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REVIEWS

Phase and Extraction Equilibriums in Aqueous Segregable Systems with Protolytic Interaction

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Abstract—Data on aqueous systems mainly based on antipyrine and diantipyrylmethane derivatives, which undergo segregation as a result of protolytic interactions with acids (haloacetic, benzoic, and naphthalene-2-sulfonic acids and pyrocatechol), are presented. The results of the physicochemical analysis of the corresponding ternary and quaternary systems are given. The distribution of metal ions between liquid phases was studied, and procedures for the combined determination of many metal ions in alloys and environmental materials are proposed. The advantage of the above extraction systems is the exclusion of the use of an organic solvent.

Keywords: extraction, antipyrine, diantipyrylalkanes, segregable systems
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The major advantage of aqueous segregable systems with protolytic interaction over traditional extraction systems is the absence of organic solvents. The low toxicity of pyrazolone derivatives and some organic acids reacting with them, for example, sulfosalicylic and naphthalene-2-sulfonic acids, is responsible for the safety of extraction processes and compliance with green chemistry requirements.

Extraction systems without an organic solvent belong to multicomponent systems, in which separation into two liquid phases is observed at certain component concentrations. The most complete picture of phase equilibriums in these systems, which is necessary for the optimization of extraction processes, can be obtained using physicochemical analysis and the construction of corresponding solubility diagrams. These diagrams make it possible not only to determine the boundaries of a segregation region and a numerical ratio between phase volumes in the system but also to make conclusions on interactions between the components.

Systems with antipyrine. For the first time, the presence of an equilibrium region of two liquid phases in the water–antipyrine–organic acid ternary systems was established in the 1950s. Chloral hydrate [1], benzoic acid [2], salycilic acid [3], phenol [4], and resorcinol [5] were used as acidic components. Many of the test systems were separated into two liquid phases only at elevated temperatures. The presence of the liquid two-phase equilibrium region in the water–antipyrine–organic acid ternary systems makes them potentially suitable for the extraction of metal ions. Extraction can occur due to the formation of both cationic complexes with antipyrine and the ion associates of metal acid complexes with the protonated form of the reagent. Studies on the extraction capabilities of these systems were initiated at the Department of Analytical Chemistry of the Perm University in the early 1980s [6].

As an example, Fig. 1 shows a solubility diagram of the water–antipyrine–naphthalene-2-sulfonic acid (NSA) system. The liquid two-phase equilibrium region (II) (16.7% of the total area of the diagram) is surrounded from all sides by the region of homogeneous solutions (I) (41.2%). We failed to examine in detail the bottom part of the concentration triangle with high concentrations of solid components because of a long equilibration time and difficulty in phase separation. The eutonic and peritonic compositions were not determined; therefore, the boundary lines of crystallization fields were drawn tentatively.

It is possible to assume the occurrence of the crystallization fields of antipyrine (III) and NSA (IV); the crystal hydrates of antipyrine (VIII) and NSA (XI); the chemical compound antipyrine·NSA (VII); the three-phase equilibrium of the crystals of antipyrine, the chemical compound antipyrine·NSA, and a solution of the composition E_1 (V); the crystals of NSA, the chemical compound, and a solution of the composition E_2 (VI); the crystallization of antipyrine, its

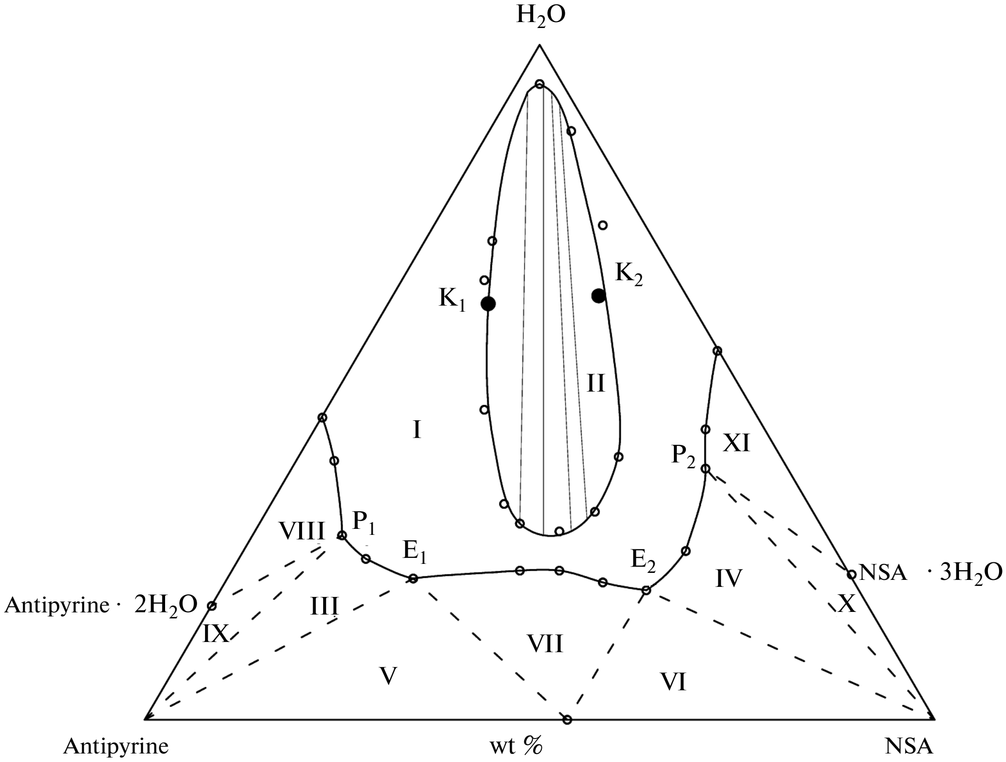

Fig. 1. Solubility isotherm of the water–antipyrine–NSA ternary system at 293 K (for I–X, see the text).

crystal hydrate, and a solution of the composition P_1 (IX); and the crystallization of NSA, its crystal hydrate, and a solution of the composition P_2 (X). The region of segregation has two critical points. The following compositions correspond to the critical points: K_1, 26.5 wt % antipyrine, 12.5 wt % NSA, and 61.0 wt % water; K_2, 11.5 wt % antipyrine, 26.0 wt % NSA, and 62.5 wt % water. The compound, which corresponds to the empirical formula $C_{11}H_{12}N_2O \cdot C_{10}H_7SO_3H$, was preparatively isolated as odorless white powder (mp 97°C; solubility, 0.9 g/100 g H_2O).

Currently available data on phase equilibriums in separable systems containing antipyrine and an organic acid make it possible to trace the influence of the organic acid (a phase-forming agent) on the properties of these systems.

The phase diagrams of the systems of antipyrine with pyrocatechol [7] at 50°C, trichloroacetic acid (TCA) at 30°C [8], NSA, monochloroacetic acid (MCA) [9], and monobromoacetic acid (MBA) [10] at 20°C are analogously shaped. The region of segregation is closed, and it has two critical points and borders on the areas of unsaturated solutions. The nodes of the segregation region form a fan-shaped round toward the antipyrine–organic acid binary system to confirm chemical interaction between the components. The greatest diameters of concentric isotherms in the region of segregation correspond to the addition product of antipyrine and the organic acid in a ratio of 1 : 1. Table 1 summarizes the areas of segregation regions determined from the solubility isotherms. In all cases, two of three binary systems belong to eutectic type systems with respect to the solubility of solid phases. The third antipyrine–organic acid binary system is a system with chemical interaction. Segregation in the ternary systems is caused by the limited solubility of the solvates of chemical compounds formed. An increase in the temperature causes the thermal dissociation of chemical compounds and increases their mutual solubility with water; because of this, all of the test systems have an upper triple critical point. In the systems with pyrocatechol, MCA, and NSA, the temperatures of the upper triple critical points are 383, 353, and 348 K, respectively, and this temperature in the water–1-hexyl-3-methyl-2-pyrazoline-5-one (HMP)–TCA system is 375 K.

