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BEHAVIOR OF AMINOMETHANESULPHONIC ACID – 3d-METAL SALT – WATER SOLUTIONS.

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Based on direct pH, redox and conductometry data, the features of the acid-base and electrochemical behavior of aqueous solutions of aminomethanesulfonic acid (AMSA) with 3d metal salts (manganese(II), iron(II), cobalt(II), nickel(II), copper(II) sulfates and cobalt(II), nickel(II), copper(II) chlorides) were established. The behavior of aqueous solutions of AMSA – 3d metal salts was studied by the ligand saturation method (equilibrium shift) at C_M^{2+} = 0.025 mol/l; C_{AMSA}/C_M^{2+} = 0.08÷4.00. The composition of the formed complexes was judged by the positions of extrema and kinks in the integral pH, redox-metric curves, and extrema in the corresponding differential curves, as well as by kinks in the conductometric curves. In the studied solutions, complex compounds of the composition $[M(NH_2CH_2SO_3)]^+$ (**I**), $[M_2(NH_2CH_2SO_3)_3]^+$ (**II**), $M(NH_2CH_2SO_3)_2$ (**III**), $[M_2(NH_2CH_2SO_3)_5]^-$ (**IV**), $[M(NH_2CH_2SO_3)_3]^-$ (**V**), are realized. So, as the products of the reaction of metal ions with AMSA, in addition to the above-mentioned complex compounds, including hydroxonium ions, which are characterized by increased movability, the value Dk (Dk = k_3 - k_2 - k_1, where k_1 - k_2 - k_3 – specific of the electrical conductivity of water solutions M_zAn_2, AMSA and M_zAn_2 from AMSA, respectively) acquire positive values. Based on a developed physicochemical model taking into account the law of mass action, the material balance of AMSA and the metal, and the principle of electroneutrality, the ion-molecular composition of the studied solutions was calculated, and the concentration constants of complexation were estimated.

Correlations were found between the formation constants of these complexes. The relative stabilities of 3d-metal ion complexes with AMSA correlate with literature data on similar values for taurine and its derivatives. The highest stability is predominantly demonstrated by compounds of Cu^{2+} ions with the studied ligand.

Keywords: aminomethanesulfonic acid, 3d-metal cations, complexation, acid-base interactions, complexation constants, stability.

INTRODUCTION. Aminomethanesulfonic acid (AMSA) and its N-alkylated derivatives (YAMSA) are easily synthesized from inexpensive reagents; the pK_a values of amino groups are in the range of physiological pH values (6.8–7.8); their salts are easily soluble in water and poorly soluble in non-polar solvents [1–4]. That is, they meet four of the seven criteria that were put forward for the components of buffer solutions that can be used in biological and biochemical research [5]. Unlike aminoethanesulfonic acid (taurine, Tau), AMSA and YAMSA exhibit antibacterial and antiviral properties [2, 11, 12]. Despite the fact that AMSA (sulfur analog of glycine) is the first representative in the homologous series of aminoalkanesulfonic acids, data on the complexing ability of this ligand are absent in the literature. Only the results of studying the reactivity of Tau in reactions with metal cations are known [6–10]. Metal complexes based on aminoalkanesulfonic acids are promising precursors for the creation of new antibacterial and antiviral agents. AMSA complexes with 3d-metal cations can be used as models for studying the interaction of metal ions with amino acids in living organisms. They may have antitumor, antibacterial, and antifungal activity.

The aim of this work is to identify the features of the acid-base and electrochemical behavior of AMSA during complexation with salts (chlorides and sulfates) of 3d metals in aqueous solutions.

EXPERIMENT AND DISCUSSION OF THE RESULTS. In the studies, $MnSO_4 \times H_2O$, $FeSO_4 \times 7H_2O$, $CoSO_4 \times 7H_2O$, $CoCl_2 \times 6H_2O$, $NiCl_2 \times 6H_2O$, $CuSO_4 \times 5H_2O$, $CuCl_2 \times 2H_2O$ and $ZnSO_4 \times 7H_2O$ of analytical grade were used; AMSA was synthesized according to an original method [13]. Working solutions were prepared with a concentration of 0.05 M of the specified salts and 0.20 M AMSA. This is due to the limited solubility of AMSA in water, which at 298 K is 0.41 M. The preparation of a saturated AMSA solution is energetically complicated and requires preliminary heating (to ~333 K) of the mixture of a given content of components (AMSA and H_2O) for complete dissolution of aminosulfonic acid, followed by cooling to a given temperature. The behavior of aqueous solutions of AMSA – 3d metal salts was studied by the ligand saturation method (equilibrium shift). From the working solutions of AMSA and M^{2+} a series of solutions was prepared ($C_{M^{2+}}$ = 0.025 M; $C_{AMSA}/C_{M^{2+}}$ = 0.08÷4.00). Conductometric and pH-metric studies were carried out similarly to [14] at 298 K.

