

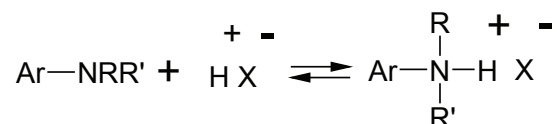
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Dvoryanskaya str. 2, 65082, Odessa, alexch@ukr.netTHE ELECTRON DONATING PROPERTIES
OF NITROGEN-CONTAINING ORGANIC BASES IN MIXED MEDIA

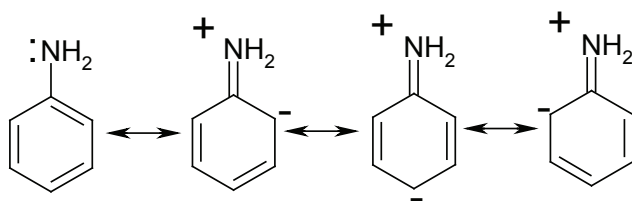
The thermodynamic ionization constants of aniline, pyridine and octylamine in water-dimethylformamide and water-dioxane media were determined by potentiometric titration method. Mathematical models that adequately describe the change of the nitrogen-containing organic bases pK were constructed by varying characteristics of chemical systems.

Key words: nitrogen-containing organic bases, ionization constants, mathematical modeling.

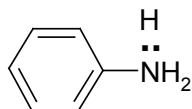
The nitrogen-containing organic bases (**NOB**) have pronounced electron donating properties, manifested in their basic nature. The basic properties of NOB are caused by the existence of nitrogen atom lone electron pair. Aliphatic amines are strong bases that easily attach a proton. Aromatic amines are weaker bases, than the aliphatic. Proton is connecting to the nitrogen atom:



Nitrogen atom in aniline is attached to sp^2 - hybridized carbon atom, however, what is more important is that its lone electron pair can interact with delocalized π -orbitals of aromatic rings.

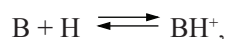


Any such interaction in anilinium-cation that was produced by protonation of aniline is prohibited, if it's leading to stabilization, because e-pair on nitrogen atom ceases to be free:



As a result an aniline molecule is more stable than anilinium-cation. Because of this, protonating isn't "profitable" for aniline energetically. In the case of heteroaromatic NOB, e.g. pyridine, nitrogen atom is in sp^2 - hybridized state and gives one electron to the system of 6π -electrons and at the same time a lone pair of electrons remains in the nitrogen atom (located on sp^2 - hybridized orbital), so that pyridine is base. Its basicity is lower than the basicity of aliphatic amines. That low basicity is typical for the bases where nitrogen atom is connected by multiple connections. This is explained by the fact that nitrogen atom lone electron pair is located on the orbital increasingly approaching in nature to the s-orbital, as the multiplicity of relations in it. This electron pair moves closer to the nucleus of nitrogen atom, in consequence of which it becomes less available for making connection with proton, and that leads to a basicity decrease in connection.

According to the Brønsted-Lowry theory of protolytic equilibrium in solutions NOB can be described by the following scheme:



and can be described the corresponding ionization constant (**pK**). The pK values are defined only in the aqueous or non-aqueous solvents for many amines. The study of NOB electron donating abilities changes in mixed media of different nature is especially interesting, because it is necessary to operate their pK values in a wide range of temperatures and organic solvents content, that are affecting their power figures, to create simple differentiated methods for NOB determination. The acquisition of required experimental data is difficult because of e.g. measurements at the level of devices uncertainty, which leads to the questionable reliability of the obtained results. In these cases, the actual problem is the creating of mathematical models [1] describing the protolytic properties changes of researched nitrogen-containing toxicants by varying the composition and characteristics of the solution [2, 3].

We have chosen the representatives of the different NOB classes: aniline (**AN**), pyridine (**Py**) and octylamine (**OA**) as objects of study, because of their heavy tonnage production, widespread use in various industries. The main aim of this work was the protolytic properties study of NOB data in mixed media, as well as the identification of existing mathematical regularities.

