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Specificity of Interionic Interaction As a Factor in the Selective Extraction of "Soft" Anions from Aqueous Media Using 2(4)-Octylaminopyridines

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Abstract—The specificity of interionic interaction in associates with inorganic anions is discussed, based on results from physical studies of 2(4)-octylaminopyridine (2(4)-OAP) salts and their distribution in a water–chloroform two-phase system. The redistribution of electron density in the aromatic cation as a function of the nature of the anion is attributed to observed violations of the order of anion exchange extraction and the selectivity of the extraction of "soft" anions (according to Pearson) with 2(4)-OAPs from aqueous media.

INTRODUCTION

Because they exhibit a number of new and interesting properties, aromatic amines (AAs) are more promising extractants than aliphatic amines and quaternary ammonium bases (QABs) [1]. The specificity of AAs as potential coordination-active reagents was discussed in [2]. The laws governing the anion-exchange extraction with AAs are still poorly understood. Results from studying extractant 2-octylaminopyridine (2-OAP) show [3, 4] that the relationships characteristic of the extraction of anions with aliphatic amines and QABs are in this case violated [5–7]. Other processes with the participation of aromatic cations show emergent properties [8, 9]. It was therefore of interest to study the specificity of interionic interaction, which affects the selectivity of the extraction of "soft" anions (according to Pearson) with AAs using the example of 2(4)-OAPs, which are increasingly used for the extractive isolation and separation of platinum and other rare metals (particularly iridium and rhodium) from aqueous solutions of complex compositions [10, 11].

EXPERIMENTAL

Reagents and Equipment

The reagents used in this work were 4-aminopyridine (98%, Acros Organics), sodium amide (99%, Acros Organics), octyl iodide (98%, Acros Organics), dioxane (analytical grade), chloroform (reagent grade), ethyl alcohol (rectified), hexane (high-purity grade), isopropyl alcohol (reagent grade), acetic acid (reagent grade), hydrochloric acid (reagent grade), hydrobromic acid (reagent grade), hydroiodic acid (reagent grade), perchloric acid (analytical grade), potassium hydroxide (analytical grade), and bidistilled water H_2O prepared using a laboratory distillation apparatus.

Reagent-grade KX ($X = F^-$, Cl^-, Br^-, NO_3^-), NH_4SCN, and $NaClO_4$ salts were dried in a vacuum at $60–70°C$ before preparing solutions.

2-Octylaminopyridine and 4-OAP were synthesized as described in [12] and [13], respectively. The 2(4)-OAP halides and the $(2\text{-OAP})^+[GaCl_4]^-$ associate were prepared by shaking a 0.2 mol/L 2(4)-OAP solution in chloroform with concentrated solutions of hydrohalic acids and a 2 mol/L gallium(III) solution in 6 mol/L HCl, respectively, until the organic phase was saturated. Chloroform was evaporated from the extract, and the residue was dried in a vacuum to remove the solvent.

2-Aminopyridine (2-AP) hydrochloride was synthesized by saturating a 2-AP solution in chloroform with dry hydrogen chloride. The solvent was evaporated in a vacuum. The 2-AP and 2(4)-OAP salts were identified according to the content of mineral acids.

Volumes of liquids were sampled using analytical graduated vessels. The weights of the substances were measured on a Nevskie VSL-200/0.1A analytical balance.

Potentiometric measurements were made at temperatures of 20 ± 2°C using a Multitest KSL-101 potentiometer and hydrogen and silver chloride glass reference electrodes. SF-16 and UV-1800 spectrophotometers (Shimadzu) with quartz cells ($l = 1$ cm) were used to record the electronic spectra and measure the absorbance of the solutions.

Infrared (IR) spectra were recorded on a Nicolet IS 10 Fourier transform IR spectrometer equipped with a SMART attachment (germanium crystal).

Proton magnetic resonance (PMR) spectra were recorded on a Bruker MSL-300 pulsed Fourier transform spectrometer with an operating frequency of 300 MHz. To do so, we prepared 0.1 mol/L solutions of samples in deuterated chloroform with tetramethylsilane as an internal standard.

Electron spectroscopy for chemical analysis (ESCA) spectra were recorded on a Riber SIA-200 spectrometer.

Extraction

2(4)-Octylaminopyridines are organic bases. The distribution of 2(4)-OAP in a water (HCl)–chloroform two-phase system was studied in [14], where the example of experimentally determined constants was used to show the extraction of acids with 2(4)-OAP via neutralization and extraction through anion exchange are described by similar equations, as with aliphatic amines [7]. It is noteworthy that the hyperstoichiometric extraction of HCl is weak with 2-OAP (about 30% from 12 mol/L HCl), but it is 100% from 6 M HCl when using 4-OAP.

The laws governing anion exchange extraction were studied using 2-AP and 4-OAP. With 2-OAP, the hydrophobic octyl radical was removed while keeping the active site of the reagent unchanged to reduce the extraction of the amine salt into the low-polar organic phase and eliminate possible effects of the association and aggregation of the extracted compounds. The extractability of anions with 2(4)-OAP was characterized by constants of the distribution of the corresponding salts in a two-phase water–chloroform system, proportional to the respective exchange constants.

