

A Potentiometric Study of the Acid Dissociation and Cationic Homoconjugation Equilibria in Substituted Pyridine N-Oxide Systems in Binary Polar Solvents, Acetonitrile – Acetone and Acetonitrile – Dimethyl Sulfoxide

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Acid dissociation constants of protonated substituted pyridine N-oxides and cationic homoconjugation constants of these acids with conjugate N-oxides have been determined by potentiometric titration in mixed polar non-aqueous solvents (acetonitrile – acetone and acetonitrile – dimethyl sulfoxide) with increasing (from 0 to 1) mole fraction of acetonitrile. In acetonitrile – dimethyl sulfoxide mixtures, the acid dissociation constants (expressed as pK_a) and cationic homoconjugation constants (expressed as $\log K_{BHB^+}$) vary non-linearly with increasing mole fraction of acetonitrile. In systems with the least basic N-oxides, local minima of pK_a have been observed. In acetonitrile-acetone mixtures, both the pK_a and the cationic homoconjugation constant values changed irregularly in the acid-base systems studied and the character of those variations could not be unambiguously determined.

Key words: binary solvents systems, acid-base equilibria, substituted pyridine N-oxides

Solvent mixtures provide novel media for chemical reactions in solutions. On the one hand, the solutes can be solvated by solvent molecules, and on the other, interactions between two solvents can affect the solvent – solute interactions [1]. For instance, the solute acidity in solvent mixtures is affected not only by electrostatic forces [2,3], as predicted by Born's theory. Deviations from Born's equation are probably due to variations in relative electric permittivity in the vicinity of the solvation spheres of ions [4]. The distances between the ions, at which the variations in relative electric permittivities occur, have been found to be a function of composition of a solvent mixture [5]. Both the non-linear variations of the pK_a of weak acids as a function of composition of the solvent mixtures [6,7] and the local extremal pK_a values are likely to be the consequences of deviations from Born's equation. Similar non-linear variations as a function of composition of solvent mixtures have also been reported for the anionic homoconjugation constants [6]. Nevertheless, reports on the linearity of variations of the acidity constants as a function of composition of solvent mixtures

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seem to preponderate [8–10]. Due to this discrepancy in respect to the nature of the variations of the acidity constant values in binary solvent mixtures, potentiometric studies have been initiated in this laboratory on acid-base equilibria in solvent mixtures for systems involving organic bases. Consequently, in such non-aqueous media the objects of investigations on acidic-basic interactions in systems containing organic bases are first of all fundamental acid-base equilibria, namely those of dissociation of cationic acids:



and cationic homoconjugation:



where B is the base molecule and BH^+ is a cation of protonated base B. Results of the preliminary investigations [11] have shown, that in systems of weak acids used as standards in potentiometric measurements (picric acid, 2,6-dinitrophenol), pK_a varied in a non-linear manner with varying composition of the binary solvent mixture. Further studies with organic bases (heterocyclic amines, their N-oxides and N-oxides of aliphatic amines) in mixtures of polar solvents, protophobic aprotic acetonitrile – amphiprotic methanol, revealed non-linear variations of both the dissociation constants of the cationic acids conjugated to the bases and of the cationic homoconjugation constants of the bases with conjugate cationic acids as a function of composition of the solvent mixtures [12].

The purpose of this study was to check whether these variations are non-linear also in solvent mixtures consisting of two polar aprotic solvents. Consequently, acid dissociation constants of protonated substituted pyridine N-oxides and cationic homoconjugation constants of these acids with conjugate N-oxides have been determined by potentiometric titration in two mixed polar non-aqueous solvent systems. In order to differentiate the tendency towards cationic homoconjugation, apart from the weakly basic protophobic acetonitrile ($\text{DN} = 14.9$ [13]), selected for this study were the protophobic acetone with relatively high basicity ($\text{DN} = 17.0$ [13]) and the strongly basic protophilic dimethyl sulfoxide ($\text{DN} = 29.8$ [13]). According to [14–16], formation constants of homocomplexes usually increase with decreasing solvation capacity and basicity of solvents. This can be attributed to a stronger solvation of the cationic acids by those of the stronger basic solvent molecules, which results in weakening of the bonding between the cationic acid and conjugate base, *i.e.* weakening of the homocomplex as a whole [17]. It can thus be assumed that in solvent mixtures, the increased content of a more basic solvent in a less basic one should suppress the capacity of formation of homocomplexes.