Materials and methods

Previously all NOB were distilled under vacuum, the purity of obtained fractions was controlled by the refraction index. The series of 0,1M water-organic NOB solutions with the content of dioxane (DO) or dimethylformamide (DMF) 10, 20, 40, 50, 70 vol.% were preparing for pK determination in mixed solvents. All the measurements were carried out in isothermal conditions and the range of temperatures of $20\div 40^\circ\text{C}$ degrees, every 5°C degrees. Ionometer И-130 and electrode pair (glass electrode ЭСЛ-43-07 and silver chloride reference electrode ЭБЛ-1М3), previously was calibrated with standard buffer solutions. We introduced NOB solution (20ml 0,01M) in the dry glass, let down the electrodes and titrated by 0,1M chloride acid solution of 0,1 ml doses, and near the point of equivalence of 0,05ml. The given temperature was maintained with accuracy of $\pm 0,1^\circ\text{C}$ degrees by thermostat UTU-4. The equilibrium was established after titrant adding, and then we were taking readings and continuing titration until the establishment of permanent pH values. The pK values were determined according to Albert and Sergeant [4].

The dielectric permittivity of studied water-organic solutions was calculated according to Silberstein equation at the corresponding temperature (table 1):

$$\varepsilon' = \frac{V}{100} \varepsilon_1 + \frac{100-V}{100} \varepsilon_2,$$

where ε' - dielectric permittivity of the solution, V and ε_1 - the volume and dielectric permittivity of the organic solvent, $100 - V$ and ε_2 - volume and dielectric permittivity of water.

Table 1

Dielectric permittivity of water-dimethylformamide and water-dioxane solutions

| The c-n. of org. solv., % | Dielectric permittivity | | | | | | | | | |
|---------------------------|-------------------------|-------|-------|-------|-------|---------------------|-------|-------|-------|-------|
| | H ₂ O-DMF | | | | | H ₂ O-DO | | | | |
| | 20°C | 25°C | 30°C | 35°C | 40°C | 20°C | 25°C | 30°C | 35°C | 40°C |
| 10 | 76,93 | 74,18 | 72,51 | 70,94 | 69,24 | 72,38 | 70,74 | 69,14 | 67,67 | 66,05 |
| 20 | 71,67 | 70,01 | 68,43 | 66,96 | 65,40 | 64,59 | 63,14 | 61,70 | 60,39 | 58,94 |
| 40 | 63,17 | 61,68 | 60,29 | 58,98 | 57,65 | 49,02 | 47,92 | 46,82 | 45,85 | 44,73 |
| 50 | 58,92 | 57,53 | 56,37 | 55,00 | 53,78 | 41,24 | 40,32 | 39,39 | 38,57 | 37,63 |
| 70 | 50,41 | 49,19 | 48,08 | 47,02 | 46,03 | 25,60 | 25,11 | 24,51 | 24,02 | 23,41 |

The amendment was introduced that taking into account the composition of water-organic systems, because of different scales of acidity for aqueous and non-aqueous solutions [5]. All used reagents had qualifications not lower than «for analysis». The received results were treated by methods of mathematical statistics.

Results and discussion

As a result of our research work we investigated the acid-basic NOB properties in the water-dimethylformamide (H₂O-DMF) and water-dioxane (H₂O-DO) solutions by varying the content of organic solvent and the temperature of the system and determined the pK values (table 2).

It was showed that the changes of acid-basic properties of studied NOB are described by the equations of the surface of the first order on the basis of the data (table 3) using mathematical modeling methods.

The obtained mathematical models are characterized by the small value of the relative error, on average not exceeding 3,63%, and this allows us to conclude that they adequately describe changes in acid-base properties of studied NOB by varying the temperature and composition of the system.

