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Electrometric determination of cu (ii) cations, Zn (ii) and Cr (iii) in aqueous, water-non-aqueous and mixed solutions

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Abstract: This work presents the results of the potentiometric determination of aqueous, non-aqueous and mixed solvents of copper (II), zinc (II) and chromium (III) cations: (propanol-2, acetone, methyl ethyl ketone, toluene, carbon tetrachloride, dimethylformamide) and their mixtures with water in a ratio of 1:1 and 1:19 by volume, the ratios of acid-base titrations are given. The quantitative results of the titration on a per kilote basis for the indicated cations Cu2+, Zn2+ and Cr3+ are based on the acidity constants of these cations assessed in the solvent environment specified above. The influence of the physical and chemical properties of solvents on acid-base titrations was studied. Due to the increase in the proportion of non-aqueous solvent in the solution, the dielectric constant of the solution decreases, and this leads to an increase in the ability to quantify acid-base titrations.

Keywords: Potentiometry, metal cations, copper, zinc, chromium, dielectric constant, acidity constant.

Introduction: It is known that heavy metal cations in solutions have their own acidic properties. Therefore, they are also called aprotic acids or Lewis acids. The acidic properties of metal ions depend on their position in the periodic table, on the ionic charge and on the number of anions associated with the cation. The cations Cu2+, Zn2+ and Cr3+ are aprotic acids, which do not retain protons, and have wetting acidic properties of varying strength in solutions depending on their ionic charge. According to the literature, there are few works on their titrimetric acid-base determination. Given their acidic properties, ions can be titrated as acids in a mixed aqueous-non-aqueous solution. Because of this, we carried out their titrimetric analysis in non-aqueous solvents mixed with water. It was of interest to determine the content of aprotic acids, which play an important role in the life of living organisms. To develop methods for the analysis of these aprotic acids, model solutions of the substances under study were taken and titrated based on acid-base reactions. As shown above, aprotic acids exhibit acidic properties of varying strength. Of the above aprotic acids, copper and zinc are dibasic acids, and chromium is a tribasic acid. Taking into account the acidity of various solutions of aprotic acids, methods of their acid-base potentiometric titration can be recommended. In aqueous solution they are mainly titrated according to the second acidity constant. The addition of non-aqueous water-miscible solvents to water improves the conditions for titration of aprotic acids. In this case, it can be ensured that they can be titrated against all acidity constants.

METHODS

The chosen objects were chlorides and sulfates of aprotic acids of copper (II), zinc (II) and chromium (III). Thus, ethanol, 2-propanol, acetone, methyl ethyl ketone, toluene, carbon tetrachloride, dimethylformamide and their mixtures with water were used as solvents.

During titration, solutions of potassium ethoxide and potassium propylites in ethanol and 1-propanol, as well as solutions of potassium acetate in suitable solvent media, were used as titrants. As a research method, we used potentiometric titration from electrochemical analysis methods. To estimate pKa values, the Henderson method was used, based on potentiometric titration with glass hydrogen-selective and silver-silver chloride electrodes. The essence of the method is that, under the same conditions, two acids are titrated with a strong alkali solution: one of them serves as a standard, and the second as the acid being studied. For a standard acid, the acidity constant in a given solvent must be known. Based on the results of potentiometric titration, titration curves are constructed and from these curves the values of half-titration potentials are determined and the values of acidity constants are calculated using the formula:

$$pK_x = pK_o \pm \frac{E^x_{1/2} - E^o_{1/2}}{\theta} \qquad (1)$$

Which is: $\mathrm{pK_x}$ – indicator of the acidity constant of the acid under study; $\mathrm{pK_o}$ – indicator of the acidity constant of the acid standard; $\mathrm{E^x_{1/2}}$ – half-titration potential of the acid under study, мВ; $\mathrm{E^o_{1/2}}$ – half-titration potential of acid standard, мВ; θ=58 (above 20^0C) мВ or θ=59 (above 25^0C) мВ. Benzoic acid was used as the standard acid. A hydrogen-selective electrode was used as an indicator electrode, which was adjusted according to the method attached to the pH meter using two buffer solutions (in an aqueous solution). The reference electrode was a silver chloride electrode filled with a saturated aqueous solution of doubly recrystallized potassium chloride.

RESULTS

Table 1 shows the results of the determination of chromium (III) $\mathrm{CrCl_3}$ in the form and $\mathrm{Cr_2(SO_4)_3}$ not only in alcohols, but also in ketones, DMP, toluene and carbon tetrachloride. As can be seen from the data in Table 1, by decreasing the amount of acids in the test solution, the relative standard deviation increases slightly. For chromium (III), the relative standard deviation of the determination also depends on both the amount of the substance and the composition of the solvent and the dielectric constant of the medium. Thus, when titrating small amounts of chromium (III), it is higher.

