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## APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

# Synthesis of New Electrolytes in Solutions with dc Current

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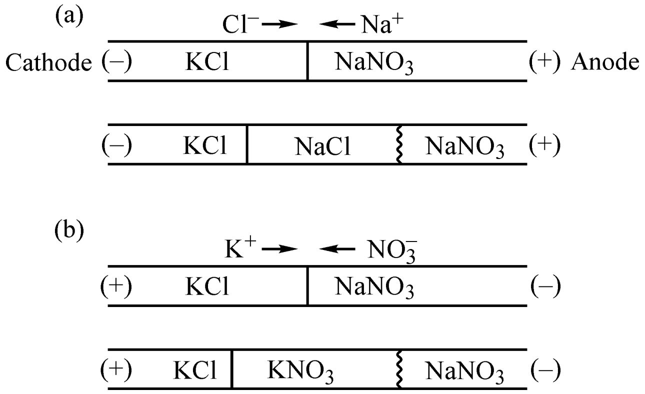
**Abstract**—Conditions under which new pure electrolyte solutions can be obtained by passing dc electric current through contacting solutions with four different ions were considered. Electrolytes were synthesized in capillary columns by various procedures.

The study is concerned with synthesis of electrolytes in which a new solution is obtained by passing dc electric current through electrolytes brought in contact. The possibility of such a synthesis was mentioned by Kohlrauch [1], who wrote that, if electric current is passed across the interface between contacting electrolytes, one more electrolyte is to be formed. A review devoted to isotachophoresis [2] reported, with reference to [1], that such a synthesis of new electrolytes is possible. However, conditions for synthesis of a pure solution were not formulated, procedures for synthesis of new electrolytes were not systematized, and the synthesis itself was not carried out experimentally in [2].

According to Kohlrauch's concept, a new electrolyte can be obtained in interaction of two solutions containing four different ions. This condition is necessary, but not sufficient for obtaining a new pure electrolyte. Let us illustrate this with the following example. In scheme 1a, two electrolytes are represented: KCl (catholyte) and $NaNO_3$ (anolyte). These solutions contain $K^+$, $Na^+$, $NO_3^-$, and $Cl^-$ ions. On applying an electric field, $K^+$ and $Na^+$ ions will move toward the cathode, and $NO_3^-$ and $Cl^-$ ions, toward the anode. In the course of electrolysis, a new NaCl solution is formed at the place of contact between the solutions. Because the mobility of the potassium ion ($u_{K^+}$) exceeds that of the sodium ion ($u_{Na^+}$), a stable interface moving toward the cathode is formed between the KCl and NaCl solutions [3, 4]. No stable boundary is formed at the other end of the column of the NaCl solution, because the mobility of chloride ions ($v_{Cl^-}$) exceeds that of nitrate ions ($v_{NO_3^-}$), which will lead to mixing of NaCl and $NaNO_3$ solutions (Scheme 1a). The width of the mixing zone will increase with the time of electrolysis.



**Scheme 1.** Motion of ions: (a) in interaction of KCl (catholyte) and $NaNO_3$ (anolyte) solutions; (b) upon a change of the polarity across the electrodes (*wavy lines* correspond to mixing of solutions).

In the case of a change of polarity across the electrodes, a $KNO_3$ solution will form at the place of contact between the solutions (Scheme 1b). However, the $KNO_3$ and $NaNO_3$ solutions will mix because $u_{K^+} > u_{Na^+}$. To synthesize from two electrolytes, $C_1A_1$ and $C_2A_2$, containing four different ions a pure electrolyte $C_2A_1$ not mixed with the starting solutions in the column, it is necessary that the following inequalities should be observed:

$$u^C_{C_1} > u^S_{C_2}, \tag{1}$$

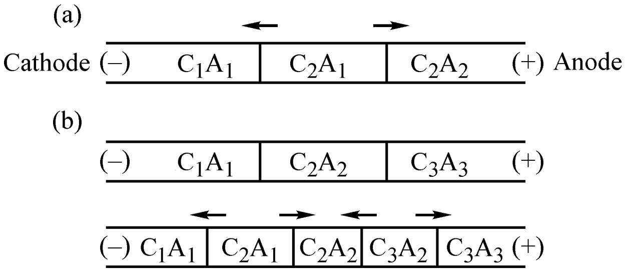
$$v^S_{A_2} < v^A_{A_2}, \tag{2}$$

where $u^C_{C_1}$ and $u^S_{C_2}$ are the mobilities of the cations of the catholyte and the electrolyte being synthesized, respectively; $v^C_{A_1}$ and $v^A_{A_2}$, mobilities of the anions of the anolyte and the electrolyte being synthesized, respectively.