Table 2

The ionization constants of nitrogen-containing organic bases in mixed media

| The c-n. of org. solv., % | pK | | | | | | | | | |
|---------------------------------|----------------------|-----------|-----------|-----------|-----------|---------------------|-----------|-----------|-----------|-----------|
| | H ₂ O-DMF | | | | | H ₂ O-DO | | | | |
| | 20° | 25° | 30° | 35° | 40° | 20° | 25° | 30° | 35° | 40° |
| | Aniline | | | | | | | | | |
| 10 | 3,51±0,03 | 3,55±0,07 | 3,59±0,05 | 3,66±0,03 | 3,71±0,06 | 3,61±0,02 | 3,67±0,01 | 3,70±0,01 | 3,76±0,04 | 3,78±0,03 |
| 20 | 3,37±0,02 | 3,40±0,04 | 3,47±0,01 | 3,52±0,02 | 3,57±0,06 | 3,53±0,02 | 3,59±0,03 | 3,67±0,03 | 3,72±0,05 | 3,76±0,03 |
| 40 | 3,27±0,01 | 3,33±0,04 | 3,37±0,03 | 3,43±0,02 | 3,45±0,03 | 3,26±0,03 | 3,30±0,06 | 3,35±0,04 | 3,39±0,02 | 3,43±0,03 |
| 50 | 3,19±0,02 | 3,21±0,03 | 3,28±0,03 | 3,33±0,05 | 3,39±0,03 | 3,07±0,04 | 3,15±0,03 | 3,21±0,04 | 3,24±0,06 | 3,29±0,03 |
| 70 | 2,92±0,06 | 2,97±0,04 | 3,01±0,02 | 3,05±0,03 | 3,13±0,05 | 2,67±0,06 | 2,72±0,05 | 2,79±0,03 | 2,82±0,02 | 2,87±0,04 |
| | Pyridine | | | | | | | | | |
| 10 | 3,76±0,02 | 3,85±0,02 | 3,93±0,06 | 3,99±0,03 | 4,01±0,03 | 3,83±0,05 | 3,73±0,03 | 3,61±0,05 | 3,45±0,01 | 3,31±0,03 |
| 20 | 3,68±0,06 | 3,74±0,03 | 3,81±0,05 | 3,85±0,02 | 3,92±0,04 | 3,71±0,07 | 3,54±0,05 | 3,35±0,07 | 3,22±0,02 | 3,08±0,08 |
| 40 | 3,46±0,03 | 3,53±0,03 | 3,62±0,04 | 3,65±0,05 | 3,71±0,03 | 3,20±0,05 | 3,10±0,02 | 2,92±0,03 | 2,84±0,05 | 2,63±0,03 |
| 50 | 3,33±0,05 | 3,38±0,02 | 3,42±0,03 | 3,48±0,04 | 3,53±0,05 | 3,03±0,02 | 2,94±0,03 | 2,75±0,05 | 2,64±0,03 | 2,38±0,06 |
| 70 | 3,14±0,04 | 3,21±0,02 | 3,26±0,07 | 3,30±0,06 | 3,34±0,04 | 2,67±0,07 | 2,51±0,05 | 2,40±0,03 | 2,28±0,02 | 2,13±0,04 |
| | Octylamine | | | | | | | | | |
| 10 | 9,04±0,05 | 8,90±0,03 | 8,85±0,01 | 8,80±0,03 | 8,74±0,06 | 9,96±0,04 | 9,75±0,07 | 9,47±0,01 | 9,15±0,04 | 8,94±0,02 |
| 20 | 8,97±0,07 | 8,86±0,03 | 8,82±0,02 | 8,75±0,01 | 8,67±0,06 | 9,01±0,03 | 8,70±0,02 | 8,45±0,02 | 8,18±0,04 | 8,04±0,07 |
| 40 | 8,92±0,05 | 8,83±0,01 | 8,81±0,03 | 8,72±0,03 | 8,63±0,05 | 8,91±0,03 | 8,65±0,04 | 8,40±0,01 | 8,13±0,05 | 7,91±0,02 |
| 50 | 8,87±0,07 | 8,79±0,05 | 8,75±0,02 | 8,68±0,02 | 8,60±0,01 | 8,85±0,02 | 8,49±0,02 | 8,33±0,01 | 8,10±0,03 | 7,76±0,05 |
| 70 | 8,82±0,03 | 8,75±0,06 | 8,69±0,04 | 8,62±0,03 | 8,57±0,05 | 8,60±0,03 | 8,38±0,02 | 8,21±0,06 | 7,90±0,05 | 7,62±0,05 |

Data analysis of mathematical models has showed that the temperature and the content of organic solvent in the solution influence equally on pK values of AN and Py in these systems, but the temperature significantly influences on pK values of AO. The coefficients' value and the signs point at orientation of the functional relation of $pK = f(T, C)$, which is the surface of the first order (i.e. plane) in three-dimensional space.