To perform the purpose of this contribution, the acid dissociation and cationic homoconjugation constants in systems involving substituted pyridine N-oxides in acetonitrile (AN) + acetone (AC) and acetonitrile + dimethyl sulfoxide (DMSO) bi-

nary solvent systems, where the mole fraction of acetonitrile x_{AN} was varied between 0 and 1, at $\Delta x = 0.1$ or 0.2, were determined. The N-oxides of 4-N',N'-dimethylaminopyridine (4NMe₂PyO), 4-methylpyridine (4PicO), pyridine (PyO), and 4-nitropyridine (4NO₂PyO) covered a relatively wide range of acid-base properties. For comparison, the acid-base equilibrium constants in these binary solvent systems were also determined for quinoline N-oxide (QNO), trimethylamine N-oxide (Me₃NO) and pyridine (Py), the representatives of binuclear heterocyclic N-oxides, aliphatic N-oxides and heterocyclic amines, respectively.

EXPERIMENTAL

The solvent mixtures of variable composition were prepared on the volume basis using purified solvents. Acetonitrile [18], dimethyl sulfoxide [19] and acetone [20] were purified by standard procedures. Simple 1:1 perchlorates of the N-oxides were prepared by the modified Szafran method [21]. The glass electrode used in potentiometric measurements was standardized before each series of measurements against a buffer solution consisting of tetra-n-butylammonium picrate and picric acid. A modified calomel electrode was used as a reference one placed in a shortened salt bridge filled with a 0.01 M solution of tetra-n-butylammonium perchlorate in the equimolar solvent mixtures. The modification consisted in replacing the aqueous KCl solution by a 0.1 M tetra-n-butylammonium chloride solution in a solvent mixture of composition identical with that in the salt bridge. Both the procedure employed and the equipment used are described elsewhere [22]. Potential readings were taken with the accuracy of ± 0.1 mV by using a multifunctional CX-731 (ELMETRON) apparatus. All measurements were carried out at 298.1 ± 0.1 K.

RESULTS AND DISCUSSION

There is no literature value for the pK_a of picric acid, used here as a reference compound in the standardizing system with tetra-n-butylammonium picrate in the solvent mixtures studied. There are only literature values in particular solvents, used for the preparation of the binary mixtures. These are 11.0, 6.3 and 1.0 for acetonitrile [23], acetone [24] and dimethyl sulfoxide [25], respectively. In this situation, pK_a values in the solvents mixtures studied were determined by the following procedure: first, rough pK_a values were determined from the difference in the e.m.f. of solutions containing equimolar proportions of both buffer components in the solvent mixture and in one of mixture components, based on the following equations:

$$pK_a^x = \frac{(E_{1/2}^x - E_{1/2}^R) \cdot \Delta pK_a}{\Delta E_{1/2}} + pK_a^R \quad (3)$$

where:

$$\Delta pK_a = pK_a^{AN} - pK_a^R \quad (4)$$

$$\Delta E_{1/2} = E_{1/2}^{AN} - E_{1/2}^R \quad (5)$$

pK_a^x is the pK_a value of picric acid in a mixture of acetonitrile with another solvent R (acetone or dimethyl sulfoxide in this case) whose concentration in the mixture is shown by the mole fraction x ; pK_a^R – the pK_a value of picric acid in solvent R; pK_a^{AN} – the pK_a value