Table 1. Results of potentiometric determination of chromium (III) in solvents with different dielectric constants

(n=5, $\bar{x} \pm \Delta x$, P=0,95)

Aprotic acid	Solute	ε	Introduced, mg	Found, mg	S	S_r
$\mathrm{CrCl_3}$	Water	78,3	8,64	8,66±0,05	0,04	0,005
	Ethanol-water (1:1)	51,3	6,94	6,71±0,02	0,02	0,003
	Ethanol	24,3	6,48	6,61±0,04	0,03	0,005
	Propanol-2	18,3	10,26	10,07±0,05	0,04	0,004
	Acetone-water (1:1)	49,6	5,41	5,40±0,05	0,04	0,007
	Acetone	20,9	6,48	6,76±0,10	0,08	0,012
	MEK- water (1:1)	48,3	5,67	5,74±0,07	0,06	0,010
	MEK	18,4	8,64	8,62±0,07	0,06	0,007
	DMPA- water (1:1)	57,5	5,67	5,72±0,11	0,09	0,015
	DMPA	36,7	6,21	6,50±0,10	0,08	0,012
	Acetone -toluene (1:1)	11,7	5,67	5,56±0,11	0,09	0,017
	Acetone -$\mathrm{CCl_4}$ (1:1)	11,6	5,67	5,68±0,12	0,10	0,018

$Cr_2(SO_4)_3$	water	78,3	11,92	12,04±0,09	0,07	0,006
	Ethanol - water (1:1)	51,3	5,67	5,77±0,12	0,10	0,018
	Ethanol	24,3	9,22	9,18±0,11	0,09	0,010
	Propanol-2	18,3	6,94	6,96±0,12	0,10	0,015
	Acetone - water (1:1)	49,6	6,59	6,58±0,14	0,11	0,017
	Acetone	20,9	4,77	4,64±0,07	0,06	0,014
	MEK- water (1:1)	48,3	4,96	4,80±0,12	0,10	0,022
	MEK	18,4	6,59	6,68±0,11	0,09	0,014
	DMPA- water (1:1)	57,5	6,47	6,58±0,16	0,13	0,019
	DMPA	36,7	5,46	5,58±0,11	0,09	0,016
	Acetone -toluene (1:1)	11,7	4,46	4,34±0,20	0,16	0,037
	Acetone -CCl_4 (1:1)	11,6	4,96	4,80±0,12	0,10	0,022

As the data in Table 1 show, the relative standard deviation of the determination decreases with an increase in the proportion of non-aqueous solvent and a decrease in the dielectric constant of the medium. The exception is mixtures of acetone with toluene and carbon tetrachloride. In these solvents, although the dielectric constant is lower, the relative standard deviation is higher. It follows that the accuracy of the determination is influenced not only by the nature of the conjugate base (anion) of the acid being determined and the physical properties of the solvent, but also by its chemical nature. The accuracy of the determination of chromium (III) ions also depends on the conjugate base. Since chloride ions are a weaker base than sulfates, the accuracy of the determination of chromium chlorides is higher than the accuracy of the determination of sulfates. The same pattern persists when titrating zinc ions in mixed solvents. Table 2 shows the results of the determination of zinc chloride and sulfate in various solvents.

Table 2. Results of potentiometric determination of various in Zn^{2+} solvents with different dielectric constants

(n=5, $\bar{x} \pm \Delta x$, P=0,95)

Aprotic acid	Solute	ε	Introduced, mg	Found, мг	S	S_r
$ZnCl_2$	Water	78,3	15,26	15,24±0,10	0,08	0,005
	Ethanol-water (1:1)	51,3	12,58	12,60±0,16	0,13	0,010
	Ethanol	24,3	16,78	16,88±0,07	0,06	0,004
	Propanol -2	18,3	15,26	15,52±0,12	0,10	0,007
	Acetone-water (1:1)	49,6	10,18	10,47±0,11	0,09	0,008
	Acetone	20,9	13,24	13,09±0,04	0,03	0,002
	MEK-water (1:1)	48,3	13,24	13,66±0,07	0,06	0,005
	MEK	18,4	15,26	15,02±0,12	0,10	0,007
	DMPA-water (1:1)	57,5	12,22	11,85±0,12	0,10	0,009
	DMPA	36,7	13,24	13,53±0,12	0,10	0,007
	Acetone -CCl_4 (1:1)	11,6	10,18	10,17±0,16	0,13	0,013
	Acetone - toluene (1:1)	11,7	13,24	13,52±0,16	0,13	0,009