The amine distribution between phases can be described by the equation

$$Am_0 + H_w^+ + A_w^- \leftrightarrow (AmH^+A^-)_0 + AmH_w^+. \quad (1)$$

The extraction of singly charged anions with 0.1 mol/L 2-AP in chloroform was studied at 25 ± 2°C; a 30 min duration of phase contact, which was sufficient for establishing equilibrium; an equal ratio of aqueous and organic phases; and an identical ionic strength produced by 0.2 mol/L KX (X = F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, SCN⁻, ClO₄⁻) and 0.3 mol/L H₃PO₄. The phases were separated via centrifugation. 2-Aminopyridine transitioned almost entirely into the aqueous phase, where it was protonated, while the AmH⁺A⁻ associate transitioned into the organic phase. The concentration of protonated amine in the organic phase after extraction was found spectrophotometrically at a wavelength of 300 nm using calibration curve

$$C_{AmH_0^+} = (19.2A + 0.16) \times 10^{-5} \quad (R = 0.999) \quad mol/L,$$

where A is the absorbance of the extract. A 0.001 mol/L 2-AP hydrochloride solution in chloroform was used as the standard solution. The reference solution was chloroform preliminarily subjected to contact (30 min) with an aqueous phase solution of the same composition as the one used in our experiments on distribution.

The extraction of singly charged anions with 1×10^{-4} mol/L 4-OAP in chloroform was studied at 25 ± 2°C, a 30 min duration of phase contact, an equal ratio of aqueous and organic phases, and an identical ionic strength produced by 1×10^{-3} mol/L KX (X = F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, SCN⁻, ClO₄⁻) and 1×10^{-2} mol/L H₃PO₄. The phases were separated via centrifugation. The concentration of protonated amine in the aqueous phase after extraction was found spectrophotometrically at a wavelength of 270 nm using calibration curve

$$C_{AmH_w^+} = (0.178A + 0.052) \times 10^{-5} \quad (R = 1) \quad mol/L,$$

where A is the absorbance of the extract. A 1×10^{-4} M 4-OAP solution in 0.01 M phosphoric acid was used as the standard solution. The reference solution was chloroform preliminarily subjected to 30 min of contact with an aqueous phase solution of the same composition as the one used in our experiments on distribution. The choice of initial concentrations of amine, salts, and phosphoric acid was due to the conditions of the spectrophotometric determination of protonated amine in the aqueous or organic phase.

The constants of the distribution of 2-APH⁺A⁻ salts were calculated according to the equation

$$\begin{aligned} K_{AmH^+X^-} &= \frac{[AmH^+X^-]_0}{[AmH^+]_w[X^-]_w} \\ &= \frac{C_{AmH_0^+}}{(C_{Am}^0 - C_{AmH_0^+})(C_{KX}^0 - C_{AmH_0^+})}, \end{aligned} \quad (2)$$

since almost all of the 2-AP was in cationic form, and the only species in the organic phase was AmH⁺X⁻ salt (our experiment showed that the extraction of phosphate ions can be ignored). Here, C_{Am}^0 (0.1 mol/L) and $C_{AmH_0^+}$ are the concentration of 2-AP in the organic phase before and after extraction, respectively, and C_{KX}^0 (0.2 mol/L) is the concentration of the respective salt in the aqueous phase before extraction.

Table 1. Constants of the distribution of salts 2-AP (25 ± 2°C, $\mu \approx 2$) and 4-OAP (25 ± 2°C, $\mu \approx 0.12$) between chloroform and water and thermodynamic characteristics of anion hydration in infinitely dilute solutions at 298 K [15]

Anion, X^-	$\log K_{AmH^+X^-}$		$-\Delta H_h$, kcal/mol	$-\Delta S_h$, kcal/(mol deg)	$-\Delta G_h$, kcal/mol	R, Å
	2-AP	4-OAP				
I^-	-2.32 ± 0.05	3.84 ± 0.04	67	8.05	64	—
SCN^-	-2.74 ± 0.06	3.65 ± 0.03	74	20*	68	1.95
ClO_4^-	-3.13 ± 0.10	3.63 ± 0.04	54	13.30	50	2.36
Br^-	-3.24 ± 0.05	3.12 ± 0.03	76	13.42	72	—
NO_3^-	-3.27 ± 0.04	2.99 ± 0.02	74	16.90	69	1.89
Cl^-	-3.31 ± 0.07	2.48 ± 0.02	84	17.10	79	—
F^-	-3.35 ± 0.09	1.63 ± 0.01	116	30.70	107	—

* Calculated from correlation dependence $\Delta S_h = f(R, Å)$, where R is the radius of polyatomic ions in water [15].

Constants of the distribution of 4-OAP salts were calculated according to results from the spectrophotometric determination of the protonated amine concentration in the aqueous phase:

$$K_{AmH^+X^-} = \frac{[AmH^+X^-]_0}{[AmH^+]_w[X^-]_w}$$
$$= \frac{(C_{Am}^0 - C_{AmH_w^+})}{C_{AmH_w^+}(C_{KX}^0 - C_{Am}^0 + C_{AmH_w^+})}. \quad (3)$$

Here, C_{Am}^0 (1×10^{-4} mol/L) and $C_{AmH_w^+}$ are the concentrations of 4-OAP in the organic and aqueous phases before and after extraction, respectively, and C_{KX}^0 (1×10^{-3} mol/L) is the concentration of the respective salt in the aqueous phase before extraction.