of picric acid in acetonitrile; $E_{1/2}^x$ – the e.m.f. in solution containing equimolar quantities of picric acid and conjugate anion in a mixture of acetonitrile with solvent R of concentration x expressed in mole fraction; $E_{1/2}^R$ – the e.m.f. in solution of equimolar quantities of picric acid and conjugate anion in solvent R; $E_{1/2}^{AN}$ – the e.m.f. in solution of equimolar quantities of picric acid and conjugate anion in acetonitrile. In the next step, the rough pK_a^x values of picric acid estimated from (3) served as the basis for the determination of its precise value in the solvent mixture containing x acetonitrile by a procedure based on the ‘general’ method of Kostrowicki and Liwo [26–28]. For all the solvent mixtures investigated, as well as for their components, there was a linear relationship between e.m.f. and the logarithm of the concentration ratio of the components of the standardizing system and the slopes of the glass electrode characteristics were close to the theoretical Nernst value 59.14 mV. The pK_a^x values of picric acid determined in this way enabled to calibrate the measuring system in the solvent mixtures studied. Further, the s (slope of the glass electrode characteristics) and E^o (standard e.m.f.) values taken from the potentiometric titration curves in the standardizing system together with the results of titrations in the organic base systems (cationic acid conjugated with the base – the base) enabled the determination of the acid dissociation and cationic homoconjugation constant values in the solvent mixtures studied. They were determined by using the ‘general’ method of Kostrowicki and Liwo [26–28].

The pK_a values are easily determinable for the dimethyl sulfoxide – acetonitrile mixtures and are burdened with respectively small values of standard deviation (Table 1). Obviously, the standard deviation values are considerably greater than in the case of acidity constants determined in individual solvents. On the other hand, they are comparable and even smaller than those characteristic for acetonitrile – methanol solvent systems [12]. It is worth of pointing that the standard deviations in the solvent systems have to be increased by the respectively high inaccuracy of pK_a determination for substances used as potentiometric standards [11]. pK_a values determined in the dimethyl sulfoxide – acetonitrile mixtures increase from the values characteristic for dimethyl sulfoxide up to maximum ones in acetonitrile. The nature of these variations for all the bases studied is distinctly non-linear, the most pronounced variations being observed at low concentrations of dimethyl sulfoxide in acetonitrile. In systems involving the strongest bases, *e.g.* 4NMe₂PyO (*cf.* Fig. 1, plot a), the variations are less pronounced. They become still more pronounced in systems of lower basicity in such a manner that the pK_s ’s of the protonated bases in mixed solvent are lower than those in dimethyl sulfoxide, thus suggesting the existence of local minima of the pK_a values, especially for the weakest base studied, 4NO₂PyO (within the DMSO mole fraction range of 0.3 to 0.5; Fig. 1, plot b). Similar local minima have also been found in mixed solvents of the acetonitrile – methanol type [12]. In Fig. 1 (as well as in Fig. 3) the discussed experimental points are located beneath a straight line (dashed one) linking the pK_a values in acetonitrile and dimethyl sulfoxide (acetone in Fig. 3), which corresponds to pK_a values expected on the basis of the additivity rule.

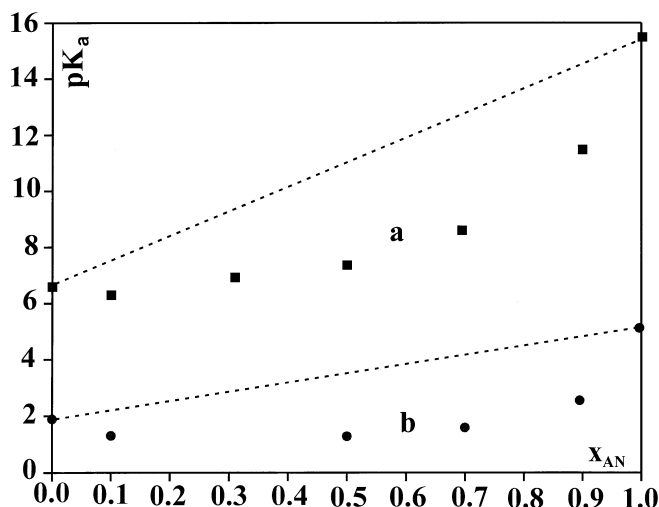


Figure 1. Plots of pK_a values of protonated 4-N',N'-dimethylaminopyridine N-oxide (plot a, squares) and protonated 4-nitropyridine N-oxide (plot b, circles) against composition of the binary solvent acetonitrile – dimethyl sulfoxide at 298.1 K.