The nature of the organic acid substantially influences the acidity range of the occurrence of a segregation region (Table 1). An increase in the strength of the acid shifts the segregation region toward low values of pH.

In the case of the systems with TCA and pyrocatechol, the region of a three-phase monotectic equilibrium of two liquid phases and one solid phase additionally appears as the temperature is decreased to 20–25°C. The region of segregation also occurs in the system with sulfosalicylic acid (SSA) [11]. Phase equilibriums in the water–antipyrine–MCA–sodium

Table 1. Acidity ranges of the occurrence of a segregation region and its area (*S*) in the isotherm of the corresponding ternary system

System	pK_a	Acidity range of the occurrence of a segregation region	*S*, %
Water–antipyrine–pyrocatechol	9.45	pH 1.5–6.0	33.3
Water–antipyrine–MCA	2.86	pH 1.4–3.5	23.6
Water–antipyrine–MBA	2.90	pH 1.4–3.6	30.5
Water–antipyrine–TCA	0.65	to 5 M H_2SO_4	22.1
Water–antipyrine–NSA	0.57	pH 2.0–5 M H_2SO_4	16.7
Water–thiopyrine–TCA	0.65	to 5 M H_2SO_4	43.9
Water–HMP–TCA	0.65	pH 8.4–8 M H_2SO_4	36.3

monochloroacetate quaternary system were studied [12].

In addition to antipyrine, amidopyrine (4-dimethylaminoantipyrine) forms segregable systems with salycilic acid [13] and chloral hydrate [14]. The extraction capabilities of these systems were not studied. The sulfur-containing analog of antipyrine thiopyrine also causes the segregation of the aqueous solutions of TCA [15] and α-bromophenylacetic acid [16]. Phase equilibriums in the water–thiopyrine–TCA–orthophosphoric acid quaternary system were studied [17]. The replacement of antipyrine by thiopyrine led to an increase in the area of the segregation region. Furthermore, the viscosity of the bottom phase decreased to cause the more rapid separation of phases.

The water–antipyrine–MCA system was the first system used in analytical practice [18]. According to Petrov and Rogozhnikov [19], Sc, Ti, Zr, Mo(VI), Fe(III), and Th were quantitatively extracted into the bottom phase at pH 2–3. The maximum degrees of extraction were the following, %: In, 93; Tl(III), 91; Hg(II), 90; Ga, 85; V(IV), 82; Sn(II), 77; Be, 73; Al, 65; Bi, 55; Y, 19; and Pb, 9. The ions of alkaline earth metals, Zn, Cd, Mn, Co, and Ni are not extracted. The extraction of Cu and rare-earth elements does not exceed 2–3%.

The ability of an extract obtained in the water–antipyrine–MCA system dissolve in water creates favorable conditions for chelatometric analysis because the stage of back extraction or heterophasic titration is excluded. Petrov and Rogozhnikov [20] proposed a method for the determination of 0.5–25.0 mg of scandium based on its quantitative extraction at pH 2 followed by the dissolution of the extract in 100–150 mL of water and titration with a solution of EDTA using a xylenol orange indicator. Large amounts (2–4 g) of the salts of Mg, Ca, Ba, Sr, Zn, Cd, Y, rare-earth elements, Cr(III), Mn(II), Al, Co, Ni, etc., cause no interference in the determination of 4.5 mg of scandium.

The ions of a number of metals are extracted as colored compounds: the compounds of Fe(III) and Cr(III) are red and green, respectively, whereas the compounds of Au(III), Pt(IV), Ti(IV), Tl(III), and U(VI) are yellow.

The reaction of antipyrine with Fe(III) is most sensitive ($\varepsilon_{425} = 9.5 \times 10^3$). The procedure developed for the hybrid extraction–photometric determination of iron(III) is characterized by high selectivity [21]. In the determination of 22 μg of Fe(III), 10000-fold molar amounts of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} ions; 5000-fold amounts of Mn^{2+}; 2500-fold amounts of Al^{3+} and Pb^{2+}; 1000-fold amounts of Be^{2+}, Ga^{3+}, In^{3+}, Sc^{3+}, Y^{3+}, La^{3+}, Zr(IV), Hf(IV), and Th(IV); 500-fold amounts of Hg^{2+}, Sn^{4+}, and Bi^{3+}; 100-fold amounts of Cr^{3+}; 50-fold amounts of Cu^{2+}; etc., cause no interference. Titanium(IV), molybdenum(VI), and uranium(VI) interfere with the determination. The procedure was tested with the standard samples of aluminum, nickel, their alloys, and bronze.

The kinetic inertness of the aqua complex of chromium(III) affects the distribution of chromium(III). Extraction is insignificant at room temperature. Because the water–antipyrine–MCA system has an upper critical point, it becomes homogeneous at $T >$ 353 K. Under these conditions, complexation occurs in 5–10 min. The system is separated into layers on cooling; in this case, chromium(III) is quantitatively concentrated in the bottom phase at pH ≥ 2.5 [22]. The 100-fold molar amounts of Mg, Ca, Sr, Ba, Zn, Cd, Co, Ni, and Mn cause no interference in the extraction–photometric determination of 2.1 mg of chromium(III). The interfering influence of Fe(III) is removed by the introduction of thioglycolic acid.

The range of extracted metal ions can be extended by the additional introduction of anions capable of forming acid complexes with the metals. In the presence of SCN^- at pH_{opt} 1.5–2, the blue thiocyanate complex of cobalt quantitatively passes into the bottom phase, whereas it is not extracted in the ternary system [23]. A procedure for the determination of 20–200 μg of cobalt based on its extraction in the water–antipyrine–MCA–NH_4SCN system was proposed

[24]. The 1000-fold molar amounts of alkaline earth metals, Al, Sn, Mn(II), and Ni; 500-fold amounts of Cd and Cr(III); and 100-fold amounts of Cu, Be, Zn, In, Sc, La, Zr, Pb, Bi, W, etc., do not interfere with the extraction–photometric determination of 124 μg of Co. The interfering influence of iron(III) is removed by the introduction of $SnCl_2$ into the system. The quantitative extraction of the thiocyanate complexes of Fe(III), Co, and a number of other metals made it possible to develop a procedure for the chelatometric determination of Ni, which remained in the raffinate after the extraction removal of a matrix.

It was proposed to add well-known photometric reagents, for example, Arsenazo III [25] and Dithizone [26] in the cases of thorium and mercury, respectively, for the photometric determination of the elements that are quantitatively extracted as colorless complexes in the water–antipyrine–MCA system.

