THE ELECTRICAL CONDUCTIVITY OF TERNARY SYSTEMS COMPOSED OF AMINES, ACETIC ACID AND WATER

S. P. Miskidzhyan and I. A. Volina

Systems, composed of amines, acid and water, have long served as subjects to attract the attention of electrochemists from the viewpoint of their utilization for the preparation of various oxidation and reduction products of amines by electrolysis [1].

The purpose of our work was to study the electrical conductivity of a number of ternary systems, composed of amines (aniline, quinoline, pyridine), acetic acid and water, with the formation of complexes in them being taken into consideration. We failed to find any data in the literature on the electrical conductivity of the indicated ternary systems. Only for the system aniline-acetic acid-water do the data of Pound [2] exist, who, although measuring the electrical conductivity of a large number of solutions of the indicated system, failed to take into consideration interaction between the components of the system.

EXPERIMENTAL

The aniline, quinoline and pyridine were purified by the technique of drying them over potassium hydroxide and subsequent distillation. For our work the following fractions were taken: aniline 183-184°, quinoline 283°, and pyridine 115°. Their specific gravities at 20° were respectively 1.022, 1.0939 and 0.984. The acetic

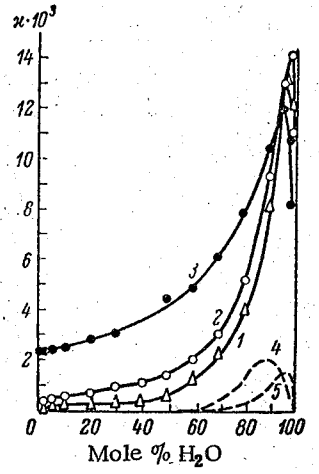

Figure 1. Electrical conductivities of the systems: 1) $C_9H_7N \cdot CH_3COOH - H_2O$; 2) $C_9H_7N \cdot 2CH_3COOH - H_2O$; 3) 12 mole % C_9H_7N and 88 mole % $CH_3COOH - H_2O$; 4) $C_9H_7N - CH_3COOH$; 5) $CH_3COOH - H_2O$.

TABLE 1

Amount of H_2O (in mole %)	Specific electrical conductivity $\kappa^{20} \cdot 10^3$	
	$C_9H_7N \cdot CH_3COOH - H_2O$	$C_9H_7N \cdot 2CH_3COOH - H_2O$
2	0.0431	0.4233
5	0.0581	0.4786
10	0.0616	0.5282
20	0.0789	0.6593
30	0.1859	1.008
40	0.3950	1.138
50	0.5986	1.518
60	1.201	2.143
70	2.256	3.148
80	3.919	5.141
90	8.016	9.397
95	13.0	13.19
98	12.02	14.32
99	—	11.405

acid was obtained from the commercial grade of glacial acetic acid by the technique of repeated freezings. The acid obtained in this manner had m. p. 16.45°. The water that we used had been distilled twice. The mixtures were prepared by the gravimetric technique, and stored in special dark-colored flasks fitted with ground-glass stoppers, which, in turn, were kept in a desiccator. The electrical conductivity of these mixtures was measured in the usual manner at 20 ± 2°.

Quinoline-Acetic Acid-Water System

Puschin and Rikovski [3] studied the binary quinoline-acetic acid system by the fusion method, and Puschin and Matavulj [4] studied it by the refractive index method. The diagrams of these properties indicate that two compounds are formed in the system: $C_9H_7N \cdot CH_3COOH$ and $C_9H_7N \cdot 2CH_3COOH$, both showing thermal decomposition into their components. Proceeding from this, we consider it expedient to study the solutions, corresponding to the composition of these compounds, in water.* In view of the fact that the specific electrical conductivity isotherm of solutions of the binary system quinoline-acetic acid, studied by Puschin and Tutundzhic [5], shows a maximum, corresponding to a composition of 12 mole % quinoline, we deemed it necessary to also measure the electrical conductivity of this solution in water.

Our measurement results for the specific electrical conductivities of all of these solutions are given in Table 1 and plotted in Fig. 1.

For the sake of comparison we have also shown by dotted lines in Fig. 1 the specific electrical conductivity isotherms for the binary systems: quinoline-acetic acid, based on the data of Puschin and Tutundzhic [5], and acetic acid-water, based on the data of N. A. Trifonov and S. I. Cherbov [6].

Aniline-Acetic Acid-Water System

The physicochemical analysis method has been used to study many of the properties of the binary system aniline-acetic acid [7-9]. The diagrams of all of the studied properties agree in indicating the formation in the system of a compound with composition $C_6H_5NH_2 \cdot 2CH_3COOH$. Only a few authors also indicate the formation of a second compound with the composition $C_6H_5NH_2 \cdot CH_3COOH$.