Initial solutions of 3d-metal salts have pH 2.70 ($FeSO_4$), 6.40 ($MnSO_4$) due to cation hydrolysis [15]:

$$M^{2+} + H_2O \rightleftharpoons M(OH)^+ + H_3O^+ \qquad (1)$$

$$K_g = \frac{[M(OH)^+] \cdot [H_3O^+]}{[M^{2+}]} \qquad (2)$$

According to the obtained data (Fig. 1), an increase in the $C_{AMSA}/C_{M^{2+}}$ ratio leads to a decrease in the pH of the studied solutions due to the course of reaction (3), except for solutions with $MnSO_4$, $CuCl_2$, and $ZnSO_4$. In the case of $CuCl_2$ solutions, initially with an increase in $C_{AMSA}/C_{M^{2+}}$ (up to 1.0:1.0), a decrease in pH is observed, then pH stepwise acquires constant values in the sections $C_{AMSA}/C_{M^{2+}}$ 1.0:(1.0÷2.0), 1.0:(2.5÷3.0), and 1.0:(3.5÷4.0).

$$kM^{2+} + n\overset{+}{N}H_3CH_2SO_3^- + nH_2O \rightleftharpoons [M_k(NH_2CH_2SO_3)_n]^{2k-n} + nH_3O^+, \qquad (3)$$

where k and n are stoichiometric coefficients.

$$K = \frac{[M_k(NH_2CH_2SO_3)_n^{2k-n}]\cdot[H_3O^+]^n}{[M^{2+}]^k\cdot[\overset{+}{N}H_3CH_2SO_3^-]} \quad (4)$$

AMSA solutions at $C_{AMSA}/C_M^{2+} < 1.0$ by decreasing pH values, cations in the presence of sulfates and chlorides can be arranged in the following series, respectively:

$Co^{2+} > Mn^{2+} > Zn^{2+} > Ni^{2+} > Cu^{2+} > Fe^{2+}$;

$Co^{2+} > Ni^{2+} > Cu^{2+}$.

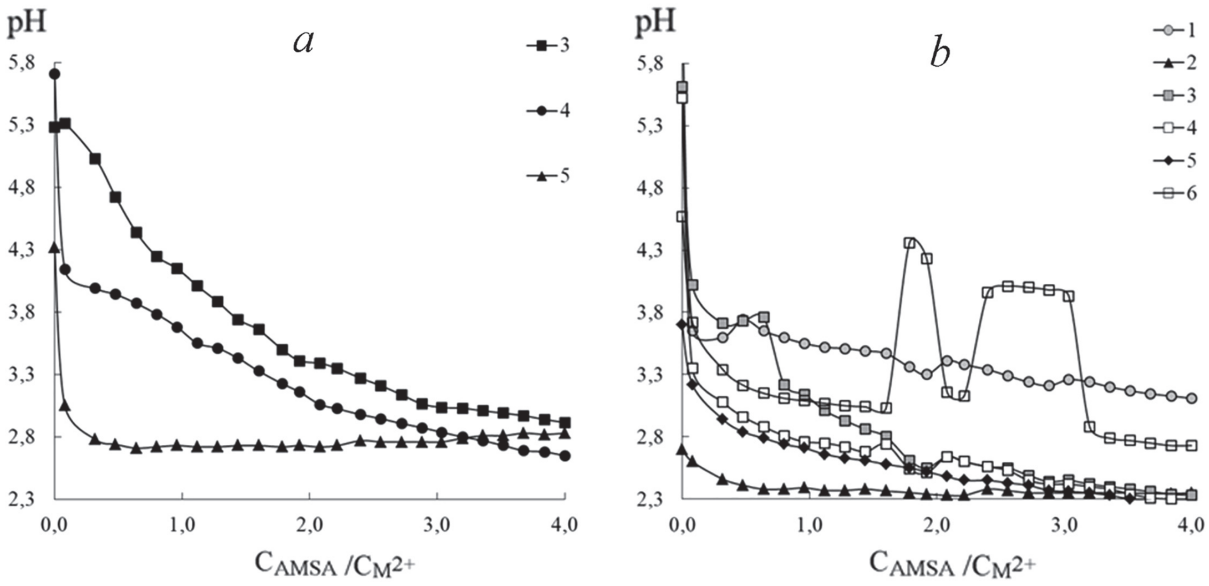

Fig. 1. Integral curves of pH dependence on the ratio C_{AMSA}/C_M^{2+}. C_M^{2+} = 0,025 M. M^{2+}: Mn^{2+} (1), Fe^{2+} (2), Co^{2+} (3), Ni^{2+} (4), Cu^{2+} (5), Zn^{2+} (6). An^{z-}: SO_4^{2-} (*a*), Cl^- (*b*).

The composition of the formed complexes (n:k ratio) was determined by the positions of extrema and inflection points on the integral pH-metric curves (Fig. 1) and extrema on the differential curves (Fig. 2), the characteristics of which are presented in Table 1.

According to pH-metry data for $MnSO_4$ solutions, the formation of three compounds with C_{AMSA}/C_M^{2+} ratios of 1.5:1.0, 2.0:1.0, and 3.0:1.0 was observed; for $NiSO_4$ and $NiCl_2$ – three compounds with C_{AMSA}/C_M^{2+} ratios of 1.0:1.0, 1.5:1.0, and 2.0:1.0. For $FeSO_4$, $CoSO_4$, and $ZnSO_4$, the formation of four compounds is characteristic. In solutions of $CoCl_2$, $CuCl_2$, and $CuSO_4$, five compounds are formed.

The data from redox-metric study of the interaction in AMSA – M^{2+} – H_2O solutions are presented in Figs. 3 and 4. At $C_{AMSA}/C_M^{2+} < 4.0$, the redox potential values of the studied solutions decrease in the following sequence depending on the cation: $Fe^{2+} > Cu^{2+} > Zn^{2+}$ [3] Mn^{2+} (for sulfates; i.e., the same series as for pH, but in reverse order) and $Co^{2+} > Ni^{2+}$ (for chlorides).

