine N-oxides in acetonitrile (AN) + nitromethane (NM) binary solvent systems, where the mole fraction of acetonitrile x_{AN} was varied between 0 and 1, at $\Delta x = 0.1 - 0.3$, were determined. The N-oxides of 4-methylpyridine (4PicO), pyridine (PyO), and 4-nitropyridine ($4NO_2PyO$) covered a relatively wide range of acid-base properties. For comparison, the cationic homoconjugation equilibrium constants in these binary solvent systems were also determined for trimethylamine N-oxide (Me_3NO) and pyridine (Py), the representatives of aliphatic N-oxides and heterocyclic amines, respectively.

Purification procedures for acetonitrile [5] and nitromethane [6], as well synthesis of simple perchlorates of the *N*-oxides [7] were described elsewhere. The solvents were mixed at appropriate mole fractions on a volume basis using purified solvents. The solvent mixtures of variable composition were prepared on the volume basis. Both the potentiometric procedure employed and the equipment used are described elsewhere [6,8]. All measurements were carried out at 298.1 ± 0.1 K.

The cationic homoconjugation constants determined in the acid-base systems formed by the bases in the binary acetonitrile – nitromethane systems are collected in Table 1. As a basis for the determination of the constants in mixed solvents served parameters **s** (slope of the response of the glass electrode) and $\mathbf{E^o}$ (standard e.m.f.), obtained from potentiometric titrations in standardising systems together with the results of the potentiometric titrations performed in the systems BH^+/B. The constant values were calculated from the results of e.m.f. measurements by the general method of Kostrowicki and Liwo [9–11]. The values of the constants were calculated under consideration of an equilibrium model involving acid dissociation and cationic homoconjugation in the BH^+/B systems.

Table 1. Log K_{BHB^+} values with their standard deviations, for protonated substituted pyridine N-oxides in acetonitrile – nitromethane binary solvents at 298.1 K. Those for trimethylamine N-oxide and pyridine are shown for comparison.

x Base	0	0.1	0.2	0.5	0.8	0.9	1
4PicO	4.27[a]	3.29 (0.07)	2.87 (0.09)	2.28 (0.11)	2.64 (0.09)	2.69 (0.11)	3.57[b]
PyO	3.59[a]	3.45 (0.04)	3.38 (0.04)	3.31 (0.04)	3.28 (0.03)	3.26 (0.03)	3.22[b]
$4NO_2PyO$	1.91[a]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]
Me_3NO	3.92[a]	3.49 (0.20)	3.37 (0.19)	3.63 (0.18)	4.83 (0.20)	4.52 (0.15)	5.95[b]
Py	1.83[a]	1.80 (0.14)	1.87 (0.13)	1.73 (0.11)	–[c]	–[c]	–[c]

[a]From ref. 6; [b]From ref. 14; [c]Missing values of homoconjugation constants could not be determined from potentiometric measurements.

The main shortcoming of the potentiometric measurements carried out in the mixed solvents was the lack of the pK_a of picric acid, used as the standardising compound. There are only literature values in particular solvents, used for the preparation of the binary mixtures. These are 11.0 and 10.55 for acetonitrile [12] and nitromethane [13], respectively. In this situation, pK_a values in the solvents mixtures studied were determined by the procedure described in [1–4].

For all the solvent mixtures investigated, as well as for their components, there exists a linear relationship between e.m.f. and the logarithm of the concentration ratio of the components of the standardising system and the slopes of the glass electrode characteristics were close to the theoretical Nernst' value 59.14 mV. It should be also noted that the relationship between pK_a and mixed solvent composition is linear (Table 2). A similar relationship of pK_a *vs.* mole fraction of acetonitrile in the solvent mixture has been found for the majority of the acid-base systems studied in this work, formed by 4PicO, PyO, Me_3NO and Py. Only with the least basic *N*-oxide, $4NO_2PyO$, the relationship is distinctly non-linear – within the acetonitrile mole fraction range of 0.3 to 0.5 (Table 2). Similar relationship was observed with weakly basic *N*-oxides in the acetonitrile – dimethyl sulfoxide [1] and acetonitrile – methanol [2] systems.

Table 2. pK_a values with their standard deviations, for picric acid and protonated 4-nitropyridine N-oxide in acetonitrile – nitromethane binary solvents at 298.1 K.

x Acid	0	0.1	0.2	0.5	0.8	0.9	1
HPi	10.55[a]	11.07 (0.28)	10.99 (0.28)	11.06 (0.18)	11.04 (0.13)	10.82 (0.27)	11.0[b]
$4NO_2PyOH^+$	4.93[c]	4.48 (0.03)	4.13 (0.07)	4.22 (0.05)	4.58 (0.12)	4.98 (0.07)	5.63[d]

[a]From [13]; [b]From [12]; [c]From [6]; [d]From [14].

The values of cationic homoconjugation are easily determinable for the N-oxide systems in acetonitrile – nitromethane mixtures and are charged with respectively small values of standard deviation (Table 1). Obviously, the standard deviations are considerably greater than in the case of constants determined in individual solvents, *i.e.* acetonitrile and nitromethane in this case. On the other hand, they are comparable and even smaller than these characteristic for acetonitrile – methanol solvent systems [2]. The values of cationic homoconjugation decrease from the value characteristic for nitromethane down to those characteristic in acetonitrile. The nature of these variations for substituted the N-oxides studied is distinctly non-linear. For the 4PicO system, they vary from the values characteristic for nitromethane down to the value characteristic in acetonitrile over the values lower than these in pure acetonitrile. This suggests the existence of a local minimum. Such a local minimum at *ca* 0.3 mole fraction of acetonitrile is distinct in the Me_3NO system. It can be, therefore, concluded that the non-linear nature of these variations increases with the increasing basicity of the N-oxide. This hypothesis can be supported by the finding that with pyridine N-oxide, the less basic *N*-oxide than 4PicO and Me_3NO, the relationship, being distinctly non-linear, does not exhibit a local minimum. With the least basic $4NO_2PyO$, the homoconjugation constants are undeterminable in all the mixed solvents studied, as is the case in pure acetonitrile [14].

With pyridine, the cationic homoconjugation constants are only determinable in a mixture with excessive contents of nitromethane, where the homoconjugation constant for the pyridine system, albeit small (its logarithm is 1.83 [6]) is still determinable. In the mixed systems with a high content of acetonitrile, the homoconjugation constants are undeterminable, similar as in acetonitrile [15]. This observation leads to another interesting conclusion about the existence of a critical acetonitrile content in mixtures with nitromethane, characteristic for a particular system, above which the cationic homoconjugation constants become indeterminable for a particular acid-base system.

These findings, concerning the influence of composition of the acetonitrile – nitromethane solvent system on cationic homoconjugation constants in the amine *N*-oxide systems, enable to reach a general conclusion, supporting a preceding one based on measurements carried out in the acetonitrile – acetone [1], acetonitrile – dimethyl sulfoxide [1] and acetonitrile – methanol [2] solvent systems, of the non-linear nature of these variations. They also support the hypothesis of the possibility of occurring of local minima in similar relationships.

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