The cationic homoconjugation constant values in the acetonitrile – dimethyl sulfoxide solvent systems are also collected in Table 1. Owing to strong basicity of dimethyl sulfoxide, addition of this solvent to acetonitrile characterized by relatively high homoconjugation constants (with the exception of the least basic $4NO_2PyO$) causes that hydrogen bond bridges in the homocomplexed BHB^+ ions are broken. The basicity of dimethyl sulfoxide and the inherent capacity of its molecules to solvate cationic acids, a process precluding the formation of homocomplexed cations, is so strong that the cationic homoconjugation constants in the acetonitrile – dimethyl sulfoxide systems are determinable only for two strongest bases, namely Me_3NO and $4NMe_2PyO$. However, for the latter base the constants could not be determined in mixtures at high dimethyl sulfoxide contents and in pure DMSO. Similar to the pK_a values, also the logarithms of the cationic homoconjugation constants are non-linear functions of composition of the solvent mixtures. With the Me_3NO system, they vary from the values characteristic for dimethyl sulfoxide up to the maximum ones in acetonitrile over the values lower than those in dimethyl sulfoxide (Fig. 2, plot a). This suggests the existence of a local minimum. Such a local minimum at *ca* 0.3 mole fraction of dimethyl sulfoxide is distinct in the $4NMe_2PyO$ system (Fig 2, plot b). Plot 2b leads to another interesting conclusion about the existence of a critical DMSO content in mixtures with acetonitrile, characteristic for a particular system, above which the cationic homoconjugation constants become indeterminable for a particular acid-base system. Consequently, in Fig. 3 the straight line (dashed one) linking the $\log K_{BHB^+}$ values in acetonitrile and dimethyl sulfoxide (acetone in Fig. 4) and corresponding to $\log K_{BHB^+}$ values expected on the basis of the additivity rule can be drawn for the Me_3NO system only.

Table 1. pK_a and $\log K_{\text{BHB}^+}$ values with their standard deviations, for protonated substituted pyridine N-oxides in acetonitrile – dimethyl sulfoxide binary solvents [$X_{\text{AN}} + (1 - X)_{\text{DMSO}}$] at 298.1 K. Those for quinoline N-oxide, trimethylamine N-oxide and pyridine are shown for comparison.