For $MnSO_4$ solutions, redox-metry provides little information about the composition of the formed compounds (Fig. 3). In the case

of $NiCl_2$, it allows the detection of an additional compound with C_{AMSA}/C_M^{2+} = 2.5 : 1.0, besides the indicated 1.5 : 1.0 and 2.0 : 1.0 ratios (Figs. 3, 4; Table 2). For $CuSO_4$, extrema on the differential redox-metric curves were also observed at C_{AMSA}/C_M^{2+} = 1.0:1.0 and 2.5:1.0. In $FeSO_4$ and $CoCl_2$ solutions, all five compounds are formed.

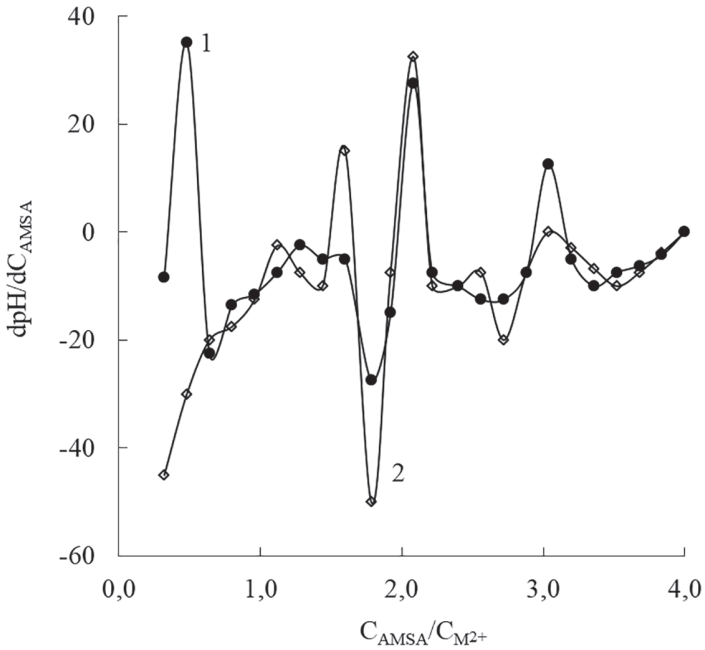

Fig. 2. Differential curves of dpH/dC_{AMSA} dependencies on the C_{AMSA}/C_M^{2+} ratio

C_M^{2+} = 0.025 M. Salts: $MnSO_4$ (1), $NiSO_4$ (2).

Table 1

pH-metry characteristics of aqueous AMSA solutions with 3d-metal salts

Effect	C_{AMSA}/C_M^{2+}	Integral curve		Differential curve	
		type	pH	type	dpH/dC_{AMSA}, L/mol
$MnSO_4$					
I	1.5	-	3.50	maximum	35.0
II	2.0	minimum	3.35	second-kind discontinuity	0
III	3.0	minimum	2.26	maximum	27.5
$FeSO_4$					
I	1.0	maximum	2.40	maximum	2.5
II	1.5	maximum	2.40	maximum	2.5
III	2.0	second-kind discontinuity	2.33 , 2.38	-	-3.0
IV	2.5	-	2.38	maximum	12.5
$CoSO_4$					
I	1.0	-	4.15	maximum	-24.0

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Table 1

Effect	C_{AMSA}/C_M^{2+}	Integral curve		Differential curve	
		type	pH	type	dpH/dC_{AMSA}, L/mol
II	1.5	-	3.74	minimum	-35.5
III	2.0	break point	3.39	minimum	-5.0
IV	2.5	-	3.21	minimum	-20
$NiSO_4$					
I	1.0	break point	3.55	minimum	-32.5
II	1.5	-	3.43	minimum	-25.8
III	2.0		3.06	maximum	-16.5
$CuSO_4$					
I	1.0	-	2.62	plateau	-7.5
II	1.5	second-kind discontinuity	2.57 , 2.95	maximum	95
III	2.0	minimum	3.00	minimum	-7.5
IV	2.5	maximum	3.04	maximum	10
V	3.0	minimum	3.00	minimum	-12.5
$ZnSO_4$					
I	1.5	second-kind discontinuity	3.03 , 4.36	maximum	333
II	2.0	second-kind discontinuity	4.23 , 3.16	minimum	-268
III	2.5	maximum	4.01	maximum	208
IV	3.0	jump	3.93	minimum	-263
$CoCl_2$					
I	1.0	break point	4.15	maximum	-24
II	1,5	-	3.74	maximum	-5
III	2.0	break point	3.39	minimum	-35.5
IV	2.5	-	3.21	minimum	-20
V	3.0	break point	3.04	minimum	-18.5
$NiCl_2$					
I	1.0	break point	3.70	minimum	-32.5
II	1.5	-	3.33	minimum	-25
III	2.0	break point	3.06	minimum	-25.8
$CuCl_2$					
I	1.0	plateau	2.73	maximum	2.5
II	1.5	plateau	2.73	maximum	2.5
III	2.0	plateau	2.72	maximum	2.5
IV	2.5	plateau	2.76	maximum	10
V	3.0	plateau	3.00	plateau	0