Table 3
The relation between electron-donor properties of nitrogen-containing organic bases, the concentration of the organic component in mixed media and temperature of system

| H ₂ O – DMF | | H ₂ O – DO | |
|------------------------------------|-------------------|------------------------------------|-------------------|
| Mathematical model | D ₀ ,% | Mathematical model | D ₀ ,% |
| Aniline | | | |
| $pK = 3,4083 - 0,0098C + 0,0100t$ | 1,66 | $pK = 3,5967 - 0,0157C + 0,0085t$ | 2,56 |
| Pyridine | | | |
| $pK = 3,6133 - 0,0103C + 0,0125t$ | 1,02 | $pK = 4,5633 - 0,0193C - 0,0270t$ | 1,51 |
| Octylamine | | | |
| $pK = 9,3267 - 0,0037C - 0,01250t$ | 1,3 | $pK = 11,1667 - 0,0227C - 0,0490t$ | 3,63 |

The graphic dependence of NOB from the inverse of the dielectric permittivity was built of H₂O-DMF (Fig. 1 a,b,c) and H₂O-DO (Fig. 2 a,b,c) solutions to study the influence of nature and physico-chemical features of medium on the acid-base properties of NOB.

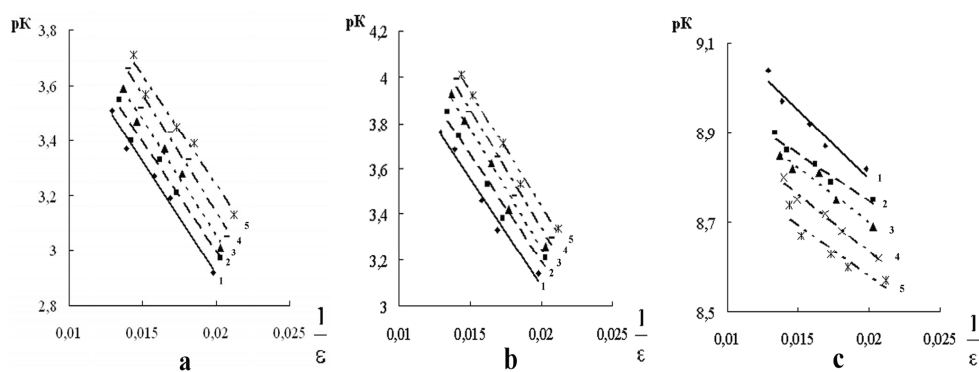


Fig. 1. The relation between NOB pK and the inverse of the dielectric permittivity of: a – system H₂O-DMF-AN; б – system H₂O-DMF-Py, в – system H₂O-DMF-OA; 1-20; 2-25; 3-30; 4-35; 5-40°C.

The dependence of NOB pK values and $1/\epsilon$ in the H₂O-DMF solutions (figure 1 a,b,c) tends to linear ($R^2 0,96\div 0,98$) for all temperatures, which corresponds with the Izmailov

theory [6]. The linear dependence shows the fact that the change of the components ratio and, as a result, the whole dielectric permittivity of the medium did not lead to significant changes in solvation characteristics of the DMF regarding studied NOB irrespective of their nature.

The depending series AN→Py→OA on fig. 2 (a, b, c) gradually distorted down to the lack of linearity ($R^2 0,36 \div 0,45$) for OA in the system H₂O-DO (fig. 2 c), that can be associated with substitute of solvent DMF to DO, which has some physical and chemical characteristics and solvation ability. It significantly influences on changes of pK values of DO dielectric permittivity. Of special note is that the traced functional dependence in system H₂O-DO-AN(fig.2a) significantly disturbed in the case of H₂O-DO-Py (fig. 2b), and for system H₂O-DO-OA (fig. 2c) there has been a change in the course of the curve, which manifests itself in the presence of two distinct areas of different directions with respect to the x-axis. So the first area is characterized by a sharp decrease in pK value of (the content is up DO<40 vol.%) and almost parallel to the vertical axis, and the second one with almost a straight-line course and a slight angle on the x-axis is accompanied by a smooth pK change of NOB. Such behavior of Py and OA can be explained by analyzing the number of hydrophilic-lipophylic balance (HLB) [7] of studied NOB.