The superscripts refer: *C* to the catholyte, *S* to the solution being synthesized, and *A* to the anolyte; the subscripts $C_1$, $C_2$, $A_1$, and $A_2$ denote the cations and anions of the respective solutions.

If inequalities (1) and (2) are observed, the boundaries between the solution being synthesized and the catholyte and anolyte are stable in an electric field and move in opposite directions. The boundary between the solution being synthesized and the catholyte will move toward the cathode, and that between the solution and the anolyte, toward the anode (Scheme 2a). The number of gram-equivalents of the substance being synthesized will be $I\tau F$, where $I$ is the current (A); $\tau$, time (s); and F, Faraday number (C g-equiv$^{-1}$). This formula follows from the fact that, if inequalities (1) and (2) are observed, only the anion passes across the boundary between the solution being synthesized and the catholyte, and only the cation, across the interface with the anolyte.

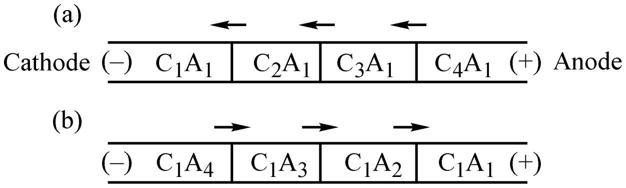
However, the potentialities of synthesis may markedly exceed that of the variant considered. Let us demonstrate this by the following example:



**Scheme 2**. (a) Synthesis of $C_2A_1$ solution from $C_1A_1$ (catholyte) and $C_2A_2$ (anolyte) in the case when inequalities (1) and (2) are observed; (b) simultaneous synthesis of two solutions, $C_2A_1$ and $C_3A_2$, from three solutions $C_1A_1$, $C_2A_2$, and $C_3A_3$. The *arrows* show the directions in which the boundaries of the electrolytes being synthesized move under the action of electric current.

Let us consider a column charged with three electrolytes. Let these be the following solutions: $C_1A_1$ (catholyte), $C_2A_2$ (middle solution), and $C_3A_3$ (anolyte) (Scheme 2b). If these solutions are chosen in such a way that, on passing an electric current, $C_2A_1$ solution is synthesized from the first pair of solutions ($C_1A_1$ and $C_2A_2$), and $C_3A_2$ solution from the second pair of solutions ($C_2A_2$ and $C_3A_3$), then two different substances will be simultaneously synthesized in the column. Such a synthesis is possible if inequalities (1) and (2) are observed for each pair of solutions ($C_1A_1$ and $C_2A_2$) and ($C_2A_2$ and $C_3A_3$) and for the solutions being synthesized ($C_2A_1$ and $C_3A_2$).

In this case, $I\tau$/F gram-equivalents of a new substance will be synthesized from each pair of solutions on passing $I\tau$ coulombs of electricity. The number of electrolyte pairs can be raised. In addition to the variants considered, replacement of one ion for another of the same sign in solution under the action of dc electric current should be regarded as synthesis of electrolytes. It is known that all the zones of the solutions acquire a common anion in the course of electrolyses in cationic isotachophoresis, and, by contrast, a common cation, in anionic isotachophoresis [3, 4]. The zones obtained in cationic and anionic isotachophoreses are shown schematically in Scheme 3. If $C_2A_2$ solution is placed instead of $C_2A_1$ solution in the column for cationic isotachophoresis, a stable zone of $C_2A_1$ solution will be obtained in the course of electrolysis. Thus, anion $A_2$ can be replaced with anion $A_1$ in the starting $C_2A_2$ solution. Similarly, one cation can be replaced with another in the starting solution by means of anionic isotachophoresis. One ion is frequently replaced with another in separation of electrolyte mixtures in practice of analytical capillary isotachophoresis [5, 6]. However, this method has not been regarded as synthetic and has not been used to synthesize new compounds.



**Scheme 3.** Distribution of zones in isotachophoresis. Variant: (a) capillary and (b) anionic.

To carry out this synthesis procedure experimentally, it is necessary to chose electrolytes and solution concentrations and to evaluate the ion mobilities. Let us describe a possible way to calculate the solution concentrations and ion mobilities for synthesizing a new electrolyte solution with the use of catholyte and anolyte (Scheme 2a).

This way can be put into effect only for the steady state (with the time-independent solution concentrations satisfying the controlling relation) [7]. To perform a calculation, it is necessary to know the catholyte concentration and have plots of the ion transference numbers with respect to the solvent against the solution concentrations for the catholyte, solution being synthesized, and anolyte. With this information available, the calculation can be performed as follows.