Petrov and Afendikova [27] studied the distribution of metal ions in the water–antipyrine–pyrocatechol system. Upon the introduction of V(V), Mo(VI), Nb(V), or W(VI) salts into the system, the bottom phase became intensely colored; this fact is indicative of the extraction of the mixed-ligand complexes of metal ions with antipyrine and pyrocatechol. The selective determination of vanadium(V) in the presence of the other metal ions can be performed at pH 4–5 (670 nm, $\varepsilon = 1.4 \times 10^4$) [28]. Conditions for the extraction and the subsequent determination of molybdenum ($\lambda_{max} = 350$ nm, $\varepsilon = 5000$) [29], tungsten (pH_{opt} 1.9–3.1, $\lambda_{max} = 340$ nm, $\varepsilon = 3000$), and niobium ($pH_{optт}$ 1.9–2.2, $\lambda_{max} = 350$ nm, $\varepsilon = 1.5 \times 10^{-4}$) can be produced by varying the range of pH (pH_{opt} 1.9–3.1).

The red complexes of iron(III) are quantitatively extracted at pH from 2 to 6, and the yellow complexes of titanium(IV) ($\lambda_{max} = 410$ nm, $\varepsilon = 7.5 \times 10^3$), at pH 3–7.5. The maximum extraction of indium was 93%. At pH from 4 to 8, scandium was quantitatively extracted into the bottom phase. The maximum extraction of rare-earth elements was shifted to the region of higher pH values. The complexes of Sc, Y, and rare-earth elements are colorless [7]. For the studied rare-earth elements (La, Sm, Tb, Dy, and Er), there is a correlation between pH_{50} and ionic radius (r). The following straight-line relationship was obtained by the least squares method:

$$pH_{50} = 106r - 2.17 \ (R = 0.972).$$

The selectivity of the extraction of metal ions increased in the system with TCA. In this respect, the quaternary system with sulfuric acid was especially effective because sulfate complexes are not extracted by pyrazolone derivatives and metal ions can pass into the bottom phase only as mixed-ligand complexes. Thus, the extraction of Hg(II) was 93%; in this case, In, Tl(III), Sc, Zr, Sn(II), Bi(III), Mo(VI), and Fe(III) were partially extracted, whereas the ions of metals such as Cu, Be, Mg, Zn, Al, Ga, Y, La, V(IV), Cr(III), Mn(II), Co, and Ni were not extracted at all. The recovery of Hg(II) upon repeated extraction was as high as 98%. Under the optimum conditions of mercury distributing (2 M H_2SO_4), a procedure for the extraction–chelatometric determination of mercury was developed. The large amounts (1–2 g) of the sulfates or nitrates of In, Zr, Bi, Fe(II), Cu(II), Be, Mg, Zn, Cd, Al, Ga, V(IV), Cr(III), Mn(II), Co, and Ni did not interfere with the determination of 40 mg of mercury [30].

The selective extraction of gallium in the water–antipyrine–TCA–HCl (6–7 M) system made it possible to develop a procedure for its extraction–chelatometric determination [31]. The recovery of gallium after double extraction was as high as 98–99%. The large amounts of the salts of Mg, Ca, Sr, Sc, Y, La, V, Cr, Ni, etc., did not interfere with the determination of 14 mg of gallium.

The distribution of 2×10^{-4} mol of some metal ions in the water–antipyrine–NSA system was studied. In the absence of an inorganic acid, scandium, iron (III), and uranium(VI) were quantitatively extracted into the bottom phase. As can be seen in Fig. 2a, the introduction of sulfuric acid leads to a sharp decrease in the extraction of the elements because of the protonation of the reagent and the destruction of cationic metal complexes.

Figure 2b illustrates the effect of HCl on the extraction of the elements. The metal ions that form chloride acid complexes, such as gallium and iron(III), exhibit a second extraction maximum. The highly stable tetrachlorothallate is formed even at small concentrations of chloride ions; therefore, the quantitative extraction of thallium(III) is observed in a range of 0.1–3.0 M HCl. A decrease in the extraction of thallium(III) at high concentrations of HCl can be explained by a decrease in the volume of the bottom phase. In addition to the metal ions shown in Fig. 2, uranium(VI) was quantitatively extracted at pH 2.8–3.0 [32].

The distribution of thallium(III) is of interest because the ions of other metals are nonquantitatively extracted in the presence of HCl. The selectivity of thallium(III) separation can be increased by the extraction of thallium from sulfuric acid solutions in the presence of small amounts of chloride ions. The maximum selectivity of the extraction of thallium(III) was achieved with the use of 1.5–2.5 M H_2SO_4 in the presence of 0.05–0.2 M chloride ions. The fivefold molar amounts of Cu(II), Sc, Th, and La and the twofold amounts of Fe(III), Zn, Cd, In, and Ga cause no interference with the extraction–chelatometric determination of thallium(III). The ions of calcium subgroup metals form precipitates and interfere with the determination of thallium(III) in more than equimolar amounts.

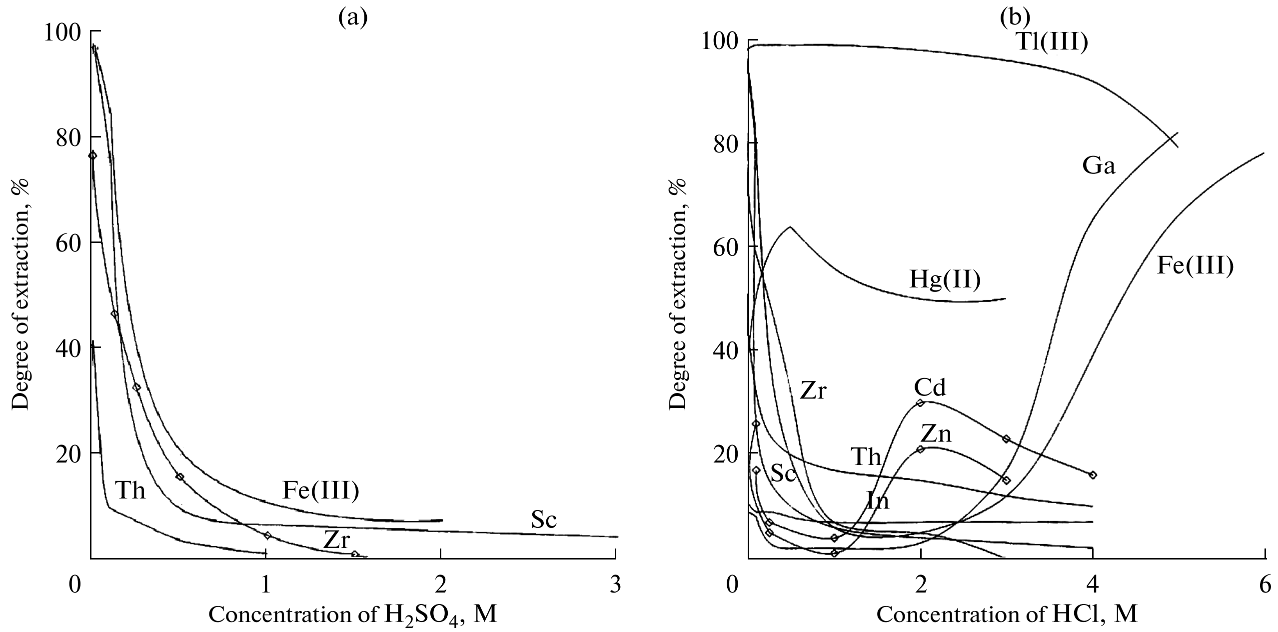

Fig. 2. Distribution of 2×10^{-4} mol of metal ions in the (a) water–antipyrine–NSA–H_2SO_4 and (b) water–antipyrine–NSA–HCl systems ($n_{\text{antipyrine}} = n_{\text{NSA}} = 0.005$ mol; $V_{\text{total}} = 20$ mL).