Constant N-oxide	DMSO		0.1		0.3		0.5		0.7		0.9		AN	
	pK_a	$K_{\text{BHB}^+}^a$	pK_a	$K_{\text{BHB}^+}^a$	pK_a	$K_{\text{BHB}^+}^a$	pK_a	$K_{\text{BHB}^+}^a$	pK_a	$K_{\text{BHB}^+}^a$	pK_a	$K_{\text{BHB}^+}^a$	pK_a	$K_{\text{BHB}^+}^a$
4NMe ₂ PyO	6.59 (0.23)	^b	6.29 (0.21)	^b	7.79 (0.33)	3.21 (0.17)	6.89 (0.46)	1.69 (0.93)	7.77 (0.15)	2.43 (0.06)	11.47 (0.26)	3.14 (0.03)	15.63 (0.28)	4.49 (0.05)
4PicO	2.92 (0.05)	^b	2.76 (0.08)	^b	2.64 (0.09)	^b	2.53 (0.13)	^b	3.15 (0.12)	^b	7.48 (0.53)	^b	10.63 (0.29)	3.60 (0.02)
PyO	1.55 (0.08)	^b	1.86 (0.21)	^b	1.54 (0.09)	^b	1.87 (0.23)	^b	2.43 (0.19)	^b	7.14 (0.39)	^b	9.03 (0.32)	3.28 (0.06)
4NO ₂ PyO	1.89 (0.24)	^b	1.56 (0.38)	^b	^b	^b	1.49 (0.14)	^b	1.59 (0.47)	^b	2.13 (0.43)	^b	4.75 (0.03)	^b
QNO	1.54 (0.19)	^b	1.49 (0.29)	^b	1.87 (0.02)	^b	1.68 (0.03)	^b	1.83 (0.43)	^b	7.56 (0.50)	1.48 (0.06)	9.17 (0.31)	2.85 (0.04)
Me ₃ NO	11.19 (0.02)	3.80 (0.02)	9.64 (0.06)	3.42 (0.01)	10.08 (0.50)	4.01 (0.07)	9.57 (0.32)	3.56 (0.04)	9.06 (0.28)	3.60 (0.09)	13.99 (0.56)	4.39 (0.10)	18.68 (0.24)	5.96 (0.29)
Py	3.83 (0.07)	^b	3.48 (0.07)	^b	2.43 (0.39)	^b	3.37 (0.05)	^b	6.07 (0.42)	^b	8.02 (0.20)	1.41 (0.38)	11.64 (0.26)	1.53 (0.72)

^aLogarithms of cationic homoconjugation constant values.

^bMissing values of homoconjugation constants could not be determined from potentiometric measurements.

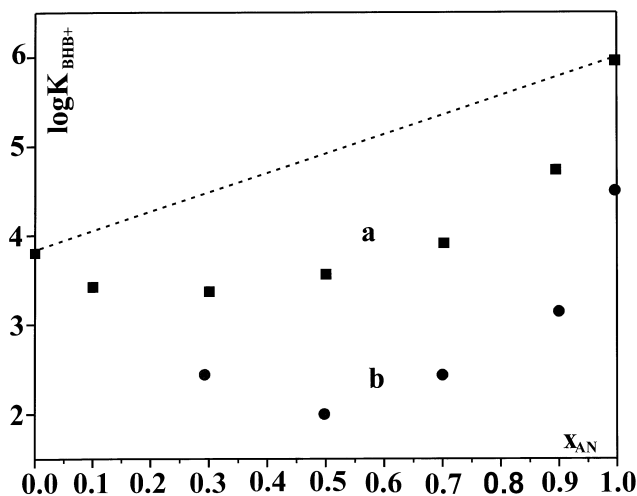


Figure 2. Plots of logarithms of the cationic homoconjugation constant for trimethylamine N-oxide (plot a, squares) and 4-N',N'-dimethylaminopyridine N-oxide (plot b, circles) against composition of the binary solvent acetonitrile – dimethyl sulfoxide at 298.1 K.

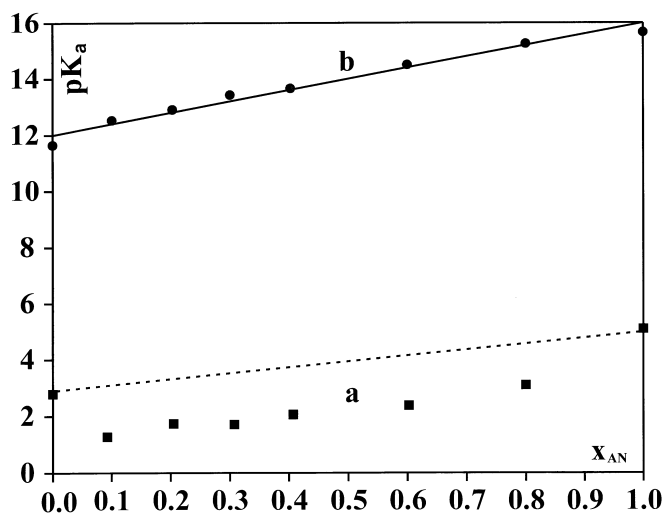


Figure 3. Plots of pK_a values of protonated 4-nitropyridine N-oxide (plot a) and protonated 4-N',N'-dimethylaminopyridine N-oxide (plot b) as a function of composition of the binary solvent acetonitrile – acetone at 298.1 K.