Results from determining constants as the average of ten experiments are shown in Table 1. The order of exchange extraction for the extraction of singly charged anions with 2(4)-OAP has the form

$$F- < Cl^- < NO_3^- < Br^- < ClO_4^- < SCN^- < I^-.$$
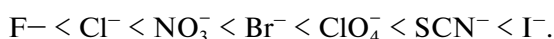
Spectroscopy

Our synthesized 2(4)-OAP halides and (2-OAPH$^+$)[GaCl$_4$]$^-$ associate were used as models of extracted compounds for physical studies. 2(4)-Octylaminopyridine and the synthesized compounds were studied via ESCA and IR and PMR spectroscopy.

N_{1s} bonding energy (eV) for 2(4)-OAPs and their chlorides are given below:

	2-OAP	4-OAP	2-OAP·HCl	4-OAP·HCl
N_{Py}	399.2	397.5	401	401
N_{Am}	399.2	400	399.9	399

The energy profile maxima were found separately for heterocyclic and amine nitrogen by decomposing the total curve into individual components, as shown in Fig. 1. The N_{1s} level of 2-OAP is degenerate (its maxima coincide), but the degeneracy is removed upon protonation. The obtained N_{1s} levels were used to determine the effective charge on nitrogen atoms, as described in [4, 16].

Table 2 lists the frequencies and their sources in the IR spectra of 2(4)-OAPs and their halides. The frequencies of the aromatic ring (ν_{CC}, ν_{CCH}, ν_{CN}) rose by 50–75 cm^{-1} upon the protonation of 2(4)-OAP. A broad and intense "ammonium" band (ν_{NH^+}) appears in the region of 2600–2800 cm^{-1} in the spectrum of 2(4)-OAP chloride. In the spectrum of the other halides and the (2-OAPH$^+$)[GaCl$_4$]$^-$ associate, this band is shifted to higher frequencies and superimposed on vibration bands ν_{CH} and ν_{NH} (2840–3050 cm^{-1}). The ν_{NH} band is shifted to the regions of low frequencies by 200–300 cm^{-1} for the halides and by 30–50 cm^{-1} for the associate.

Attributions of the chemical shifts of protons in the PMR spectra of 2(4)-OAPs and their salts is shown in Table 3. The signal of the "ammonium" proton is detected in the low-field region; with 2-OAP, the chemical shift (μ'_{NH^+}) is much lower and diminishes in the order Cl$^-$ > Br$^-$ > [GaCl$_4$]$^-$ > I$^-$. The signal of the amino group proton is shifted to the low-field region. The dependence of the position of the signal on the nature of the anion is not as strong, although the chemical shift (μ''_{NH}) diminishes slightly in the order Cl$^-$ > Br$^-$ > I$^-$ ≫ [GaCl$_4$]$^-$. The chemical shift of the protons of the methylene group adjacent to nitrogen also depends on the nature of the anion, but it diminishes in the opposite order: I$^-$ > Br$^-$ > Cl$^-$ > [GaCl$_4$]$^-$.

RESULTS AND DISCUSSION

In describing the extraction of ionic associates, it is basically assumed that any sequence of extractability of anions is possible, since it is determined by the
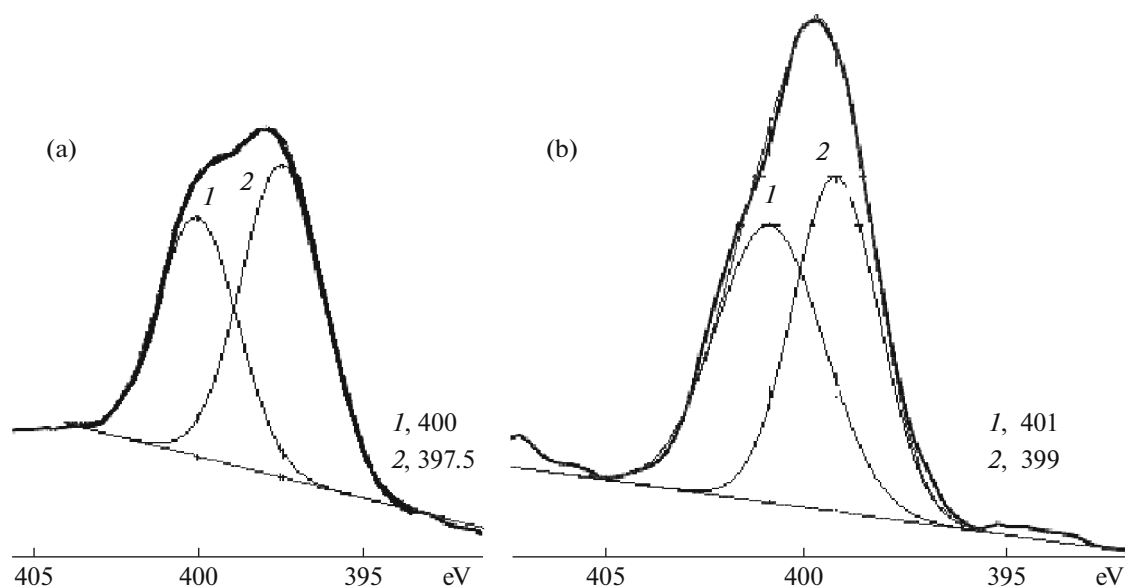
Fig. 1. Decomposition of the N_{1s} energy profile into individual components for heterocyclic and amine nitrogen: (a) 4-OAP and (b) 4-OAP·HCl.