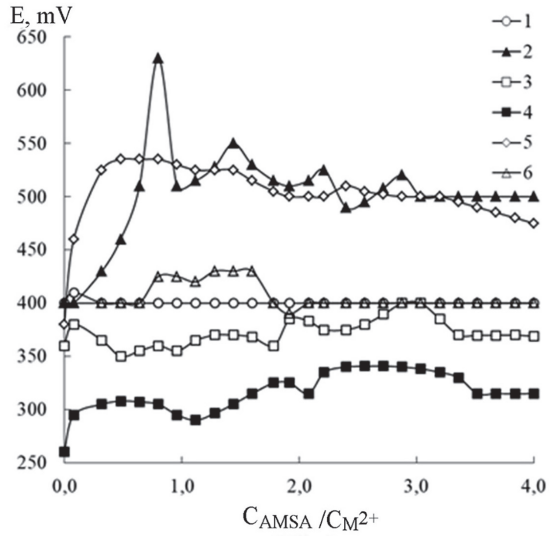

Fig. 3. Integral curves of E (mV) dependencies on C_{AMSA}/C_{M}^{2+}. C_{M}^{2+} = 0.025 M. M^{2+}: Mn^{2+} (1), Fe^{2+} (2), Co^{2+} (3), Ni^{2+} (4), Cu^{2+} (5), Zn^{2+} (6). An^{z-}: SO_4^{2-} (1, 2, 5, 6); Cl^- (2, 3).

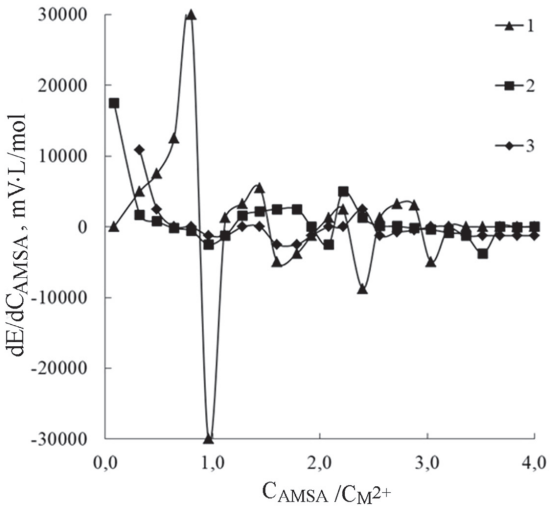

Fig. 4. Differential curves of E (mV) dependencies on C_{AMSA}/C_{M}^{2+}. C_{M}^{2+} = 0.025 M. M^{2+}: Fe^{2+} (1), Ni^{2+} (2), Cu^{2+} (3). An^{z-}: SO_4^{2-} (1, 3); Cl^- (2).

Table 2.

Redox-metry characteristics of aqueous AMSA solutions with 3d-metal salts.

Effect	C_{AMSA}/C_{M}^{2+}	Integral curve		Differential curve	
		type	E, mV	type	dE/dC_{AMSA}, mV×L/mol
$FeSO_4$					
I	1.0	minimum	510	minimum	-30000
II	1.5	maximum	550	maximum	5500
III	2.0	minimum	515	–	0
IV	2.5	minimum	490	minimum	-8750
V	3.0	plateau	500	minimum	-5000
$CoCl_2$					
I	1.0	minimum	355	minimum	-1250
II	1.5	maximum	370	–	0
III	2.0	maximum	285	maximum	6250
IV	2.5	minimum	375	–	0
V	3.0	maximum	400	–	0

Table 2.

$NiCl_2$					
I	1.0	minimum	290	minimum	-2500
II	2.0	maximum	325	minimum	-2500
III	2.5	maximum	340	plateau	150
$CuSO_4$					
I	1.0	plateau	525	minimum	-1250
II	2.0	plateau	500	minimum	-2500
III	2.5	–	510	maximum	2500
IV	3.0	plateau	500	maximum	0
$ZnSO_4$					
I	1.0	maximum	425	–	0
II	1.5	maximum	430	–	0
III	2.0	minimum	390	maximum	2500

The results of conductometric study of complex formation in AMSA – M^{2+} – H_2O solutions are presented in Fig. 5. The specific conductivity values of the studied solutions decrease for sulfates in the following sequence of metal cations:

$Zn^{2+} > Cu^{2+} > Fe^{2+} > Ni^{2+} > Co^{2+} » Mn^{2+}$ (at $C_{AMSA}/C_M^{2+} < 1.0$),

$Zn^{2+} > Cu^{2+} > Ni^{2+} > Fe^{2+} > Co^{2+} » Mn^{2+}$ (at $C_{AMSA}/C_M^{2+} > 1.0$).

The products of interaction of the studied cations with AMSA are aminomethanesulfonate complexes and hydronium ions (reaction 3). The latter are characterized by enhanced mobility. This causes Δκ to acquire positive values (Fig. 5b).

Conductometry detects only three compounds with $MnSO_4$ (similar to pH-metry), $NiSO_4$ and $NiCl_2$ (analogous to pH- and redox-metry); four compounds with $FeSO_4$, $CoSO_4$ and $ZnSO_4$ (similar to pH-metry); five compounds with $CuSO_4$ and $CuCl_2$ (similar to pH-metry) (Fig. 5; Table 3). In $CoCl_2$ solutions, five compounds are registered, similar to redox-metry.

Table 3.

Conductometry characteristics of aqueous AMSA solutions with 3d-metal salts.

Effect	C_{AMSA}/C_M^{2+}	Type	k, mS/cm	Dk, mS/cm
$MnSO_4$				
I	1.5	plateau	3.02	0.35
II	2.0	break point	3.32	0.52

Table 3.