(1) The cation transference number is found for the chosen catholyte concentration from the dependences of the ion transference numbers for the catholyte on its concentration.

(2) The concentration and the cation transference number of the electrolyte being synthesized are found graphically from the concentration dependence of the ion transference numbers of the catholyte and the electrolyte being synthesized [8].

(3) The anion transference number of this solution is found from the cation transference number of the catholyte being synthesized.

(4) The concentration and the anion transference number of the anolyte are found, also graphically, from the concentration and the anion transference number of the electrolyte being synthesized and from the concentration dependence of the ion transference numbers of the anolyte [8].

(5) The resulting solution concentrations and ion transference numbers can be used to find the mobilities appearing in relations (1) and (2).

(6) The ion mobility is calculated by the formula

$$u = T\chi/\mathrm{F}c, \tag{3}$$

where $u$ is the ion mobility (cm$^2$ V$^{-1}$ s$^{-1}$); $T$, ion transference number; $\chi$, electrical conductivity of the solution ($\Omega^{-1}$ cm$^{-1}$); F, Faraday number (C g-equiv$^{-1}$); and $c$, solution concentration (g-equiv l$^{-1}$).

However, the above calculation procedure can be only used in very rare cases because of the complete lack of data on how the ion transference numbers depend on the solution concentration at high concentrations, for which such a synthesis is the most promising. In addition, the solution concentrations do not necessarily satisfy the steady-state conditions in syntheses of new substances.

Synthesis can be performed at equal solution concentrations. In this case, the choice of starting electrolytes is not difficult if the ion mobilities are only roughly estimated (higher or lower). The electrolytes are chosen by comparing the ion mobilities of solutions having equal concentrations (g-equiv l$^{-1}$) and a common ion. This evaluation method, suggested in [9], is worthwhile in practice in studying the separation of electrolyte mixtures in concentrated solutions by ion mobilities. Let us illustrate this technique by the following example.

Let there exist two electrolytes ($C_1A_1$ and $C_2A_1$) of equal concentrations. The equivalent electrical conductivity ($\lambda$) of $C_1A_1$ solution is given by

$$\lambda_{C_1A_1} = \mathrm{F}(u_{C_1} + v_{A_1}), \tag{4}$$

and that of $C_2A_1$ solution by

$$\lambda_{C_2A_1} = \mathrm{F}(u_{C_2} + v_{A_1}). \tag{5}$$

As the solutions have a common ion (anion) the mobility of the noncommon ion (cation) will be higher for that solution, which has a higher equivalent electrical conductivity. Therefore, a stable interface between the solutions will be formed if the electrolyte having a higher equivalent electrical conductivity is situated ahead of that with a lower electrical conductivity in the direction of motion of noncommon ions in the electric field. Hence follows that synthesis of a new solution on bringing in contact two solutions containing four different ions yields an electrolyte whose equivalent electrical conductivity is lower than that of each of these solutions at a concentration equal to that of the starting solutions. Let us consider, as an example, choice of electrolytes in interaction of two solutions containing four different ions: $K^+$, $Na^+$, $Cl^-$, and $NO_3^-$. Four different compounds can be formed from these ions: KCl, $KNO_3$, NaCl, and $NaNO_3$. The equivalent electrical conductivities of aqueous solutions of these compounds at a concentration of 2.0 g-equiv l$^{-1}$ and temperature of 18°C are as follows:

| Substance | KCl | $KNO_3$ | NaCl | $NaNO_3$ |
|---|---|---|---|---|
| $\lambda$, $\Omega^{-1}$ g-equiv$^{-1}$ cm$^2$ | 92.3 | 69.0 | 66.6 | 54.4 |

It can be seen from the electrical conductivity data that the following compounds cannot be synthesized: (1) KCl, whose electrical conductivity is the highest; (2) $KNO_3$, whose electrical conductivity is lower than that of only a single solution; and (3) NaCl, whose electrical conductivity is lower than that of two solutions (KCl and $KNO_3$), but these solutions contain no sodium ions and, therefore, cannot be used in synthesis.

Only an $NaNO_3$ solution can be synthesized in pure form. As starting solutions for this synthesis can serve only $KNO_3$ and NaCl solutions containing four different ions and having an equivalent electrical conductivity exceeding that of the $NaNO_3$ solution. This principle of electrolyte selection was used when carrying out this synthesis in practice. In those cases when no data are available on the equivalent electrical conductivities of solution, the electrolytes can be chosen experimentally.