energy of hydration in the aqueous phase, the energy of solvation in the organic phase, and the energy of association in both phases. However, for all extraction systems with the participation of amines (and other substances) that have been studied to date, the energy of hydration of the anion in the aqueous phase determined its position in the order of exchange extraction. The extractability of singly charged anions thus grows in the order $F^- < Cl^- < Br^- < NO_3^- < I^- < SCN^- < ClO_4^-$. It does not depend on the structure of the QAB cation, and a correlation between the constants of exchange and the heat of hydration of the anion is observed [18]. The constants of extraction of monobasic acids with aliphatic amines via neutralization are adequately described by the equation $\log K = \log K_0 + b\Delta G_h$, where ΔG_h is the free energy of hydration for the anion; $\log K_0$ is the constant of extraction of the acid for a given diluent, the anion of which is taken as the standard ($\Delta G_h = 0$); and b is the coefficient of sensitivity, which is constant for a set of extraction systems that differ only in the nature of the anion and depends on the solvation ability of the solvent [7].

This order of the extractability of anions is violated with 2(4)-OAP. The above anions can be arranged in two orders, for which an increase in the constants of exchange is observed with a drop in the heat of hydration (free energy):

$$Br^- < SCN^- < I^- \quad \text{and} \quad F^- < Cl^- < NO_3^- < ClO_4^-.$$
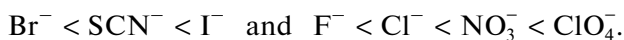
The anions constituting the first order are generally extracted more easily than those constituting the second order. A linear correlation between the logarithms of the constants of distribution, and thus those of the extraction of the respective acids and the free energy of hydration for anions, holds separately in each order (Fig. 2). However, it is not observed for the entire set of the studied anions, as it is with aliphatic amines [7]. The sensitivity of the constants to changes in the free energy of hydration for the anions constituting the first order is considerably higher than that of the second order. As with aliphatic amines, the sensitivity of the constants to changes in the free energy of hydration for the anions constituting the second order is extremely low when using chloroform, due to the strong solvation ability of the solvent [7].

A distinctive feature of the anions constituting the first order is that they form strong complexes with "soft" cations of metals (according to Pearson) and are thus classified as soft bases. Conversely, the anions constituting the second order are extremely "hard" bases. 2(4)-Octylaminopyridine exhibits selectivity in the extraction of soft anions, due apparently to the specificity of interionic interaction in 2(4)-OAP associates, as is clear from our physical study of 2(4)-OAPs and their salts in particular.

It is more convenient to interpret these results in terms of the mesomeric effect. The contribution from each canonical structure to a real molecule can be determined using the simplest theoretical model and the N_{1s} levels of energy [16]. The N_{1s} level of energy correlates with the effective charge on the nitrogen atom. A satisfactory correlation of these quantities for a large group of nitrogen-containing compounds of various structures was obtained in [16]. Effective charges on nitrogen atoms for limiting structures can be calculated using the concept of ionic character [19].

Table 2. Attributions of some frequencies (cm^{-1}) in the IR spectra of 2(4)-OAPs and their halides

Compound	ν_{NH}	ν_{CH} ν_{NH}	ν_{CC} ν_{CCH} ν_{CN}	δ_{NCH}	$\delta_{CH_3}^{as}$ δ_{CCH}	$\delta_{CH_3}^{s}$	ν_{CH} δ_{CCH}	ν_{CC} δ_{CCH}
2-OAP	3460 3360 3270	2910 2845	1609 1560 1510	—	1470	1380	1330 1290	1090 1015
4-OAP	3230 3138 3022	2956 2923 2849	1600 1529	—	1467	1353	1320 1215	1086 984
2-OAP·HCl	3240 3180 3100	3000 2910 2840	1655 1625 1585	1495	1470	1380	1280 1230	1170 1100
4-OAP·HCl	3210 3118 3083	3022 2957 2931 2859	1653 1589 1546	—	1472	1379	1264 1204	1193 1107
2-OAP·HBr	3230 3180 3120	3050 3000 2910	1660 1620 1580	1492	1465	1380	1280 1230	1170 1100
4-OAP·HBr	3206 3119 3080	3044 3024 2957 2930	1652 1590 1544	—	1471	1380	1267	1182 1098
2-OAP·HI	3230 3180 3120	3050 3000 2910	1620 1580	1490	1470	1380	1330 1290	1170 1095
4-OAP·HI	3243 3132 3083	3061 2960 2932 2860	1655 1586 1544	—	1471	1367	1255 1199	1183 1076
(2-OAPH$^+$)[GaCl$_4$]$^-$	3330 3200	3085 2915 2845	1665 1635 1580	1495	1475	1385	1330 1290	1170 1095

Table 3. Chemical shifts of protons (ppm) in the PMR spectra of 2(4)-OAPs and their halides and degree of delocalization of the charge in the cation as a function of the polarizability of H−X bonds [17] (0.1 mol/L 2(4)-OAP and 2(4)-OAPH$^+$X$^-$ in chloroform; tetramethylsilane is the internal standard)