In the acetonitrile – acetone mixtures, the acid dissociation constants of the protonated bases decrease (higher pK_a 's) with increasing acetonitrile contents in the solvent mixture (Table 2). Only in the case of the strongest acid, protonated 4NO₂PyO (Fig. 3, plot a) the variations are strictly non-linear. In the remaining systems the values vary irregularly raising from a minimum for acetone to a maximum for acetonitrile. In this situation it is difficult to identify the nature of these variations, and the relation between pK_a and composition of the mixed solvent can roughly be described

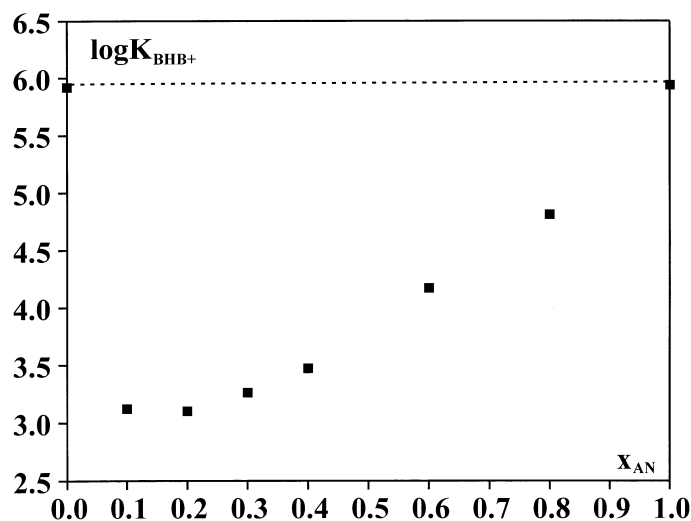


Figure 4. Plots of logarithms of the cationic homoconjugation constant for trimethylamine N-oxide as a function of composition of the binary solvent acetonitrile – acetone at 298.1 K.

by a straight line. In Fig. 3 (plot b) an example of linear relationship between pK_a values for protonated 4NMe₂PyO in binary solvent mixtures (pK_a^x) and their compositions expressed as mole fraction of acetonitrile (x_{AN}) is given:

$$pK_a^x = 3.8 (0.3) x_{AN} + 12.2 (0.2) \quad (6)$$

where the correlation coefficient R equals to 0.9780. Such a variability of the acid dissociation constant values of the protonated bases can be explained in terms of small differences in pK_a 's of these species in the two solvents, most probably attributable to the lack of distinct interactions between them. This lack of interactions, together with small differences in solvation capacities of acetonitrile and acetone, are responsible for the similar shape of variations also in the case of cationic homoconjugation constants. Clearly non-linear are only relationships for cationic homoconjugation constants of the most basic N-oxides (trimethylamine N-oxide and 4-N',N'-dimethylaminopyridine N-oxide), thus those of the most pronounced tendency to homoconjugation. In Fig. 4 the non-linear variation of $\log K_{BHB^+}$ for Me₃NO system from the values characteristic for dimethyl sulfoxide up to the maximum ones in acetonitrile through the local minimum at *ca* 0.15 mole fraction dimethyl sulfoxide is presented. Finally, it is worth noting that with small additions of one solvent to the other, in particular of acetonitrile to acetone (as clearly seen in Fig. 4), a considerable decrease in the constant values is observed, which subsequently increase up to comparable contents of both solvents. To sum up the above observations, it can be stated that the acid dissociation constants, expressed as pK_a values, have been found to vary in a non-linear manner with increasing mole fraction of acetonitrile in its mixture with dimethyl sulfoxide in all the acid-base sys-

Table 2. pK_a and $\log K_{BHB^+}$ values with their standard deviations, for protonated substituted pyridine N-oxides in acetonitrile–acetone binary solvents [$X_{AN} + (1 - X)_{AC}$] at 298.1 K. Those for quinoline N-oxide, trimethylamine N-oxide and pyridine are shown for comparison.