Effect	C_{AMSA}/C_M^{2+}	Type	k, mS/cm	Dk, mS/cm
III	3.0	minimum	3.76	0.61
$FeSO_4$				
I	1.0	maximum	2.59	0.02
II	1.5	break point	2.76	0.04
III	2.0	break point	2.96	0.04
IV	2.5	break point	3.08	0.01
$CoSO_4$				
I	1.0	break point	2.74	0.12
II	2.0	break point	3.39	0.42
III	2.5	break point	3.54	0.42
IV	3.0	break point	3.83	0.57
$NiSO_4$				
I	1.0	break point	3.14	0.50
II	1.5	break point	3.51	0.72
III	2.0	break point	3.88	0.95
$CuSO_4$				
I	1.0	break point	2.90	0.43
II	1.5	break point	3.33	0.68
III	2.0	break point	3.75	0.95
IV	2.5	break point	4.06	0.95
V	3.0	break point	4.49	1.38
$ZnSO_4$				
I	1.0	break point	4.09	1.20
II	2.0	break point	5.25	2.34
III	2.5	break point	5.74	2.50
IV	3.0	second kind break point	6.57 , 4.92	3.04 , 1.50
$CoCl_2$				
I	1.0	break point	4.66	0.70

Table 3.

Effect	C_{AMSA}/C_M^{2+}	Type	k, mS/cm	Dk, mS/cm
II	1.5	break point	5.02	0.91
III	2.0	break point	5.53	1.22
IV	2.5	break point	5.75	1.29
V	3.0	plateau	6.17	1.60
$NiCl_2$				
I	1.0	break point	3.90	0.13
II	1.5	break point	4.22	0.28
III	2.0	plateau	4.53	0.40
$CuCl_2$				
I	1.0	break point	5.00	1.08
II	1.5	plateau	5.80	1.73
III	2.0	plateau	6.63	2.37
IV	2.5	plateau	7.18	2.70
V	3.0	plateau	7.92	3.37

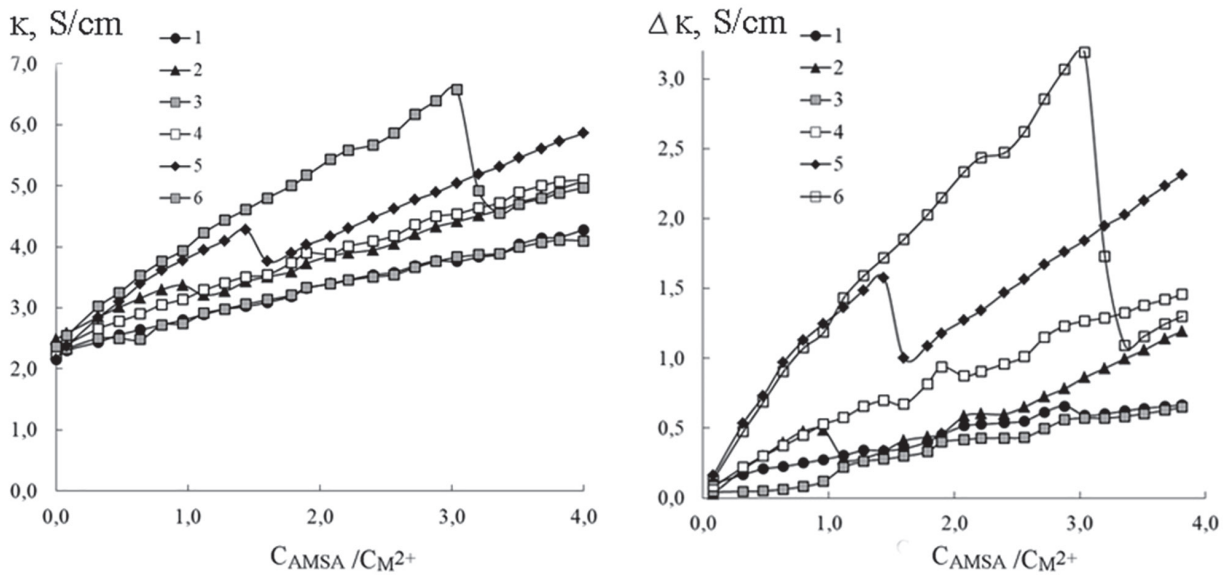

Fig. 5. Curves of κ (a) and Δκ (b) dependencies on the C_{AMSA}/C_M^{2+} ratio.
C_M^{2+} = 0.025 M. M^{2+}:Mn^{2+} (1), Fe^{2+} (2), Co^{2+} (3), Ni^{2+} (4), Cu^{2+} (5), Zn^{2+} (6). An^{z-}: SO_4^{2-}

Physicochemical model

Thus, the formation of five complex compounds $[M(NH_2CH_2SO_3)]^+$ (**I**), $[M_2(NH_2CH_2SO_3)_3]^+$ (**II**), $[M(NH_2CH_2SO_3)_2]$ (**III**), $[M_2(NH_2CH_2SO_3)_5]^-$ (**IV**) and $[M(NH_2CH_2SO_3)_3]^-$ (**V**) was detected in the studied solutions, which are described by equation (5). In addition, reactions of water autoprotolysis (7), AMSA dissociation (8) [2, 16, 17], and cation hydrolysis (1) occur. A mathematical model was developed that takes into account the law of mass action (2), (4), (6), (9), material balance for AMSA (10) and metal (11), as well as the principle of electroneutrality (12), similar to [2, 3, 14, 16, 17].