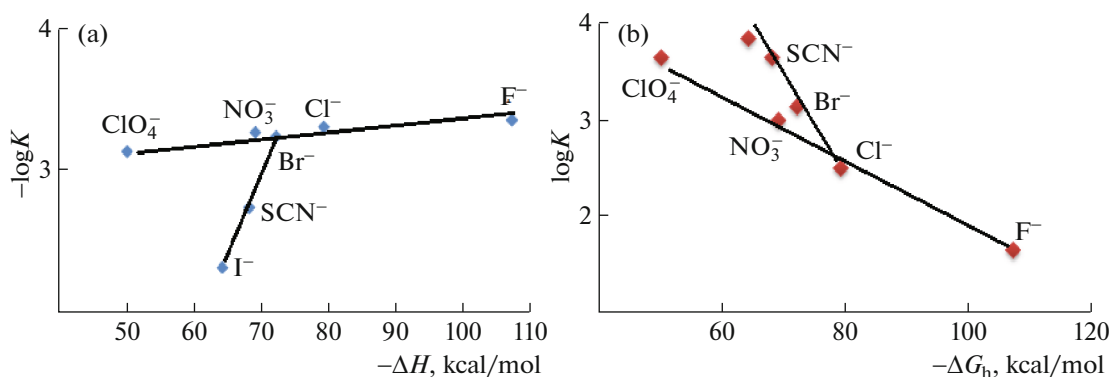| Compound	μ'_{NH^+}	μ''_{NH}	α-H(Py)	N−CH$_2$−	−(CH$_2$)$_6$−	−CH$_3$	α, %	P, cm^3
2-OAP	—	4.60	8.07	3.23	1.31	0.86	—	—
AmH$^+$[GaCl$_4$]$^-$	11.20	6.90	7.81	3.25	1.31	0.86	61	—
2-OAP·HCl	15.10	8.70	7.73	3.31	1.31	0.86	62	6.7
2-OAP·HBr	14.10	8.50	7.78	3.33	1.31	0.86	64	9.6
2-OAP·HI	9.20	8.40	7.83	3.41	1.31	0.86	92.5	13.7
4-OAP	—	5.25	8.74	3.75	1.89	1.48	—	
4-OAP·HCl	9.01	6.53	7.80	3.19	1.19	0.79	30	
4-OAP·HBr	8.50	6.53	7.96	3.22	1.21	0.83	35	
4-OAP·HI	8.05	6.61	7.89	3.27	1.22	0.83	46	

Fig. 2. Dependence of the logarithm of the distribution constants of salts (a) 2-AP and (b) 4-OAP in a water−chloroform two-phase system on the free energy of hydration for the anion.
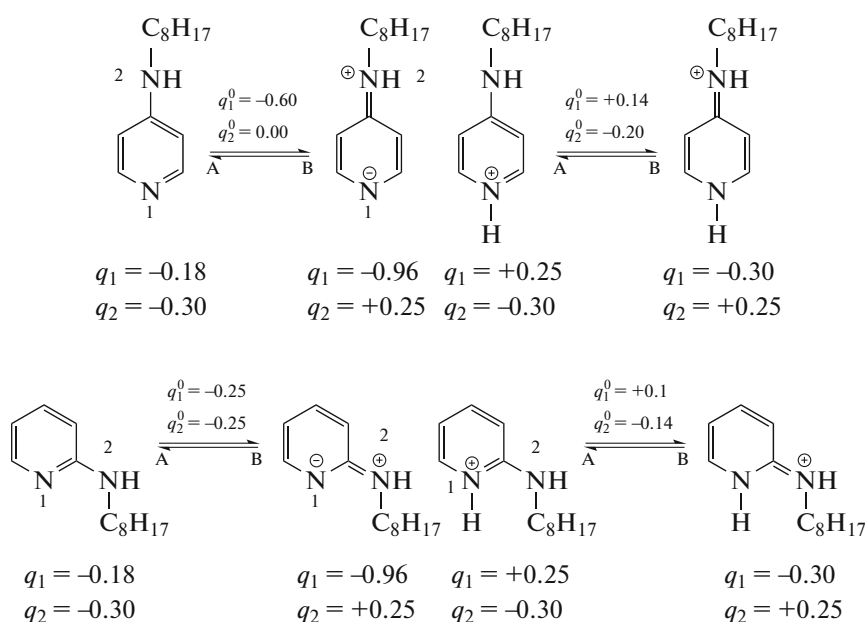

Fig. 3. Canonical structures of the 2(4)-OAP (A) molecule and the 2(4)-OAP (B) cation. Calculated (q_1, q_2) and experimental effective charges (q_1^0, q_2^0) on nitrogen atoms (B = 2(4)-OAP·HCl) are presented.

The canonical structures of 2(4)-OAPs and their cations are shown in Fig. 3, along with the calculated effective charges on nitrogen atoms for these structures and a real molecule. Using the equations for charge balance on nitrogen atoms, the contribution from the pyridonimine structure (B) in the 2-OAP and 4-OAP molecules was estimated at 9 and 54%, respectively.

To a first approximation, we may assume that the 2(4)-OAP molecule is a resonance structure with a contribution from pyridonimine component B. This feature ensures a higher basicity of heterocyclic nitrogen than that of pyridine, due to the pumping of electron density from the amino group in the *ortho*- and *para*-positions of the pyridine ring and the partial delocalization of the charge in the cation. Since the depth of resonance is higher for 4-OAP, its basicity is two orders of magnitude higher than the basicity of 2-OAP.