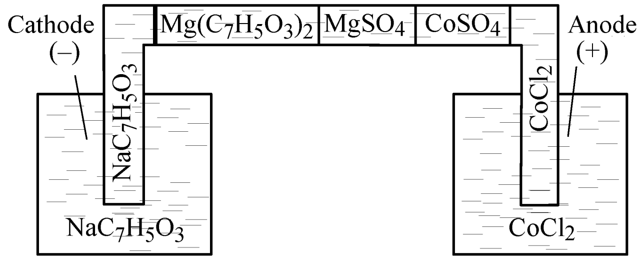
## EXPERIMENTAL

Any of the synthesis variants considered above can be performed experimentally using devices for capillary isotachophoresis, described in [10, 11]. These devices have an extended detector that makes it possible to monitor the course of synthesis over a long part of the capillary column. ∏-shaped removable capillaries with an inner diameter of 0.05–0.8 mm can be used in the devices. The capillaries employed in this study had inner and outer diameters of 0.2–0.5 and 0.4–1 mm, respectively. The capillaries were 30 to 50 cm long, with a horizontal part of 20 to 30 cm. The ends of the capillaries were pointed as pipette tips, which made it possible to raise the hydrodynamic resistance of the capillaries and to virtually eliminate solution overflow. To carry out the synthesis, the capillaries were filled with the starting solutions and mounted in the device. This was done in such a way that like solutions at the capillary ends and in the electrode vessels came into contact. The synthesis was performed with aqueous electrolyte solutions. The following variants of synthesis were used.

(1) Synthesis of a solution (LiCNS) from a catholyte (2.0 N KCNS solution) and anolyte (2.0 N LiCl solution). The electrolysis was terminated when the solution being synthesized occupied a position in the horizontal part of the capillary between two marks. The marks were preliminarily deposited onto the capillary surface with a colored lacquer.

(2) Simultaneous synthesis of two new solutions. In this experiment, a 2.0 N solution of sodium salicylate ($NaC_7H_5O_3$) served as catholyte, and a 2.0 N $CoCl_2$ solution, as anolyte. A $MgSO_4$ solution was used as a middle solution. On passing an electric current, magnesium salicylate $Mg(C_7H_5O_3)$ was synthesized from $NaC_7H_5O_3$ and $MgSO_4$ solutions, and a $CoSO_4$ solution from $MgSO_4$ and $CoCl_2$ (Scheme 4). The electric current was switched off when the $MgSO_4$ solution completely disappeared. It should be noted that the interface between the $NaC_7H_5O_3$ and $Mg(C_7H_5O_3)$ solution, obtained in this case, was wider than those between other electrolytes. This is shown by a heavier line in Scheme 4.

(3) Replacement of the chloride ion for the rhodanide, acetate, and bromate ions in solutions of chlorides of rare-earth elements samarium(III), neodymium(III), and yttrium(III), respectively. $Sm(CNS)_3$ was synthesized from a 2.0 N KCNS solution (catholyte) and 1.5 N $NiCl_2$ solution (anolyte). In synthesis of $NdAc_3$, a 2.0 N KAc solution served as catholyte, and a 1.5 N $CdCl_2$ solution as anolyte. $Y(BrO_3)$ was obtained using a 2.0 N $KBrO_3$ solution as catholyte and a 1.5 N $CdCl_2$ solution as anolyte. In the cases mentioned in item 3, a steady state was attained in the capillary column. The lengths of the zones of the electrolytes synthesized were time-independent.



**Scheme 4.** Simultaneous synthesis of magnesium salicylate $Mg(C_7H_5O_3)$ and $CoSO_4$ solutions.

After an experiment was complete, the capillary in which synthesis was carried out was removed from the device and the zone of the solution synthesized was cut off at its boundaries. New electrolyte solutions with a prescribed chemical or isotopic composition can be synthesized in capillary columns not only in a free solution, but also in a transparent filler, e.g., agar-agar. It should be noted that the synthesis procedure under consideration can be easily made ecologically safe. However, only microscopic amounts of new electrolyte solutions can be synthesized in capillary columns. Special technological apparatus should be designed to synthesize larger amounts of electrolytes.

## CONCLUSIONS

(1) Conditions for synthesis of a new electrolyte in interaction of two solutions containing four different ions were formulated.

(2) Various procedures for synthesis of new electrolytes were systematized.

(3) A rule for selection of starting electrolytes for syntheses was suggested.

(4) Various procedures for synthesis of electrolytes were carried out experimentally.

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