Complex formation

$$kM^{2+} + n\overset{+}{N}H_2CH_2SO_3^- \rightleftharpoons [M_k(NH_2CH_2SO_3)_n]^{2k-n} \quad (5)$$

$$b = \frac{[M_k(NH_2CH_2SO_3)_n^{2k-n}]}{[M^{2+}]^k \cdot [NH_2CH_2SO_3^-]^n} \quad (6)$$

Autoprotolysis H_2O

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad (7)$$

AMSA dissociation

$$\overset{+}{N}H_3CH_2SO_3^- + H_2O \rightleftharpoons NH_2CH_2SO_3^- + H_3O^+ \quad (8)$$

$$K_{AMSA} = \frac{[NH_2CH_2SO_3^-] \cdot [H_3O^+]}{[\overset{+}{N}H_2CH_2SO_3^-]^n} \quad (9)$$

$$C_{AMSA} = [\overset{+}{N}H_3CH_2SO_3^-] + [H_2NCH_2SO_3^-] + n[M_k(NH_2CH_2SO_3)_n]^{2k-n} \quad (10)$$

$$C_M^{2+} = [M^{2+}] + [M(OH)^+] + k[M_k(NH_2CH_2SO_3)_n]^{2k-n} \quad (11)$$

$$[H_3O^+] + [M(OH)^+] + 2\times[M^{2+}] + (2k\text{-}n)[M_k(NH_2CH_2SO_3)_n] = [H_2NCH_2SO_3^-] + [OH^-] + 2\times C_M^{2+} \quad (12)$$

Based on pH-metry data, the ion-molecular composition of the studied systems was calculated (for example, Fig. 6). With increasing C_{AMSA}/C_M^{2+} ratio, the content of the zwitterion mole fraction (curve 4) increases from 67% to 98%. At the same time, the relative content of unbound Cu^{2+} (curve 1) and complexed forms of AMSA (curve 6) decrease. The relative content of complexed forms of copper (curve 3) initially increases, reaching a maximum value (about 10%) at C_{AMSA}/C_M^{2+} 1.0, and then decreases. Meanwhile, the relative content of the hydrolyzed form of Cu^{2+} (basic salt – copper(II) hydroxide sulfate) and aminomethanesulfonate anion (curves 2 and 5, respectively) is less than 0.01%.

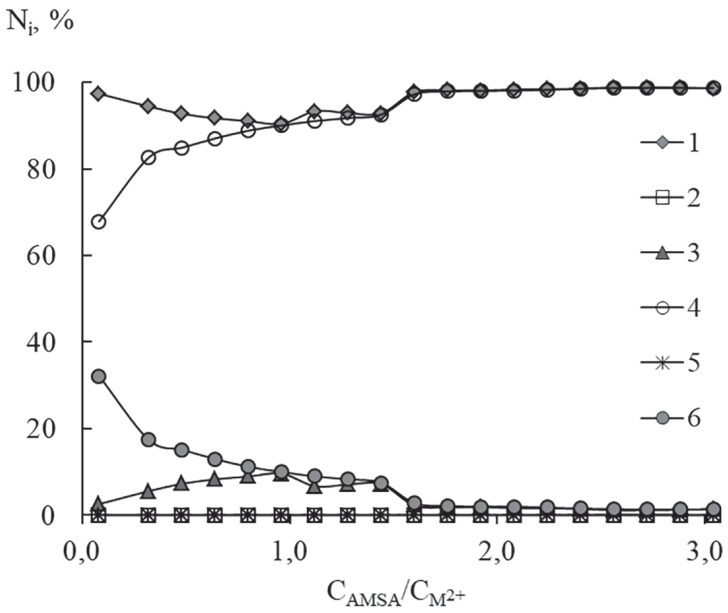

Fig. 6. Partial distribution diagrams of different forms of interaction in $CuSO_4$ – AMSA–H_2O solutions depending on C_{AMSA}/C_M^{2+}. C_M^{2+} = 0.025 M. N_i – mole fraction.

$$N_1 = \frac{[Cu^{2+}]}{C_{Cu}}; N_2 = \frac{[CuOH^+]}{C_{Cu}}; N_3 = \frac{[I] + 2[II] + [III] + 2[IV] + [V]}{C_{Cu}};$$

$$N_4 = \frac{[^+H_3NCH_2SO_3^-]}{C_{AMSA}}; N_5 = \frac{[H_2NCH_2SO_3^-]}{C_{AMSA}}; N_6 = \frac{[I] + 3[II] + 2[III] + 5[IV] + 3[V]}{C_{AMSA}}.$$

According to calculations, the ionic strength of the solutions, which is determined by equation (13), depends on the charge of the counterion in the d-metal salt and the ratio of AMSA to metal. The concentration dependencies $m = f(C_{AMSA}/C_M^{2+})$ are described by an equation of the form (14).

$$\mu = 1/2([H_3O^+] + [M(OH)^+] + 4\times[M^{2+}] + + (2k\text{-}n)^2\times M_k(NH_2CH_2SO_3)_n] + 4\times \times[^+NH_3CH_2SO_3^-] + [H_2NCH_2SO_3^-] + + [OH^-] + |z|\times 2\times C_M^{2+}) \quad (13)$$

$$\mu = A_i + B_i\times C_{AMSA}/C_M^{2+} \quad (14)$$

According to the calculation results, for chloride salts (of cobalt, nickel, and copper) $A_i \cong 3\times C_M^{2+}$; in the case of sulfates (of all studied metals) $A_i \cong 4\times C_M^{2+}$. The nature of the metal itself has almost no effect on this. The B_i values do not depend on the nature of the anion and cation and are approximately equal to $2\times C_M^{2+}$.