The same picture is observed in the 2(4)-OAP cation: the positive charge of the proton is delocalized throughout the molecule. It is noteworthy that the delocalization of the charge in the cation depends on the nature of the anion and grows in the order $[GaCl_4]^- < Cl^- < Br^- < I^-$. This is evident from the data in Table 3 and Fig. 4, where it is shown that the experimentally determined effective charge on the nitrogen atoms in the molecule of 2(4)-OAPs and their chlorides correlates with the chemical shift of the respective protons. The signals of protons in the PMR
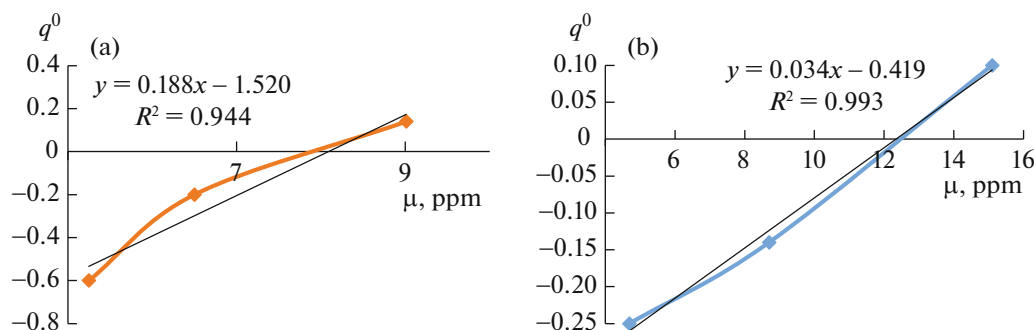
Fig. 4. Correlations between the effective charge (q^0) and the chemical shift (μ) of protons on nitrogen atoms: (a) 4-OAP and 4-OAP chloride and (b) 2-OAP and 2-OAP chloride.

spectra attributed to heterocyclic and amine nitrogen thus approach each other in this order, indicating equalization of the effective charges on the nitrogen atoms. The delocalization of the charge as a function of the nature of the anion can thus be determined quantitatively in terms of the previous model (Fig. 3).

By simultaneously solving the equations for the conservation of charge on nitrogen atoms for a protonated amine,

$$q_1^A(100 - x) + xq_1^B = 100q_1^0 \quad (4)$$

and

$$q_2^A(100 - x) + xq_2^B = 100q_2^0,$$
$$q_1^0 + q_2^0 \approx q_1^A + q_1^B = q_2^A + q_2^B, \quad (5)$$
$$q_1^A = q_2^B = q' = 0.25,$$

$$q_2^A = q_1^B = q'' = -0.30, \quad (6)$$

we obtain

$$x \approx 50(1 - (q_1^0 - q_2^0)/(q_1^0 + q_2^0 - 2q'')). \quad (7)$$

Here, x, % is the contribution from pyridonimine structure B; q_1^0 and q_2^0 are the effective charges calculated from the experimental values of the N_{1s} level for a real molecule on heterocyclic and amine nitrogen, respectively [4, 16]; and q_1^A, q_2^A, q_1^B, and q_2^B are the effective charges on nitrogen atoms for canonical structures, calculated in terms of the ionic character of the bond [4, 16] (Fig. 3).

Complete charge delocalization (α, %) is achieved with equal contributions from canonical structures A and B. The contribution from pyridonimine structure B (x) calculated with X-ray photoelectron spectroscopy data for 2-OAP and 4-OAP chlorides was 27 and 19%, respectively; $\alpha = 54$ and 38%.

The ratio of effective charges can be replaced with that of the chemical shifts of the respective protons bound to nitrogen. The delocalization of the charge is then calculated according to the equation

$$\alpha \approx 100(1 - ((\mu_1 - q_2))/(\mu_1 + \mu_2 - 2\mu'')), \quad (8)$$

where μ_1 and μ_2 are the chemical shifts of the proton on heterocyclic and amine nitrogen, respectively, and μ'' is the chemical shift of the proton on the nitrogen atom with an effective charge of -0.30, which is determined from the curves of $q^0 = f(\mu)$ correlation: 3.5 and 6 ppm for 2-OAP and 4-OAP, respectively (Fig. 4).

Results from calculating α using data on the PMR spectra are shown in Table 3. The calculations based on X-ray photoelectron and PMR spectra using the example of 2(4)-OAP chloride are in agreement to a first approximation, testifying to the correctness of our assumptions in terms of the adopted model. The delocalization of the charge in the amine cation grows in the order of increasing polarizability of the anion: $[GaCl_4]^- < Cl^- < Br^- < I^-$.

The specificity of interionic interaction in 2(4)-OAP associates is thus evident mainly as the redistribution of electron density in the aromatic cation as a function of the nature of the anion. Another factor is the formation of hydrogen bonds.