The high degree of extraction (84%) from sulfuric acid solutions in the water–antipyrine–SSA system was observed only for iron(III). The introduction of additional complex-forming anions, for example, chlorides, increases the extraction of iron(III) to 97% and zinc and cadmium, to 82 and 89%, respectively. From thiocyanate solutions, Cd, Co, Cu, and Fe are efficiently extracted. The efficient extraction of Hg(II), Sc, Sn(II), and Sn(IV) in the segregable system with antipyrine and SSA made it possible to propose procedures for their quantitative determination with Dithizone, xylenol orange, and morin, respectively [33, 34]. This system found practical application in the photometric, voltammetric, and atomic-absorption determination of Hg, Se, Cu, Pb, Cd, Zn, nitrite ions, and phenols in environmental samples (soils, plants, and aquatic ecosystems) [35–41].

The replacement of a rigid oxygen atom in the molecule of antipyrine by an easily polarizable sulfur atom in the molecule of thiopyrine led to a change in the range of the extracted metal ions. Zinc and mercury(II) were quantitatively extracted from 0–0.5 M solutions of H_2SO_4, and cadmium was extracted from 0–4.0 M solutions [42]. Procedures for the extraction–photometric determination of osmium(VIII) with thiopyrine [43] and bismuth with dithiopyrylmethane [44] were developed.

The presence of an organic acid is a characteristic property of segregable systems with antipyrine. Unlike antipyrine, HMP is capable to separate the aqueous solutions of both organic acids, for example, TCA [45], and inorganic acids, for example, perchloric and nitric acids [46], into two liquid phases. The use of acetic or phosphoric acid does not lead to the formation of a second liquid phase.

The extraction of zirconium or hafnium reached a maximum in 1 M HNO_3 or $HClO_4$, respectively. A decrease in the extraction of metal ions with decreasing acidity may be explained by the formation of hydroxo complexes. An increase in the acidity destroys cationic complexes due to the protonation of the reagent and, as a result, decreases the degree of extraction of metal ions. The higher degree of extraction of the metal ions with the use of $HClO_4$ is explained by a lower hydration energy of the perchlorate ion, which is indirect evidence for a coordination mechanism of the extraction of metal ions in the given systems. Other rigid multicharged cations, for example, of titanium(IV), scandium, and gallium, pass into an organic phase together with the ions of zirconium and hafnium. At the same time, the doubly charged cations of Zn^{2+} and Mn^{2+}, the cations of alkaline earth metals, and Al^{3+} have almost no effect on the extraction.

In addition to the system with HMP, the extraction properties of systems based on its alkyl homologs and perchloric acid were studied. 1-Heptyl-3-methyl-2-pyrazoline-5-one exhibits a maximum efficiency with respect to scandium; however, the extraction does not exceed 80% [47].

In the case of antipyrine, the region of liquid two-phase equilibrium is closed and surrounded by a region of homogeneous unsaturated solutions from all sides, and it has two critical points, whereas the region of segregation in the case of thiopyrine and HMP is separated by a limiting node from the field of the three-phase equilibrium of two liquid phases and reagent crystals.

Antipyrine can form cationic complexes with a wide range of metal ions; however, all of them are relatively unstable and occur in a narrow range of pH. The addition of strong acids leads to the destruction of complexes because of the protonation of the reagent. These circumstances make it possible to explain differences in the distribution of metal ions in the test systems.

The maximum number of metal ions will be extracted in the systems with a maximum pH value of the occurrence of a segregation region, namely, in the water–antipyrine–pyrocatechol system. The possibility of the formation of mixed-ligand complexes with the participation of pyrocatechol in the system should also be considered.

A large number of metal ions is also extracted into the bottom phase of the water–antipyrine–MCA system at pH 2–3. Data on the extraction of metals in the system with MBA are absent from the currently available literature; however, taking into account an analogous range of pH of the occurrence of a segregation region and close values of pK_a, we assume that this system exhibits analogous properties.

The selectivity of the extraction of metal ions increases in the systems with TCA or NSA. In the absence of an inorganic acid from the water–antipyrine–NSA (or TCA) system, only Sc, Fe(III), and U(VI) are quantitatively extracted into the bottom phase. The introduction of sulfuric acid leads to a sharp decrease in the extraction of metal ions. In the system with TCA, Hg(II) is extracted to a considerable degree, apparently, as the ion associate of the trichloroacetate complex of Hg(II) with the antipyrinium cation. The low value of pH in the aqueous phase of the systems with TCA and NSA explains the absence of antipyrine interactions with the majority of metals except for hard cations according to Pearson's classification, which form the most stable cationic complexes with pyrazolone derivatives. The range of the extracted metal ions can be expanded due to the introduction of additional anions capable of forming acid complexes with the metal cations. In this case, the mechanism of extraction changes from coordination to anion-exchange one.

Systems with diantipyrylalkanes. The introduction of diantipyrylmethane (DAM) or its alkyl homolog into the aqueous solutions of organic acids such as MCA [48], TCA [49], and NSA [50] leads to segregation into two liquid phases. The shape of the solubility diagrams of the water–diantipyrylalkane–organic acid systems is analogous. The region of segregation borders on the region of unsaturated solutions and the region of monotectic equilibrium between two liquid phases and the crystals of a chemical compound. As an example, Figure 3 shows a phase diagram of the water–DAM–NSA system.

The concentration triangle exhibits a developed region of two-phase liquid equilibrium (II), which occupies 11.3% of the total area, surrounded by the field of unsaturated solutions (I) (17.4% of the area) and by the region of the three-phase equilibrium of two liquid phases and DAM crystals (VIII). Because of the special features of the system, we failed to study in detail the bottom part of the phase diagram with the high concentrations of solid components; therefore, the boundary lines between the fields of crystallization were drawn tentatively. It is possible to assume the occurrence of two crystallization fields of DAM (III); the crystallization of NSA (IV) and its crystal hydrate (IX); the crystallization of the chemical compound DAM·NSA (VI); the three-phase equilibrium of DAM crystals, the chemical compound, and a solution of the composition E_1 (V); the crystals of NSA and the chemical compound and a solution of the composition E_2 (VII); and the crystallization NSA, its crystal hydrate, and the solution P (X). The nodes go off toward the DAM–NSA binary system to confirm the formation of a chemical compound between the base and the acid. The chemical compound was isolated preparatively as slightly pinkish odorless powder (mp 488 K; solubility, 0.262 g/100 mL H_2O at 293 K). The critical point of the region of liquid two-phase equilibrium is directed to the water–NSA side. It has the following composition, wt %: DAM, 13.5; NSA, 25.0; and water, 61.5.