Constant N-oxide	AC		0.1		0.2		0.3		0.4		0.6		0.8		AN	
	pK_a	$K_{BHB^+}^a$	pK_a	$K_{BHB^+}^a$	pK_a	$K_{BHB^+}^a$	pK_a	$K_{BHB^+}^a$	pK_a	$K_{BHB^+}^a$	pK_a	$K_{BHB^+}^a$	pK_a	$K_{BHB^+}^a$	pK_a	$K_{BHB^+}^a$
4NMe ₂ PyO	11.65 (0.40)	4.54 (0.02)	12.53 (0.35)	4.19 (0.09)	13.27 (0.47)	4.07 (0.05)	13.43 (0.43)	4.13 (0.08)	13.87 (0.37)	4.27 (0.04)	14.50 (0.35)	4.52 (0.03)	15.26 (0.26)	4.48 (0.02)	15.63 (0.28)	4.59 (0.05)
4PicO	6.39 (0.01)	3.19 (0.01)	8.17 (0.34)	2.95 (0.03)	4.49 (0.24)	^b	8.19 (0.18)	3.02 (0.01)	9.92 (0.10)	3.37 (0.01)	10.10 (0.38)	3.25 (0.03)	11.85 (0.35)	3.17 (0.03)	10.63 (0.29)	3.60 (0.02)
PyO	5.11 (0.02)	2.69 (0.02)	5.78 (0.15)	2.66 (0.06)	8.47 (0.24)	2.06 (0.07)	6.90 (0.17)	2.52 (0.02)	9.66 (0.39)	2.45 (0.07)	9.07 (0.20)	3.01 (0.02)	11.23 (0.18)	2.99 (0.02)	9.03 (0.23)	3.28 (0.06)
4NO ₂ PyO	2.79 (0.02)	^b	0.76 (0.53)	^b	2.50 (0.09)	^b	2.27 (0.13)	^b	2.62 (0.20)	^b	2.83 (0.06)	^b	3.09 (0.09)	^b	4.75 (0.03)	^b
QNO	6.0 (0.01)	^b	7.15 (0.67)	^b	8.01 (0.42)	^b	7.23 (0.10)	2.92 (0.09)	8.03 (0.68)	2.80 (0.09)	8.04 (0.42)	2.69 (0.06)	10.31 (0.30)	2.90 (0.04)	9.17 (0.31)	2.85 (0.04)
Me ₃ NO	14.42 (0.21)	5.92 (0.04)	12.96 (0.48)	3.12 (0.05)	13.31 (0.31)	3.10 (0.02)	13.20 (0.49)	3.26 (0.04)	14.82 (0.45)	3.47 (0.04)	15.27 (0.37)	4.17 (0.11)	16.47 (0.43)	4.81 (0.22)	18.68 (0.24)	5.96 (0.29)
Py	6.79 (0.01)	^b	9.43 (0.46)	^b	7.20 (0.27)	^b	9.57 (0.26)	^b	11.37 (0.12)	1.77 (0.06)	11.59 (0.15)	2.48 (0.02)	13.91 (0.41)	1.65 (0.33)	11.64 (0.26)	1.53 (0.72)

^aLogarithms of cationic homoconjugation constant values.^bMissing values of homoconjugation constants could not be determined from potentiometric measurements.

tems studied. In systems with the least basic N-oxides, local minima of the pK_a values have been observed. At the same time it was found that the cationic homoconjugation constants were determinable over the whole variability region of composition of these solvent mixtures only in the case of the most basic trimethylamine N-oxide. Their variations, similar to those of the acid dissociation constants, were non-linear. With the acetonitrile-acetone mixtures, both the pK_a and the cationic homoconjugation constant values changed irregularly in the acid-base systems studied and the character of those variations could not be unambiguously determined. A strictly non-linear course of the variations of the dissociation constants as a function of composition of the solvent mixtures could only be noticed with a cationic acid obtained by protonation of the least basic 4-nitropyridine N-oxide. In contrast, distinctly non-linear were variations of the cationic homoconjugation constants for the most basic N-oxides studied.