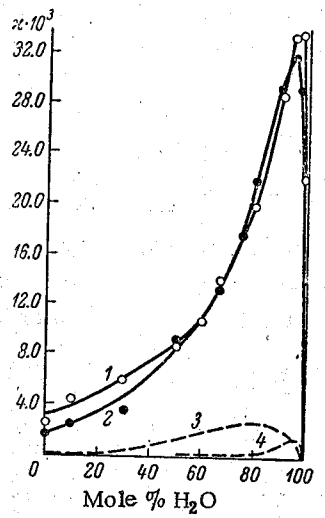

Figure 2. Electrical conductivities of the systems:
1) $C_6H_5NH_2 \cdot 2CH_3COOH-H_2O$; 2) $C_6H_5NH_2 \cdot CH_3COOH-H_2O$; 3) $CH_3COOH-C_6H_5NH_2$; 4) $CH_3COOH-H_2O$.

TABLE 2

Amount of H_2O (in mole %)	$\chi^{20} \cdot 10^3$	
	$C_6H_5NH_2 \cdot CH_3COOH-H_2O$	$C_6H_5NH_2 \cdot 2CH_3COOH-H_2O$
0.0	1.980	2.580
10.0	2.471	4.541
30.0	3.540	5.886
50.0	9.086	8.804
67.0	13.52	13.81
75.0	17.68	—
80.0	21.91	19.72
90.0	29.03	28.63
95.0	31.81	33.21
97.0	29.35	33.26
98.0	26.65	—
99.0	19.81	22.09

* We discount the possibility of interaction in the acetic acid-water system, since at the present time there fail to exist reliable data, testifying to the presence of interaction between them, while our taken amines are practically immiscible with water, with the exception of pyridine, which, although it is completely miscible with water, still apparently fails to show reaction with it, or else reacts very slightly.

The maximum on the specific electrical conductivity isotherm is found at 33 mole % aniline, i.e. it corresponds to the composition of the compound

$$C_6H_5NH_2 \cdot 2CH_3COOH.$$

In connection with this we prepared solutions for our measurements, corresponding to the composition of these compounds with water, i.e. (33.3 mole % aniline + 66.7% mole % acetic acid)-water and (50 mole % aniline + 50 mole % acetic acid)-water.

The data, obtained by us in measuring the specific electrical conductivities of the solutions of this ternary system, are given in Table 2, while the corresponding specific electrical conductivity isotherms, constructed on the basis of the data given in this table, are shown in Fig. 2. The specific electrical conductivity isotherms of the binary system acetic acid-water, constructed on the data of N. A. Trifonov and S. I. Cherbov [6], is shown below the dotted Line 3.

Pyridine-Acetic Acid-Water System

Many of the properties of the binary system pyridine-acetic acid have also been studied by physicochemical analysis methods. In particular, the fusion method was used by Puschin and Rikovski [3], the viscosity method by Faust [10] and others, and the electrical conductivity method by Petten [11], A. N. Sakhanov [12], N. A. Trifonov and S. I. Cherbov [6], A. S. Naumova [13] and others. The diagrams of these properties indicate the formation of four compounds in the system; however, reliable mention can be made of only two compounds, and specifically: $C_5H_5N \cdot CH_3COOH$ (by the fusion diagram) and $C_5H_5N \cdot 2CH_3COOH$ (by all of the other properties). The specific electrical conductivity isotherm of the system pyridine-acetic acid shows a maximum, found at approximately 80 mole % acetic acid.

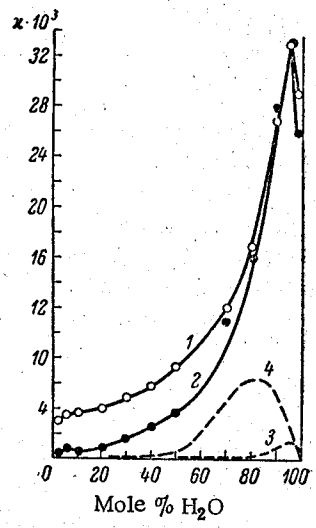

Figure 3. Electrical conductivities of the systems: 1) $C_5H_5N \cdot 2CH_3COOH-H_2O$; 2) $C_5H_5N \cdot CH_3COOH-H_2O$; 3) $CH_3COOH-H_2O$; 4) $C_5H_5N-CH_3COOH$.