Hydrogen bonds form protons on heterocyclic and amine nitrogen. With 2-OAP, e.g., the interaction between the chloride ion and the two protons on the different nitrogen atoms is clear from the presence of a broad "ammonium" band (ν_{NH^+}) in the region of much higher frequencies than those that are reasonable to expect, allowing for the basicity of the nitrogen heteroatom. This factor ensures a less pronounced separation of the above band and the ν_{CH} band than in the case of, e.g., trialkylamines [20]. At the same time, the frequency of ν_{NH^+} falls by 200 cm^{-1}. This position of the frequencies indicates a strengthening of the bond of the "ammonium" proton with heterocyclic nitrogen and a weakening of the hydrogen bond of the proton with the chloride ion, which can be attributed to a drop in the electron density on the anion due to the formation of a second hydrogen bond with ring closure.
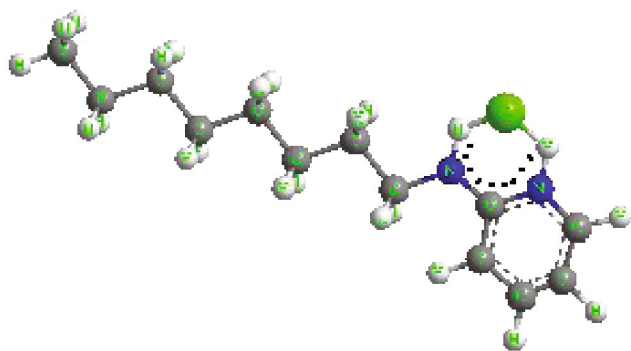
Fig. 5. Three-dimensional structure of 2-OAP halides using the example of 2-OAP chloride.

Fig. 6. Charge delocalization (α, %) in cations (*1*) 2-OAP and (*2*) 4-OAP as a function of the parameter of the softness (E, eV) of the halide in the order $Cl^- > Br^- > I^-$.

The strength of the hydrogen bonds of the anion in the ring and their equivalence depend on the nature of the anion and especially on the charge density and localization. With a drop in the charge density on a free or coordinated anion, frequency ν_{NH^+} grows negligibly in the order $Cl^- < Br^- < I^- < [GaCl_4]^-$. Frequency ν_{NH} grows in the same order, but less strongly. With $(2\text{-}OAPH^+)[GaCl_4]^-$, these frequencies overlap each other and are as little as 40–50 cm^{-1} lower than frequency ν_{NH^+} in 2-OAP. This suggests that the strength of the hydrogen ring generally falls in the order $Cl^- > Br^- > I^- > [CaCl_4]^-$. It should be noted that in the set of halides, the strength of the hydrogen bond of the heterocyclic nitrogen proton falls much faster than it does with the amino group proton. This proton becomes more "acidic" with an increase in the effective positive charge on nitrogen, due to delocalization in the order $Cl^- < Br^- < I^-$. This effect partially compensates for the effect of a drop in the charge density on the anion. A very slight change in the chemical shift of the amino group proton is therefore observed in the PMR spectra of halides (Table 3) because there is mutual compensation for contributions to the diamagnetic shielding constant due to charge delocalization and hydrogen bonding. It is this factor that is responsible for the increase in the chemical shift of the protons of the methylene group adjacent to nitrogen, which do not form hydrogen bonds, in the order $[CaCl_4]^- < Cl^- < Br^- < I^-$, in accordance with an increase in the degree of delocalization of the charge (Table 3). Conversely, the chemical shift of the amino group proton grows only slightly in the opposite order of the halides: $I^- < Br^- < Cl^-$, indicating the formation of a second hydrogen bond in the ring, the strength of which grows in the same order.

2-OAP associates thus have the following structure, which represents the number of the specificity of interionic interaction (Fig. 5).

The formation of a ring based on hydrogen bonding is a feature that distinguishes 2-OAP from 4-OAP and
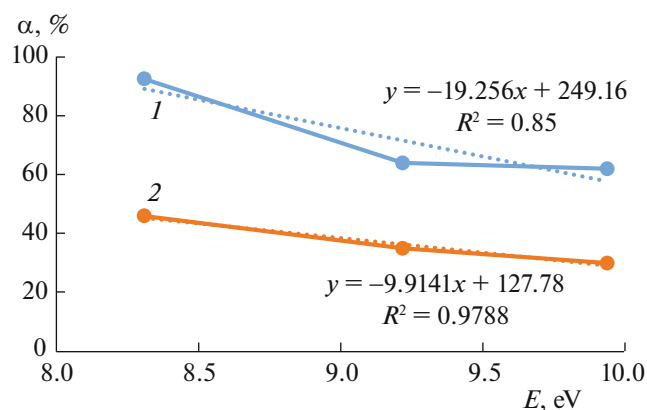
conventional nitrogen-containing anion-exchange resins. This feature in particular could be responsible for the abnormally high constants of distribution of 2-OAP chloride and extraction of HCl via the neutralization mechanism, the absence of water in the extracted salt, and the negligible hyperstoichiometric extraction of HCl [14]. The addition of a second HCl molecule apparently requires cleavage of the energetically advantageous ring. This feature also apparently contributes to the efficiency of using 2-OAP as an extractant for the isolation and separation of platinum and other rare metals from chloride, malonate, succinate, salicylate, and citrate media [21]. However, the violation of the order of exchange extraction of singly charged anions cannot be attributed to the above feature, because the strength of the ring conversely falls upon switching to an anion with higher extractability. The selectivity of the extraction of soft anions with 2(4)-OAP is thus directly attributable to the redistribution of electron density in the aromatic cation as a function of the nature of the anion.