To characterize the solubility isotherm of the water–DAM–NSA–HCl quaternary system, we studied sections with the concentrations of 1, 2, 4, and 6 M HCl [51]. The introduction of HCl into the system leads to a considerable change in the positions of fields, as compared with the diagram of a ternary system. As the concentration of HCl was increased to 1 M, the area of the region of liquid two-phase equilibrium considerably increased to 27.5%, and the region of the three-phase equilibrium of two liquid phases and DAM crystals disappeared. The region of homogeneous solutions shifted to the DAM–water side and completely surrounded the domain of the existence of two liquid phases. A further increase in the concentration of HCl led to a decrease in the area of the region of liquid two-phase equilibrium to 23.8 (2 M HCl), 21.1 (4 M HCl), or 17.5% (6 M HCl). In the solubility diagrams of the last two sections, a region of the three-phase equilibrium of two liquid phases and NSA crystals appeared.

The optimum amounts of components are 0.002 mol of DAM and 0.003 mol of NSA at a total volume of 20 mL; they provide segregation and a bottom phase volume (1.6 mL) sufficient for practical purposes [52]. Figure 4 shows data on the distribution of a number of metal ions in the water–DAM–NSA–H_2SO_4 system. The replacement of antipyrine by

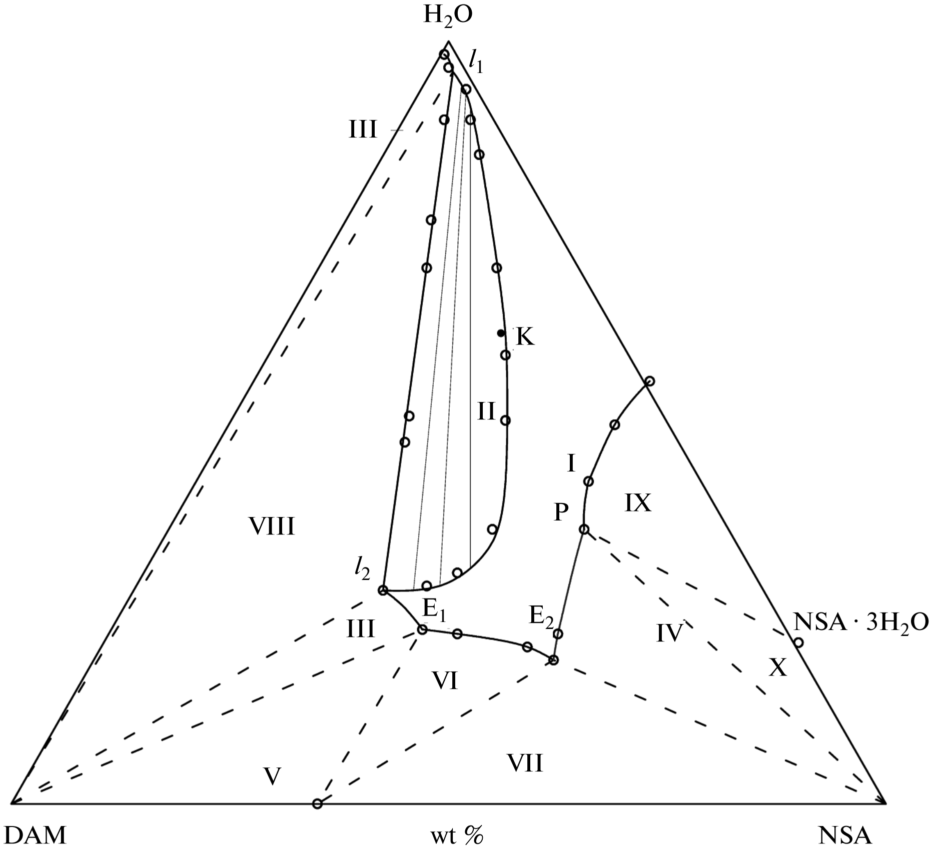

Fig. 3. Solubility isotherm of the water–DAM–NSA ternary system at 295 K (for I–X, see the text).

DAM leads to a considerable expansion of the range of metal ions quantitatively extracted into the bottom phase. In the absence of an inorganic acid, the quantitative extraction of Sc, Fe(III), Zr, Hf, Th, Bi, In, Mo (VI), and U(VI) was observed. The degrees of extraction of other metals were the following, %: La, 85; Y, 65; Ce(IV), 52; V(IV), 47; Ni, 46; Mn(II), 30; Ga, 40; Zn, 25; Cu(II), 20; Cd, 19; Ca, 26; and Ag, 12. The introduction of sulfuric acid suppresses the extraction of the majority of metal ions; however, the quantitative extraction of Zr, Hf, and Sc was observed up to 1.5 M H_2SO_4 in the system.

A procedure for the extraction–chelatometric determination of scandium was developed based on its extraction from a 0.5 M solution of H_2SO_4 with the subsequent back titration of the extract solution in an ammonium buffer solution with zinc sulfate and Eriochrome Black ET-00. In the determination of Sc, 12-fold molar amounts of Ga; ninefold amounts of Mg; eightfold amounts of Zn and La; sixfold amounts of Cr(III); fivefold amounts of Cd; and fourfold amounts of Mn(II), Ni, and Cu(II) caused no interference. The large amounts of Fe(III) interfere with the determination; at small amounts (to 15 mg), iron is preliminarily reduced with ascorbic acid [53].

Figure 5 illustrates the influence of HCl concentration on the extraction of metal ions. The quantitative extraction of the test metal ions from weakly acidic solutions can be explained by the formation of cationic complexes with DAM. With increasing the acidity, they are decomposed because of the protonation of the reagent, which leads to a decrease in the extraction of indium, lanthanum, scandium, zirconium, hafnium, and thorium ions. The second extraction maximum is observed for the ions of gallium, iron(III), uranium(VI), and copper(I), which form chloride acid complexes. The distribution of copper(I) has a maximum at an HCl concentration of 0.5 M.

A procedure was developed for the extraction–photometric determination of iron(III) in alloys based on its quantitative extraction from 4–5 M HCl. At the ratio DAM : NSA = 1 : (1–1.5), the bottom phase is a viscous fluid; therefore, the extract is diluted with acetone before the measurement of light absorption (l = 5 cm, 450 nm). In the determination of 27.0 μg of Fe(III), the 200-fold molar amounts of Ni, Mn(II), Cd, Co(II), Ca, Mg, Hf, Zr, Zn, Sc, La, In, Ga, and Hg(II) cause no interference. The procedure was tested in the analysis of the standard samples of nickel alloy and silumin.

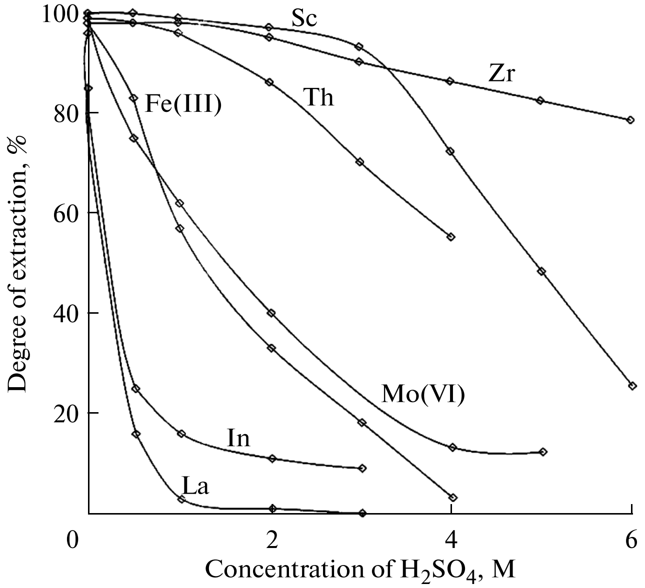

Fig. 4. Distribution of 2×10^{-4} mol of metal ions in the water–DAM–NSA–H_2SO_4 system (n_{DAM} = 0.002 mol; n_{NSA} = 0.003 mol; V_{total} = 20 mL).