TABLE 3

Amount of H_2O (in mole %)	$\chi_{20} \cdot 10^3$	
	$C_5H_5N \cdot 2CH_3COOH-H_2O$	$C_5H_5N \cdot 2CH_3COOH-H_2O$
2	0.6126	3.335
5	0.5343	3.703
10	0.7203	3.775
20	0.9793	4.354
30	1.674	4.988
40	2.365	5.758
50	3.675	7.176
60	5.997	9.024
70	11.80	12.067
80	16.29	17.43
90	28.06	27.05
95	33.07	33.09
98	26.46	29.46

For our study we prepared solutions composed of 50 mole % acetic acid and 50 mole % pyridine in water, and 33 mole % acetic acid and 67 mole % pyridine in water.

The results of our specific electrical conductivity measurements are given in Table 3, while the corresponding isotherms are shown in Fig. 3.

DISCUSSION OF RESULTS

As can be seen from the presented plots, the electrical conductivity of the studied solutions shows constant increase in measure with the addition of water to the mixtures of amine and acetic acid; here the specific electrical conductivity passes through a sharp maximum at 95 mole % water and then drops rapidly. Of interest is the fact that all of the solutions of the ternary systems show much greater electrical conductivities than do the solutions of the binary systems, composed of acetic acid and the same amines. Thus, for example, the maximum specific electrical conductivity shown by solutions of the ternary system quinoline-acetic acid-water exceeds $12 \cdot 10^{-3}\ \Omega^{-1}\ cm^{-1}$. The maximum electrical conductivity shown by solutions of the binary system quinoline-acetic acid, as can be seen from the presented specific electrical conductivity isotherm (Fig. 1, dotted line), is equal to only $2 \cdot 10^{-3}\ \Omega^{-1}\ cm^{-1}$, while the maximum electrical conductivity shown by the system acetic acid-water is even less, being of the order of $1.6 \cdot 10^{-3}\ \Omega^{-1}\ cm^{-1}$. An even greater difference in the maximum specific electrical conductivity is observed in the aniline-acetic acid system. Thus, for example, the maximum specific electrical conductivity shown by solutions of the ternary system aniline-acetic acid-water is $32 \cdot 10^{-3}\ \Omega^{-1}\ cm^{-1}$, while at the same time the maximum electrical conductivity shown by solutions of the binary system aniline-acetic acid fails to reach $3 \cdot 10^{-3}\ \Omega^{-1}\ cm^{-1}$. As a result, the addition of water to binary systems, composed of amines and acetic acid, leads to a 7- to 10-fold increase in the electrical conductivity. In isolated cases the specific electrical conductivity shown by solutions of the ternary systems is more than 3 times greater than the electrical conductivity shown by 0.1 N potassium chloride solution. This makes it possible to select the desired solution of the ternary system for running the electrolysis under optimum conditions. Such a large increase in the electrical conductivity shown by solutions of binary systems, composed of amines and acetic acid, when water is added to them, in our opinion, can be explained as follows. The electrical conductivity shown by solutions of binary systems, composed, for example, of aniline and acetic acid, is determined by the ionization of the compounds formed in this system by the following schemes:

$$1)\ C_6H_5NH_2 \cdot 2CH_3COOH \rightleftarrows C_6H_5NH_3^+ + CH_3COOH \cdot CH_3COO^-,$$
$$2)\ C_6H_5NH_2 \cdot CH_3COOH \rightleftarrows CH_3COO^- + C_6H_5NH_3^+.$$

The added water ionizes an additional amount of the acid, which is present in all of the solutions in excess, since all of the binary systems taken by us are irrational, i.e. the compounds formed in the system suffer decomposition into their components. As a result, together with the above indicated ions in the solutions of the ternary systems studied by us, there also appear H_3O^+ and CH_3COO^- ions due to ionization of the acid molecule. Naturally, this should lead to a noticeable increase in the electrical conductivity. Consequently, it can be said that the total electrical conductivity shown by solutions of the above ternary systems is an additive value, based on the electrical conductivities shown by two binary systems: amine-acetic acid and acetic acid-water.

SUMMARY

1. The electrical conductivities shown by a number of solutions of the ternary systems: quinoline-acetic acid-water, aniline-acetic acid-water and pyridine-acetic acid-water were measured.

2. It was established that the electrical conductivities shown by solutions of these ternary systems are always greater than are the electrical conductivities of the corresponding solutions of the binary systems, formed from amines and acetic acid or from acetic acid and water. In individual solutions the addition of water to solutions of the binary systems leads to a 10-fold increase and more in the electrical conductivity. This increase in electrical conductivity is explained by the independent ionization of the acid in water, and of the complex formed by the acid and amine.

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Lvov Medical Institute

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