The concentration constants of hydrolysis (equation 2) and complex formation (equation 6) were calculated, the numerical values of which are presented in Table 4. For sulfates, the following was noted:

$$p\beta_{II} = -12.05 + 1.77\times p\beta_I; R^2 = 0.9472 \text{ (except } CoSO_4); \quad (15)$$

$p\beta_{III} = 1.35 + 0.665 \times p\beta_{II}$; $R^2 = 0.9015$ (except $ZnSO_4$); (16)

$p\beta_{IV} = -4.58 + 1.46 \times p\beta_{II}$; $R^2 = 0.9093$ (except $ZnSO_4$); (17)

$p\beta_{V} = -1.30 + 0.88 \times p\beta_{II}$; $R^2 = 0.8879$ (except $ZnSO_4$). (18)

A dependence of the stability constants of complexes on the counterion of the salt used is observed (Table 4). Regardless of the nature of the complex (Co^{2+}, Ni^{2+}, Cu^{2+}), complexes with sulfates are more stable than those with chlorides. Judging from equations (5) and (8), during the formation of neutral complexes **III** from sulfate and chloride salts, the by-products are sulfuric and hydrochloric acids, respectively. Moreover,

$p\beta_{III(HCl)} = 34.49 + 3.15 \times p\beta_{III(H2SO4)}$; $R^2 = 0.9419$. (19)

The presence of correlations (15) – (19) indicates a uniform type of ligand coordination with the central atoms. The deviations of $CoSO_4$ and $ZnSO_4$ from correlations (15) and (16) – (18), respectively, are due to differences in the coordination modes of Co^{2+} and Ni^{2+} compared to other cations. The observed stabilization of complexes **III** by sulfate anions, compared to chlorides, may be caused by the salt effect (the ionic strength of sulfate salt solutions is higher than that of chlorides (Table 4)). This may also be caused by the fact that the reactivity of Cl^- toward competing coordination with M^{2+} cations is higher than that of SO_4^{2-}. For a more detailed explanation of the observed stabilization, additional experiments involving other physicochemical and quantum chemical methods are necessary.

Table 4.

Values of concentration constants of hydroxylation and complex formation in AMSA – M^{2+} – H_2O solutions.

Complex (m, M)	M^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
	MSO_4						
	pK_g	11.18	3.76	9.62	9.44	6.32	7.54
I (0.14)	pβ	-5.74	-7.43	-5.76	-7.07	-7.42	-6.26
	Δpβ	0.01	0.16	0.46	0.06	0.03	0.18
II (0.17)	pβ	-21.93	-24.95	-23.66	-24.56	-25.38	-23.60
	Δpβ	0.32	0.33	0.36	0.14	0.17	0.27
III (0.19)	pβ	-13.01	-14.98	-14.87	-15.04	-15.47	-11.41
	Δpβ	0.43	0.08	0.86	0.78	0.03	0.57
IV (0.21)	pβ	-36.26	-40.59	-40.25	-40.25	-41.81	-35.80
	Δpβ	0.12	0.27	0.72	0.72	0.83	0.73
V (0.24)	pβ	-20.28	-22.77	-22.75	-22.84	-23.65	-17.19
	Δpβ	0.20	0.07	0.21	0.27	0.07	0.30
	MCl_2						
	pK_g	-	-	8.96	9.82	7.04	-

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Table 4.

I (0.12)	pβ	-	-	-3.89	-4.94	-7.30	-
	Δpβ	-	-	0.57	0.16	0.24	-
II (0.14)	pβ	-	-	-20.26	-20.68	-23.99	-
	Δpβ	-	-	0.94	0.11	0.49	-
III (0.17)	pβ	-	-	-12.48	-12.55	-14.25	-
	Δpβ	-	-	0.75	0.52	0.21	-
IV (0.18)	pβ	-	-	-36.34	-36.45	-38.55	-
	Δpβ	-	-	0.55	0.23	0.35	-
V (0.22)	pβ	-	-	-20.64	-20.49	-21.24	-
	Δpβ	-	-	0.55	0.18	0.16	-

According to reactivity toward cation hydrolysis, sulfate salts vary in the series:

$$Fe^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}.$$

The reactivity toward formation of compounds I – V decreases in the series:

$Fe^{2+} \gg Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} \gg Mn^{2+}$ (**I**),

$Cu^{2+} > Fe^{2+} > Ni^{2+} > Co^{2+} \gg Zn^{2+} > Mn^{2+}$ (**II**),

$Cu^{2+} \gg Ni^{2+} \gg Fe^{2+} \gg Co^{2+} > Mn^{2+} > Zn^{2+}$ (**III**, **V**),

$Cu^{2+} \gg Fe^{2+} \gg Co^{2+} \gg Ni^{2+} > Mn^{2+} > Zn^{2+}$ (**IV**).

The sequence of complex stability corresponds to the Irving-Williams series ($Zn^{2+} < Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$ [18] (with the exception of Fe^{2+}), which is a consequence of the stabilizing influence of the Jahn-Teller effect for chelate octahedral compounds [19]. Similar behavior is characteristic of complex compounds of glycine, taurine, and its derivatives of composition **I** and **III** [8, 20–22]. The positioning of the relative stability of Fe^{2+} compounds outside the Irving-Williams series is probably due to a different mode of ligand coordination with this cation compared to the rest of the studied M^{2+} ions.