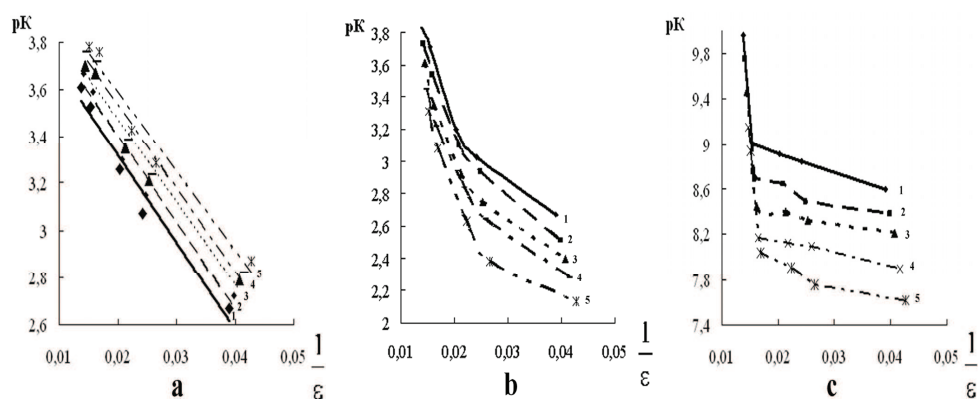


Fig. 2. The relation between NOB pK and the inverse of the dielectric permittivity of: a – system H₂O-DO-AN; б – system H₂O-DO-Py, в – system H₂O-DO-OA; 1-20; 2-25; 3-30; 4-35; 5-40°C.

In series of Py→AN→OA the value of HLB respectively decreases (3,54→3,44→2,48). Although, the HLB value for Py is a few bigger than for AN and we would expect the linear dependence for both amines in the H₂O-DO solutions. However, we have also to take into account the geometry of molecules, which influences on behavior of solvation processes and the distortion of functional dependence progress for Py (fig 2b). In the case of OA the smallest HLB value causes affinity to the interaction of the OA carbon chain with apolar DO. The capability of AO to change their spatial configuration that depends on the nature of media also influences on the process of its solvation, which leads to the significant weakening of electron-donor properties of OA (table 2).

So the thermodynamic ionization constants of AN, Py and OA were defined by potentiometric titration method in H₂O-DMF and H₂O-DO media by different concentrations of organic solvent in the temperature range of 20÷40°C degrees. It

was shown that the studied NOB nature, physico-chemical properties of media and the temperature influenced on nature and electron-donor ability ratio of change. The mathematical models were constructed, which adequately describe the change of the pK by varying characteristics of the system. On the basis of the obtained models the influence of the organic solvent content and the temperature of system on protolytic properties of studied NOB. It was established, that the linearity of $pK=f(1/\epsilon)$ is observed only in those mixed media, the changing composition of which didn't lead to significant changes in the solvation characteristics of components of the media.

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ЕЛЕКТРОНОДОНОРНІ ВЛАСТИВОСТІ НІТРОГЕНВІСНИХ ОРГАНІЧНИХ ОСНОВ У ЗМІШАНИХ СЕРЕДОВИЩАХ

Резюме

Методом потенціометричного титрування визначені термодинамічні константи іонізації аніліну, піридину і октиламіну в водно-диметилформамідних і водно-діоксанових середовищах. Побудовано математичні моделі, які адекватно описують зміну величин рК нітрогеновмісних органічних основ при варіюванні характеристик хімічних систем.

Ключові слова: нітрогеновмісні органічні основи, константи іонізації, математичне моделювання.

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ЭЛЕКТРОНОДОНОРНЫЕ СВОЙСТВА АЗОТСОДЕРЖАЩИХ ОРГАНИЧЕСКИХ ОСНОВАНИЙ В СМЕШАННЫХ СРЕДАХ

Резюме

Методом потенциометрического титрования определены термодинамические константы ионизации анилина, пиридина и октиламина в водно-диметилформамидных и водно-диоксановых средах. Построены математические модели, адекватно описывающие изменения величин рК азотсодержащих органических оснований при варьировании характеристик химических систем.

Ключевые слова: азотсодержащие органические основания, константы ионизации, математическое моделирование.