It was proposed in [22] that the "softness" of an anion as an electron donor should be quantitatively determined in terms of orbital electronegativity, which is a derivative of the energy of an appropriate orbital with respect to the number of orbital occupation. For halides in an aqueous solution, it is $Cl^- > Br^- > I^-$ (i.e., $9.94 > 9.22 > 8.31$ eV, respectively) [23]. It is evident from Fig. 6 that there is a correlation between this parameter and the calculated delocalization of the charge in the 2(4)-OAP cation.

It seems that when describing the extraction of anions as an ion-exchange process, the difference between the energy of the association of soft and hard anions, which can be comparable to or higher than the effect of anion resolvation, should not be ignored. It is therefore logical to consider the constant of the distribution of the amine salt as a two-phase constant of the stability of the associate:
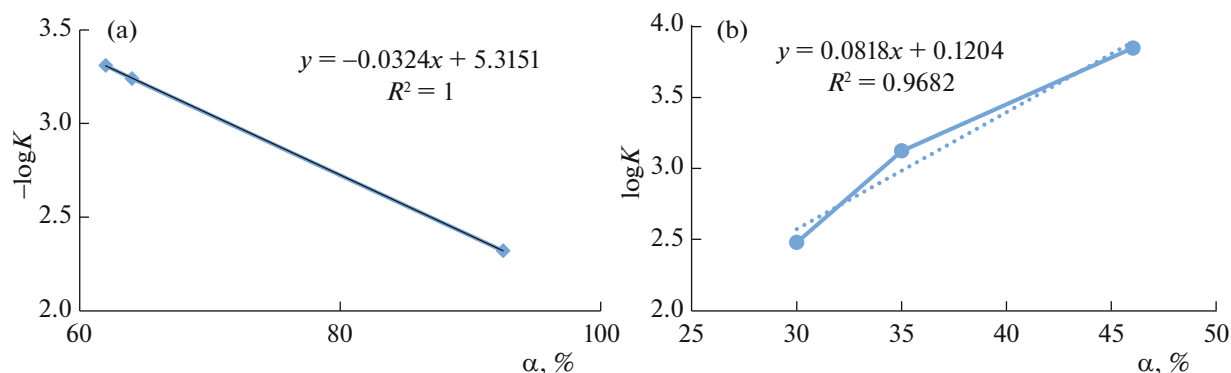
Fig. 7. Dependences of the logarithm of the constants of the distribution of (a) 2-AP and (b) 4-OAP halides in a water−chloroform two-phase system on the degree of delocalization of the charge in the aromatic cation.

$$K_{AmH^+X^-} = [AmH^+X^-]_0/[AmH^+]_w[X^-]_w = K_D K_{ass}, \quad (9)$$

where $K_{AmH^+X^-} = [AmH^+X^-]_0/[AmH^+]_w$ is the constant of the distribution of the associate in a two-phase system and $K_{ass} = [AmH^+X^-]_w/[AmH^+]_w[X^-]_w$ is the constant of the stability of the associate in water. The selectivity of the extraction of soft anions with OAPs can be attributed to the reversal of the order of stability of the associates (similar to the reversal of the order of stability during the complexation of hard and soft cations of metals [24]) due to an increase in the contribution from the delocalization component to the polar bond energy and the related effects of the environment upon switching from a hard anion to a soft anion (Fig. 7).

CONCLUSIONS

Our results are consistent with those from studies of RPy^+X^- (where RPy^+ is the long-chain alkylpyridinium ion and X^- denotes anions of different origins) ion pairs and the formation of micelles in water and organic solvents [9, 25, 26]. Charge transfer (CT) interaction was detected on the surfaces of micelles in an aqueous solution, according to an increase in the softness of the anion in the order $Br^- \ll SO_3^{2-} < N^- < I^- < S_2O_3^{2-}$. Similar interaction was observed for the ion pairs in chloroform in the order $Cl^- \ll Br^- < I^-$; it was not observed for hard ClO_4^-. No CT was observed in ion pairs or on the surfaces of micelles for hard Cl^-, NO_3^-, NO_2^-, ClO_3^-, BrO_3^-, IO_3^-, $HCOO^-$, and SO_4^{2-} and in ion pairs of hard tetraalkyl- and tetraalkylphenylammonium cations with soft Br^- and I^-. The difference between the free energy of adsorption for soft I^- and hard Cl^- on the surfaces of micelles was 1.7 ± 0.5 kcal/mol [26].

In Mulliken's formulation [27, 28], CT is attributed to the mixing of the wave functions of neighboring excited states with the wave function of the ground state. Since the ground state in an ion pair is charged and the excited state is neutral, the CT corresponds to a greater or lesser covalent contribution (energy of delocalization in terms of molecular orbitals) in associates of a soft amine cation with a soft anion, which is not present in associates with a hard ion (cation or anion).

The laws governing anion-exchange extraction with 2(4)-OAP (and apparently other AAs on the one hand, and aliphatic amines and QABs on the other) are identical only with respect to hard anions. The picture changes when extracting soft anions. Due to the specificity of interionic interaction, AAs are more selective with respect to soft anions (according to Pearson), due apparently to some acido complexes of soft cations of metals in particular (e.g., with respect to halide complexes of platinum and other rare metals that are extracted more readily by AAs than by aliphatic amines and QABs) [21, 29].

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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