$ZnSO_4$	Water	78,3	15,20	15,18±0,07	0,06	0,004
	Ethanol-water (1:1)	51,3	16,72	16,97±0,27	0,22	0,013
	Ethanol	24,3	16,72	16,91±0,17	0,14	0,008
	Propanol -2	18,3	10,14	10,86±0,22	0,18	0,017
	Acetone-water (1:1)	49,6	13,56	13,70±0,30	0,24	0,018
	Acetone	20,9	12,16	12,60±0,16	0,13	0,010
	MEK- water (1:1)	48,3	14,19	14,70±0,31	0,25	0,017
	MEK	18,4	15,20	15,30±0,39	0,31	0,020
	DMPA- water(1:1)	57,5	15,20	14,99±0,12	0,10	0,007
	DMPA	36,7	18,31	18,45±0,57	0,46	0,025
	Acetone -CCl_4(1:1)	11,6	10,14	10,47±0,16	0,13	0,012
	Acetone -toluene (1:1)	11,7	12,16	11,95±0,16	0,13	0,011

In order to more deeply study the role of the anion on the accuracy of the determination of aprotic acids, titration was also carried out with copper (II) not only chlorides and sulfates, but also acetates, which are stronger bases than sulfates and especially chlorides.

Table 3. Results of potentiometric determination of chlorides, sulfates and acetates of copper (II) in solvents of various natures

(n=4, $\overline{x} \pm \Delta x$, P=0,95)

Aprotic acid	Solute	ε	Introduced, mg	Found, mg	S	S_r
Water	78,3	$CuSO_4$	2,46	2,47±0,03	0,02	0,010
		$CuCl_2$	2,54	2,51±0,03	0,02	0,007
		$Cu(CH_3COO)_2$	3,18	3,20±0,08	0,05	0,016
Ethanol-water (19:1)	27,0	$CuSO_4$	2,72	2,73±0,03	0,02	0,007
		$CuCl_2$	2,60	2,55±0,02	0,01	0,005
		$Cu(CH_3COO)_2$	3,10	3,10±0,05	0,03	0,010
Propanol -2- water (19:1)	21,3	$CuSO_4$	3,62	3,57±0,03	0,02	0,007
		$CuCl_2$	2,65	2,60±0,02	0,01	0,005
		$Cu(CH_3COO)_2$	3,41	3,55±0,13	0,08	0,023
Propanol -1- water (19:1)	23,0	$CuSO_4$	3,22	3,10±0,03	0,02	0,008
		$CuCl_2$	2,65	2,70±0,03	0,02	0,007
		$Cu(CH_3COO)_2$	3,41	3,41±0,06	0,04	0,011
DMPA- water (19:1)	38,8	$CuSO_4$	3,22	3,24±0,03	0,02	0,008
		$CuCl_2$	3,20	3,25±0,03	0,02	0,008

		$Cu(CH_3COO)_2$	3,10	3,15±0,06	0,04	0,012
DMPA- water (1:1)	57,5	$CuCl_2$	2,65	2,68±0,05	0,03	0,012
		$Cu(CH_3COO)_2$	3,10	3,06±0,06	0,04	0,014

The results of titration of chlorides, sulfates and acetates of copper (II) in various solvents are given in

Table 3. Both anhydrous chlorides and acetate crystal hydrates were taken for analysis.

As can be seen from the data in table. 3, the accuracy of the determination of copper aprotic acids depends on the strength of the conjugate base. At similar amounts of chlorides, sulfates, and acetates, the relative standard deviation increases with increasing basicity of the anion.

The exception is mixtures of acetone with toluene and carbon tetrachloride. In these solvents, although the dielectric constant is lower, the relative standard deviation is higher. It follows that the accuracy of the determination is influenced not only by the nature of the conjugate base (anion) of the acid being determined and the physical properties of the solvent, but also by its chemical nature. Based on the developed analysis methods, the content of harmful heavy metal ions in various food products (meat, liver, spleen, milk, feta cheese, etc.) and other environmental objects was determined.

CONCLUSIONS

1. The possibility of potentiometric acid-base determination of the above metals in water, aqueous-non-aqueous and mixed solutions was studied.

2. The data obtained from potentiometric acid-base titration of aqueous aqueous-non-aqueous and mixed solutions of aprotic acids can be concluded that the studied acids are well titrated with solutions of hydroxide, ethylate, propylate, isopropylate and

potassium acetate with a properly selected solvent. A decrease in the dielectric constant and autoprotolysis constant of the solvent improves the conditions for potentiometric titration, which is expressed in an increase in the potential jump on the titration curves.

3. It has been established that the conditions for acid-base potentiometric titration improve with an increase in the proportion of non-aqueous solvent, when the dielectric constant of the medium decreases.

4. The developed methods of acid-base titrimetric analysis have been applied to the analysis of metal cations in various natural objects, such as meat, dairy products, water, soil and plants.

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