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REFERENCES

1. Bosch E., Rafols C. and Roses M., *Anal. Chim. Acta*, **302**, 109 (1995).
2. Rochester C.H. and Sclosa S.A., *J. Chem. Soc. Farad. Trans. I*, **75**, 2781 (1979).
3. Nowak B. and Pawlak Z., *J. Chem. Soc. Farad. Trans. I*, **79**, 2693 (1982).
4. Paabo M., Bates R.G. and Robinson R.A., *J. Phys. Chem.*, **70**, 247 (1966).
5. Alfenaar M and De Ligny C.L., *Rec. Trav. Chim.*, **86**, 926 (1967).
6. Leśniewski B., Pawlak Z. and Przybyszewski B., *J. Chem. Soc. Farad. Trans. I*, **80**, 1769 (1984).
7. Halle J.C. and Schard R., *Anal. Chim. Acta*, **60**, 197 (1972).
8. Ballash N.M., Robertson E.B. and Sokołowska M.D., *J. Chem. Soc. Farad. Trans. I*, **66**, 2622 (1970).
9. Bates R.G. and Pawlak Z., *J. Chem. Soc.*, **5**, 513 (1976).
10. Rochester C.H. and Wilson D.N., *J. Chem. Soc. Farad. Trans. I*, **72**, 2930 (1976).
11. Wróbel R. and Chmurzyński L., *Anal. Chim. Acta*, **405**, 303 (2000).
12. Wróbel R., Kaczmarczyk E. and Chmurzyński L., *J. Chem. Thermodyn.*, **31**, 1 (1999).
13. Barthel J., Wachter R. and Gores H.H., *Modern Aspects of Electrochemistry*, **13**, Plenum Publ. Corp. 1979, pp. 112–114.
14. Kolthoff I.M., *Anal. Chem.*, **46**, 1992 (1974).
15. D'Aprano A. and Donato I.D., *J. Chem. Soc. Farad. Trans. I*, **69**, 1685 (1973).
16. Parker A.J., *Chem. Rev.*, **69** (1969).
17. Bruss D.S. and Harlow G., *Anal. Chem.*, **30**, 1836 (1958).
18. Chmurzyński L., Wawrzynów A. and Pawlak Z., *Electrochim. Acta*, **35**, 665 (1990).
19. Chmurzyński L. and Warnke Z., *Austral. J. Chem.*, **46**, 237 (1993).
20. Chmurzyński L. and Liwo A., *J. Chem. Soc. Farad. Trans.*, **87**, 3858 (1991).
21. Szafran M., *Polish J. Chem.*, **52**, 2491 (1978).
22. Chmurzyński L., Wawrzynów A. and Pawlak Z., *J. Chem. Soc. Farad. Trans. I*, **85**, 4269 (1989).
23. Kolthoff I.M. and Chantooni M.K., Jr., *J. Am. Chem. Soc.*, **87**, 4428 (1965).
24. Coetzee J.M. and Padmanabhan G.R., *J. Phys. Chem.*, **66**, 1708 (1962).
25. Kolthoff I.M., Chantooni M. K., Jr. and Bhowmik S., *J. Am. Chem. Soc.*, **90**, 23 (1968).
26. Kostrowicki J. and Liwo A., *Comput. Chem.*, **8**, 91, 101 (1984).
27. Kostrowicki J. and Liwo A., *Comput. Chem.*, **11**, 195 (1987).
28. Kostrowicki J. and Liwo A., *Talanta*, **87**, 645 (1990).