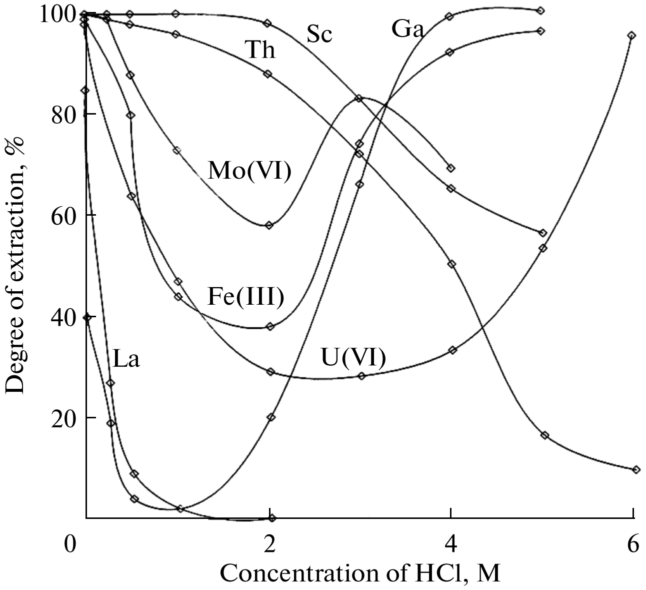

Fig. 5. Distribution of 2×10^{-4} mol of metal ions in the water–DAM–NSA–HCl system (n_{DAM} = 0.002 mol; n_{NSA} = 0.003 mol; V_{total} = 20 mL).

Upon a change in the molar ratio DAM : NSA to 1 : 4, a transparent and mobile extract is formed in the presence of 0.5–3.0 M solutions of inorganic acids; this makes it possible to measure its optical density without additional operations. Furthermore, it is not necessary to work with the weighed portions of DAM because its 0.2 M solution in a 0.8 M solution of NSA can be used.

The distribution of titanium(IV) in the segregable water–DAM–NSA system was studied at the ratio DAM : NSA = 1 : 4 [54]. The optimum conditions of the extraction of titanium(IV) are the following: 0.002 mol of DAM, 0.008 mol of NSA, and 0.002 mol of $SnCl_2$ in a 1.0–2.5 M solution of HCl with a total volume of 20 mL. The molar light absorption coefficient of the complex of titanium in the presence of tin(II) is 13250 at 400 nm. The study of the stability of the complex in time showed that the color is rapidly developed, it and remains stable for 3 h. Beer's law is obeyed in a range of 1–15 μg of titanium. Under these conditions, the 600-fold molar amounts of La, Sc, Co, Ni, Zn, Cd, Mn(II), Ga, In, Pb, Ca, and Mg and 300-fold amounts of Cr(III) and Hg(II) did not interfere with the determination of 15 μg of titanium. The procedure was tested with the standard samples of 09Kh16N4B alloy steel and KhN78T nickel-base alloy.

Interfacial distribution in the water–DAM–NSA–NH_4SCN system was studied based on the example of the trace amounts of Zn, Cd, Fe(III), and Co(II) ions. Fe(III), Co(II), and Zn were extracted quantitatively. The degree of Cd extraction was as high as 82%. Under the optimum conditions of cobalt extraction (0.2 M SCN^-, 1 M HCl), the ion associate $(LH)_2[Co(SCN)_4]$ with a blue color ($\lambda_{\max}$ = 615 nm, $\varepsilon = 2.9 \times 10^3$) was extracted. Under the same conditions, iron(III) was extracted in the form of the ion associate $(LH)_3[Fe(SCN)_6]$ ($\lambda_{\max}$ = 485 nm, $\varepsilon = 1.5 \times 10^4$). The simultaneous determination of iron and cobalt in a range of 1 : 4–50 ratios between then can be performed at 485 nm (iron) and 615 nm (cobalt). At a higher iron(III) content, iron should be preliminarily reduced with ascorbic acid. Calibration graphs for the determination of cobalt and iron(III) were linear in ranges of 20–150 and 10–100 μg, respectively. The majority of the elements did not interfere with the determination. The determination of cobalt(II) was strongly influenced by more than 0.5-fold molar amounts of iron(III) and copper(II), which form chromatic cherry-red compounds; however, they were reduced in the presence of ascorbic acid [55]. The accuracy of the procedure was confirmed by the analysis of a Nickel-91b standard sample.

Analogous results were obtained with the use of the water–diantipyrylbutane (DAB)–NSA system [56]. As compared with the system containing DAM, the system based on DAB is more effective in the extraction of the acid complexes of metals. From iodide solutions, 97% of cadmium was extracted; precipitates were formed in the case of zinc and cobalt. Co, Mo(VI), Zn, Fe(III), and Cu(II) were quantitatively extracted from 0.1 M thiocyanate solutions.

Water–diantipyrylheptane (DAH)–naphthalene-2-sulfonic acid system. Depending on the mechanism of extraction, the length of a hydrocarbon radical in the diantipyrylalkane molecule exerts different effects on the extraction capacity of reagents. DAM, which does not contain alkyl substituents, is the best reagent for the extraction of metal ions by a coordination mechanism [57]. An increase in the length of a hydrocarbon chain at the methylene carbon atom positively affects the extraction of the acid complexes of metals by an anion-exchange mechanism [58]. Upon the replacement of DAM by DAH, the more effective extraction of metal ions by the anion-exchange mechanism would be expected.

In the absence of an inorganic acid, the following amounts (%) were extracted into the bottom phase: Sc, 98; Mo(VI), 91; Fe(III), 80; Th, 73; Co, 67; Hg(II), 52; Mn(II), 39; Zn, 25; Ga, 22; Ti(IV), 21; In, 19; and Cu(I), 1.5. Sulfuric acid suppresses the extraction [59]. Figure 6 illustrates the effect of HCl on the degrees of extraction of some metal ions. The extraction in the absence of inorganic acids can be explained by the formation of cationic complexes with DAH, which are destroyed with increasing the acidity because of reagent protonation to cause a sharp decrease in the extraction. Two extraction maximums are characteristic of the metal ions that form chloride acid complexes. A highly stable tetrachlorothallate is formed at the small concentrations of chloride ions; thallium(III) is quantitatively extracted in a wide range of HCl concentrations up to 8 M. For increasing the selectivity of thallium(III) separation, it was proposed to extract thallium under the conditions of a chloride ion deficiency and high acidity with H_2SO_4. The region of the sufficiently selective extraction of Tl(III) in the water–DAH–NSA–2.5 M H_2SO_4 system occurs in a range from 0.05 to 0.2 M HCl. Under these conditions, Fe(III), Ga, Zn, Sc, rare-earth elements, and Cu(II) are not extracted, and the extraction of Mo(VI) and U(VI) is no higher than 16 and 3%, respectively.