CONCLUSIONS. Thus, based on direct pH-, redox-, and conductometry data, the formation of water-soluble complex compounds of five compositions was detected for the first time: $M(NH_2CH_2SO_3)]^+$, $[M_2(NH_2CH_2SO_3)_3]^+$, $[M(NH_2CH_2SO_3)_2]$, $[M_2(NH_2CH_2SO_3)_5]^-$ and $[M(NH_2CH_2SO_3)_3]^-$. The data from these methods confirm and complement each other. The concentration stability constants of these complex compounds in terms of p*b* values vary in the ranges: -7.43 ÷ -5.74 (**I**), -25.38 ÷ -21.93 (**II**), -15.47 ÷ -11.41 (**III**), -41.81 ÷ -35.80 (**IV**), -23.65 ÷ -17.19 (**V**) in the presence of sulfates; -3.89 ÷ -7.30 (**I**), -20.26 ÷ -23.99 (**II**), -12.48 ÷ -14.25 (**III**), -38.55 ÷ -36.34 (**IV**), -21.24 ÷ -20.49 (**V**) in the presence of chlorides. The obtained values of stability constants of 3d-metal ion complexes with AMSA correlate with similar values obtained earlier for taurine and its derivatives. The studied ligand forms the most stable complexes predominantly with Cu^{2+} ions. The relative stability of the complex compounds corresponds to the Irving-Williams series, with the exception of Fe^{2+} compounds.

In the future, synthesis and investigation

of the structure, physicochemical properties, and biological activity (particularly antibacterial and antiviral properties) of these complex compounds are planned for the development of new pharmaceutical preparations.

DETAILED DESCRIPTION OF THE AUTHORS' CONTRIBUTION.

A.M. Karych – conducting experimental research, initial processing of results. R.E. Khoma – conceptualization and research idea formulation, methodology development, writing the article. S.V. Vodzinskii – summarizing results, preparation of the initial draft of the manuscript. V.S. Kovtun – providing materials and resources, processing results.

CONFLICT OF INTEREST. The authors declare no conflict of interest.

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ПОВЕДІНКА РОЗЧИНІВ АМІНОМЕТАНСУЛЬФОКИСЛОТА – СІЛЬ 3d-МЕТАЛІВ – ВОДА

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На основі даних прямих pH-, редокс та кондуктометрії встановлено особливості кислотно-основної та електрохімічної поведінки у водних розчинах амінометансульфокислоти (AMSA) із солями 3d- металів (сульфатами марганцю(II), заліза(II), кобальту(II), нікелю (II), міді(II) та цинку(II), а також хлоридами кобальту(II), нікелю (II) та міді(II)). Поведінку водних розчинів AMSA – солі 3d-металів досліджували методом насичення за лігандом (зсуву рівноваги) при C_M^{2+} = 0.025 моль/л; C_{AMSA}/C_M^{2+} = 0.08 , 4.00. Про склад утворених комплексів судили за положеннями екстремумів та зламів на інтегральних pH-, редокс-метричних кривих та екстремумів на відповідних їхніх диференційних кривих, а також за зламами на кондуктометричних кривих. У досліджених розчинах реалізуються комплексні сполуки складу $[M(NH_2CH_2SO_3)]^+$ (**I**), $[M_2(NH_2CH_2SO_3)_3]^+$ (**II**), $[M(NH_2CH_2SO_3)_2]$ (**III**), $[M_2(NH_2CH_2SO_3)_5]^-$ (**IV**), $[M(NH_2CH_2SO_3)_3]^-$ (**V**). Оскільки продуктами реакції іонів металів з AMSA, окрім вказаних вище комплексних сполук, є іони гідроксонію, які характеризуються підвищеною рухливістю, значення Dk ($Dk = k_3 - k_2 - k_1$, де k_1, k_2, k_3 – питомі електропровідності водних розчинів M_zAn_2, AMSA та M_zAn_2 із AMSA відповідно) набувають додатних значень. На основі розробленої фізико-хімічної моделі, що враховує закон діючих мас, матеріальний баланс за AMSA та металом, а також принцип електронейтральності, розраховано йон-молекулярний склад

вивчених розчинів та оцінено концентраційні константи комплексоутворення. Зі збільшенням співвідношення C_{AMSA}/C_M^{2+} відносний вміст мольної частки цвіттеріону зростає, а незв'язаного Cu^{2+} та закомплексованих форм AMSA – зменшуються. Відносний вміст закомплексованих форм міді (спочатку зростає, набуваючи максимального значення при C_{AMSA}/C_M^{2+} 1.0, а потім спадає. Водночас відносний вміст гідролізованої форми Cu^{2+} (основної солі – гідроксиду-сульфату міді(II)) та амінометансульфонат аніону складають менше 0.01 %.

Виявлено кореляції між константами утворення зазначених комплексів. Відносні стійкості комплексів іонів 3d-металів з AMSA корелюють з літературними даними щодо аналогічних значень для таурину та його похідних. Найбільшою стійкістю характеризуються переважно сполуки іонів Cu^{2+} із досліджуваним лігандом.

Ключові слова: амінометансульфокислота, катіони 3d-металів, комплексоутворення, кислотно-основна взаємодія, константи комплексоутворення, стійкість.

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