Denisova et al. [60] compared extraction systems of different types using the extraction of 1×10^{-4} mol of iron(III) from naphthalene-2-sulfonate solutions with diantipyrylmethane and its alkyl homologs in a mixture (9 : 1) of chloroform with isopentanol and in the corresponding systems based on antipyrine and its derivatives without an organic solvent as an example. Figure 7 shows the effect of HCl concentration on the extraction of iron with the solutions of DAM, DAB, and DAH in the mixture of chloroform with isopentanol at a constant NSA concentration (0.15 M) and in the segregable systems analogous in composition. The curves of iron extraction exhibit two maximums. The complex $[FeL_2](C_{10}H_7SO_3)_3$ is extracted from weakly acidic solutions. DAM is the best of the studied reagents. The decrease in the effectiveness of reagents in the order DAM, DAB, and DAH can be explained by the appearance of steric hindrances for complexation due to alkyl substituents. In the segregable systems, iron(III) is extracted more completely than in similar systems with chloroform, in spite of the same values of pH_{eq} in an aqueous phase. This is explained by a higher reagent concentration in a small-volume bottom phase and by a higher polarity of the extractant because of the presence of water in it.

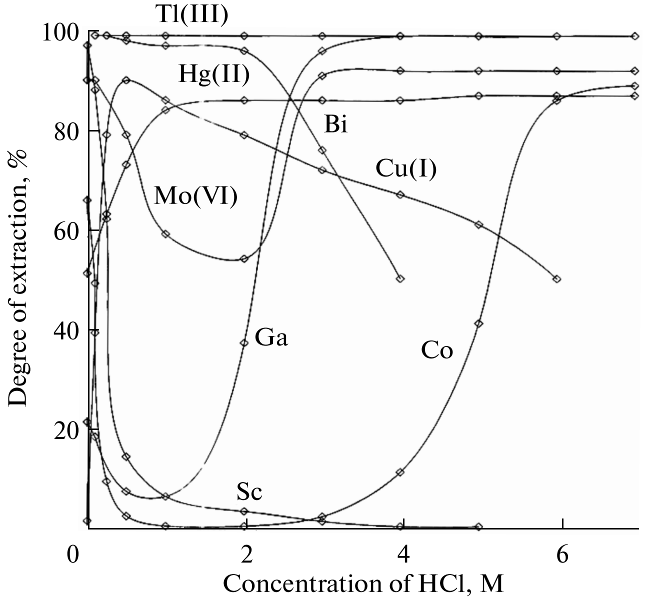

Fig. 6. Distribution of 2×10^{-4} mol of metal ions in the water–DAH–NSA–HCl system ($n_{DAM} = 0.002$ mol; $n_{NSA} = 0.003$ mol; $V_{total} = 20$ mL).

At high HCl concentrations, the acid complex of iron is extracted in the form of the ion associate with the protonated reagent $LH[FeCl_4]$ by the anion-exchange mechanism. No essential differences between the compared systems were observed. DAH with a longer hydrocarbon radical at the central carbon atom exhibited a maximum efficiency.

Water–diantipyrylalkane–benzoic acids systems. In the systems with benzoic acids, the organic phase formed at room temperature is a compact solid substance easily separable from the aqueous phase. Technically, extraction can be performed only after the preheating of the system above 50°C; that is, extraction with a melt actually occurs. Stable segregation manifests itself upon the addition of inorganic acids.

In the water–DAB (or DAH)–benzoic acid systems, the ions of Tl(III), Fe(III), Ga, Cd, Hg(II), Cu(I), Sn(II), and Sn(IV) are quantitatively extracted from acid chloride solutions [61]. A procedure was developed for the extraction–photometric determination of tin(II) in the water–DAH-benzoic acid–HCl system [62].

The extraction of Cd, Co, Hg(II), and Zn ions from thiocyanate solutions in the systems containing diantipyrylalkanes and benzoic acid was studied [63]. In these systems, Co(II) was quantitatively extracted as the ion associate $(LH)_2[Co(SCN)_4]$ [64]; this made it possible to develop a method for its determination [65].

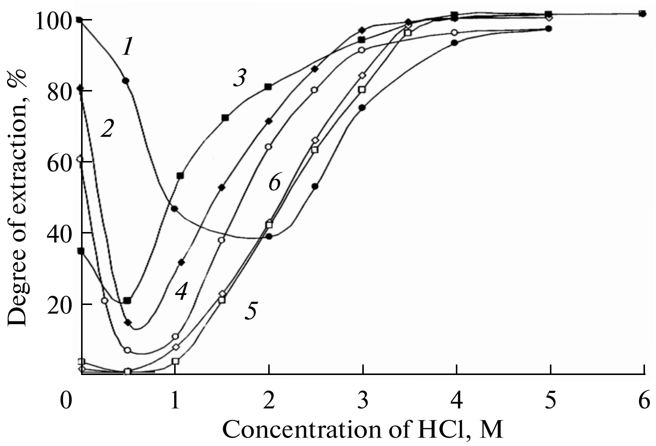

Fig. 7. Dependence of the extraction of 0.01 mol/L Fe(III) on the concentration of HCl: (*1*) water–DAM–NSA, (*2*) water–DAB–NSA, (*3*) water–DAH–NSA, (*4*) water–DAM–NSA–solvent, (*5*) water–DAH–NSA–solvent, and (*6*) water–DAB–NSA–solvent. $c_L = 0.1$ M; $c_{NSA} = 0.15$ M; solvent, a mixture of chloroform with isopentanol in a ratio of 9 : 1 by volume.

In addition to the systems with benzoic acid, data on the extraction of a number of metal ions from chloride solutions with the use of *o*-bromobenzoic acid (*o*-BBA) and dichlorobenzoic acids (DCBAs) are available. Segregation into two liquid phases in these systems is observed only at elevated temperatures (higher than 80°C) in a wide range of inorganic acid concentrations (0.01–3.0 M). The region of segregation is absent from the system with *o*-BBA and DAM [66]. If diantipyrylethane (DAE) is used as the reagent, the microphase is crystallized upon cooling, and the phase remains mobile and transparent for more than a day in the case of DAB or diantipyrylisopentane (DAIP). The extraction of molybdenum(VI) from the solutions of HCl in the system with *o*-BBA was observed. In the system with DCBAs, the extraction of zinc, cadmium, and mercury was 97, 96, and 92–94%, respectively.

Mutual solubility in the four-component water–DAM (DAH)–salycilic acid (SA)–HCl systems was studied at 25 and 50°C [67]. In the case of DAM, steady segregation appeared upon the addition of 3.0 to 4.9 wt % HCl. On the replacement of DAM by DAH, a wide region of segregation was detected in the DAH–SA–5 wt % HCl solution section. The ability of other DAM homologs—DAB, diantipyrylpentane (DAP), DAIP, and diantipyryldecane (DAD)—to segregate the aqueous solutions of the mixtures of SA and hydrochloric acid on heating to 80°C [68–71] was studied [68–71]. Fe(III), Ga(III), Tl(III), Cu(I), Sn(II), and Sn(IV) were quantitatively extracted from the chloride solutions. The extraction of the elements in the form of chloride acid complexes occurs by the anion-exchange mechanism.

There are data on the extraction of manganese(II) in the water–diantipyrylalkane–SA–HCl systems [72, 73]. It was found that the maximum extraction of manganese (58%) was reached with DAP, DAH, and DAD under the conditions of 6–7 M HCl; DAM and DAB were ineffective. The degree of manganese(II) extraction increased upon the introduction of salting-out agents. Thus, 2.0 and 0.75 M concentrations of calcium and magnesium chlorides ensured the quantitative extraction of manganese.

Summarizing information on the extraction systems with pyrazolone derivatives, note that, because of the good solubility of antipyrine in water, the extract can be dissolved in aqueous solutions. This property of the extract considerably simplifies the determination of metal ions in some hybrid methods of analysis, for example, extraction–titrimetric analysis. Furthermore, all of the reagents are used as aqueous solutions. The inconvenience of operations with the weighed portions of diantipyrylalkanes can be removed using a homogeneous aqueous solution of a reagent and NSA at the molar ratio NSA : reagent > 2 : 1.

Segregable water–organic base–acid systems. The interaction of many organic bases with organic acids is responsible for the segregation of their aqueous solutions. The water–diethylamine–TCA [74] and water–triethylamine–SA [75] (or anthranilic acid [76]) systems belong to this type. The extraction properties of these systems were not studied. The water–diphenylguanidine–TCA–HCl system [77] was proposed for the extraction of thorium complexes with Arsenazo III, whereas the water–guanidine sulfate–TCA system was proposed for the complexes of palladium with 1-(2-pyridylazo)resorcinol [78].

Upon the saturation of the aqueous solutions of N-substituted pyridine salts with sulfur dioxide, the system is segregated into two liquid phases. The study of the distribution of metal ions in these systems showed that many of them—Al, Ba, Ca, Co(II), Cr(III), Nd(III), Ni(II), Fe(III), Mn(II), VO^{2+}, and Zr(IV)—almost completely remained in the aqueous layer, whereas the ions of Ag, Bi(III), Cd, Cu(II), Pb(II), Sb(III), Sn(II), Pt(IV), Zn, W(VI), Hg(II), and Mo(VI) were concentrated in the heavy liquid phase [79–83].

The major advantage of the segregable systems with the only liquid component—water—over traditional liquid extraction is the elimination of organic diluents from the process. Because of this, the processing safety considerably increases and working conditions are improved. Table 2 summarizes published data on the applications of the above segregable systems in analytical chemistry. The wide variety of segregable systems, the possibility of changing the range of extracted metal ions, and the simplicity and high selectivity of procedures indicate that these systems are promising from both theoretical and practical points of view.

Table 2. Application of extraction in segregable aqueous systems with protolytic interaction to combined and hybrid methods of analysis

Extraction system*	Analyte ion, reference	Extraction conditions	Determination method and conditions
Water–antipyrine–MCA [9]	Sc(III), [20]	pH 2	EC with xylenol orange
	Fe(III), 3–40 μg, [21]	pH 2–3	EP ($\varepsilon_{425} = 9.5 \times 10^3$)
	Cr(III), 0.5–4 mg, [19]	pH 2.5 (heating for 10 min at 363 K)	EP
	Th(IV), 1–10 μg, [25]	pH 2–3	EP with Arsenazo III (665 nm)
	Zr(IV), 0.5–5 μg, [20]	pH 2–3	EP with 2-(3,5-dibromo-2-pyridylazo)-5-diethylaminophenol (610 nm);
	Hg(II), 2–25 μg, [26]	pH 2–3	EP with Dithizone
	Ti(IV), 1–10 μg, [9]	pH 2–3	EP with SCN^-
	Co(II), 124 μg, [23]	pH 1.5–2	EP with SCN^- ($\varepsilon_{625} = 1.9 \times 10^3$)
Water–antipyrine–MBA [10]	–	–	–
Water–antipyrine–TCA [15]	Hg(II), [30]	2 M H_2SO_4	EC
	Ga(III), [31]	6–7 M HCl	EC
Water–antipyrine–pyrocatechol [7]	V(V), [27, 28]	pH 3.5–5.5	EP ($\varepsilon_{650} = 1.4 \times 10^4$)
	Ti(IV), 8–60 μg, [7]	pH 2.4–2.8	EP ($\varepsilon_{410} = 7.5 \times 10^3$)
Water–antipyrine–NSA [32]	Tl(III), [32]	1.5–2.5 M H_2SO_4, 0.1–0.2 M NH_4Cl	EC
	U(VI), 80–800 μg, [32]	ph 2.8–3.0	EP (355 nm)
Water–antipyrine–SSA	Cd, Cu, Pb, Zn, [36, 39]	pH~1.5, 0.1 M KSCN	EVA
	Hg(II), [35, 37, 38]	0.1 M HCl	EAA, cold vapor technique
	Se(IV), [38]	0.1M HCl	EAA, hydride technique
	Sc, 2–58 μg, [33]		EP with xylenol orange (530 nm)
	NO_2^-, [40]	pH~1.5	EP
	C_6H_5OH, [41]	pH~1.5	EP

Table 2. (Contd.)

Extraction system*	Analyte ion, reference	Extraction conditions	Determination method and conditions
Water–thiopyrine–TCA [15]	Os(VIII), [42, 43]		EP
Water–dithiopyrylmethane–TCA–H_2SO_4	Bi(III), [44]		EP
Water–DAM–NSA [51]	Fe(III), 2–40 μg, [53]	pH 1–2	EP (450 nm)
	Ti(IV), 1–15 μg, [54]	1 MHCl, 0.002 mol $SnCl_2$	EP ($\varepsilon_{400} = 1.3 \times 10^3$)
	Sc, [50]	0.5 M H_2SO_4	EC
Water–DAM–NSA–NH_4SCN	Co and Fe(III), [55]	1 M HCl, 0.2 M NH_4SCN	EP Co($\varepsilon_{615} = 2.9 \times 10^3$), Fe($\varepsilon_{485} = 1.5 \times 10^4$)
Water–DAB–NSA [56]	Co(II), [56]	1 M HCl, 0.15 M NH_4SCN	EP (625 nm)
Water–DAH–NSA [59]	Tl(III), 5–60 μg, [50]	0.05 M HCl, 1 M H_2SO_4	EAE
Water–DAA–benzoic acid, SA [61]	Mo, 10–60 μg and Ti(IV) 5–30 μg, [84]	0.1–0.5 M H_2SO_4, $c_{SCN^-} = 0.25$ M	EP Mo ($\varepsilon_{465} = 2.2 \times 10^4$)? Ti ($\varepsilon_{390} = 1.9 \times 10^4$)
	Sn(II), 50–300 μg, [63]	0.4–0.8 M H_2SO_4, $c_{SCN^-} = 0.25$ M	EP with phenylfluorone ($\varepsilon_{515} = 3.9 \times 10^3$)
	Tl(III), 20–60 mg, [61]	1.5–2.0 M H_2SO_4, $c_{Cl^-} = 0.05–0.15$ M	EC with Eriochrome Black T
	Fe(III), 10–90 μg, [63]	pH 1–2; $c_{SCN^-} = 0.25$ M	EP ($\varepsilon_{480} = 8.3 \times 10^3$)
	Sn(II), 20.0–100.0 μg, [62]	0.5 M HCl	EP with pyrocatechol violet (590 nm)
	Co(II), 20–230 μg, [64]	pH 1–2, $c_{SCN^-} = 0.25$ M	EP ($\varepsilon_{625} = 2.3 \times 10^3$)

* Reference to the appropriate solubility isotherm.

Designations: EP, extraction–photometric analysis; EC, extraction–chelatometric analysis, EAA, extraction--atomic absorption analysis; EVA, extraction–voltammetric analysis; and EAE, extraction–atomic emission analysis.

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