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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Demineralization of Alkaline Soil Extracts by Electrodialysis with Inert and Ion-Exchange Membranes

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Abstract—Mass-transfer in electrodialysis of alkaline soil extracts containing pyrophosphate ions with cellophane and MA-40 and MA-41 ion-exchange membranes was studied. The transport numbers of hydroxide- and phosphorus-containing ions and the degree of demineralization of the alkaline soil extracts were determined under the conditions under study.

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An effective procedure to isolate humic acids from the organic substance of soils in a study of their qualitative and quantitative composition is extraction with a mixture of sodium hydroxide and pyrophosphate at pH 12–13 [1]. The extract obtained in this case is a polydisperse system and contains a mixture of humates and fulvates with pyrophosphate complexes of metals and an excess amount of an alkali and sodium pyrophosphate. Acidification of the extract with hydrochloric or sulfuric acid to pH 1.5–2.0 yields a poorly soluble precipitate of humic acids, with soluble fulvic acids remaining in solution. The resulting preparations of humic acids contain a considerable amount of mineral components, which requires an additional purification.

An efficient way to purify colloid systems to remove electrolytes is electrodialysis [2]. Data on use of membrane methods in, in particular, demineralization of soil extracts are scarce. It seems, however, that use of these methods to remove most part of electrolytes that accompany humic substances will yield humic acid preparations with increased purity.

The aim of this study was to determine the fundamental aspects of mass transfer in electrodialysis of soil extracts with membranes of varied chemical nature.

EXPERIMENTAL

As object of study served alkaline extracts obtained by treating samples of virgin chernozem, leached with a 0.1 M solution of sodium pyrophosphate, in a 0.1 M sodium hydroxide solution at a soil : solution mass ratio of 1 : 5 for 24 h. The resulting suspension was centrifuged and the alkaline extract of humic acids was separated from the solid phase and subjected to electrodialysis with inert or ion-exchange membranes. As inert membranes were used an unvarnished cellulose film [cellophane, GOST (State Standard) 7730–89]. In addition, the following membranes were employed: heterogeneous MK-40 based on a KU-2 sulfostyrene cation exchanger, MA-40 based on an EDE-10P low-basic anion exchanger of aliphatic nature, and MA-41 containing a AV-17 strongly basic

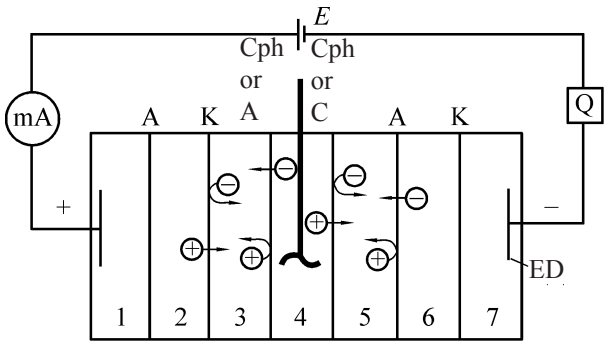

Fig. 1. Schematic of the installation for electrodialysis. (*E*) dc power source, (ED) electrodialyzer, (1–4) electrodialyzer sections, (Q) coulometer, (mA) milliammeter, (+) cations, and (–) anions. Membranes: (A) anion-exchange, (C) cation-exchange, and (Cph) cellophane.

anion exchanger with a polystyrene matrix and fixed trimethylbenzylammonium ion.

The electromembrane transfer was studied on an installation schematically shown in Fig. 1. The electrodialyzer was connected into a dc circuit including a milliammeter and a copper coulometer. An alkaline extract under study was poured into section 4 of the apparatus, equipped with a stirrer. Sections 1, 3, 5, and 7 were filled with distilled water; and buffer sections 2 and 6, with a 2 M potassium nitrate solution. The electrodialysis was performed at a current density of 10 mA cm^{-2}, which provided a high process intensity at a minimum solution heating. In the course of electrodialysis, anions from the extract under study were transferred across the cellophane or anion-exchange membrane to section 3, into which potassium cations migrated across the cation-exchange membrane from section 2. Similarly, cations from the mixture under study and nitrate ions from section 6 migrated to section 5. Every 30 min, solutions from section 3 (permeates) were discharged and the section was again filled with distilled water. In parallel, the pH was measured in a solution in section 4 (retentate) at a switched-off current with a pH-150 ion meter. The permeate and the starting extract were analyzed for the content of proton-acceptor ions by potentiometric titration.

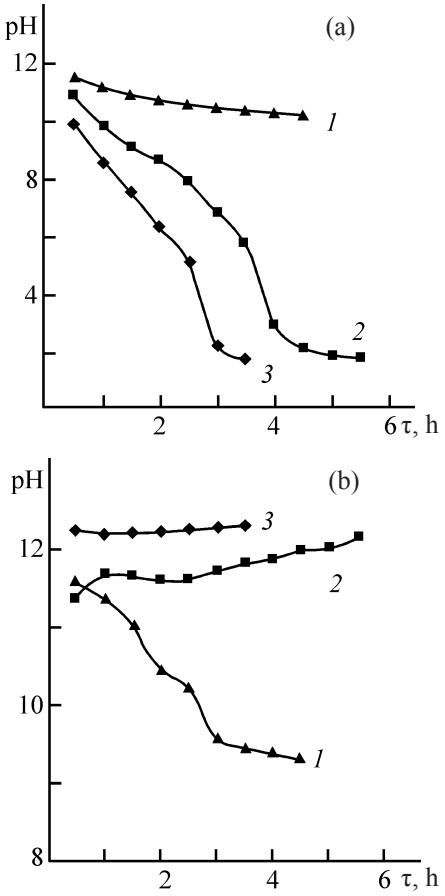

Fig. 2. pH of (a) retentate and (b) permeate vs. the duration τ of electrodialysis with (*1*) cellophane membranes and anion-exchange membranes (*2*) MA-40 and (*3*) MA-41.

The exact quantity of electricity passed through the system was found from the mass of copper deposited at the coulometer cathode [3]. The transport numbers of anions in membranes were calculated as ratios between the amounts of their equivalents in the permeates and the amount of equivalents of deposited copper. The degree of demineralization was determined as the ratio between the number of moles of phosphorus-containing ions transferred to section 3 in a given time and their initial amount.

Figure 2 shows how the pH value of the retentate (a) and permeate (b) varies in the course of electrodialysis of the alkaline extract. The runs of the curves obtained with inert and anion-exchange membranes are fundamentally different. When the anion mass transfer was performed across the inert cellophane membrane, the pH value of the retentate decreased during the process by only a single unit (Fig. 2a, curve *1*). At the same time, in an electrodialysis with ion-exchange membranes, the pH value decreased from 11 to 2 (Fig. 2a, curves *2* and *3*). This points to a substantially higher intensity of the electrodialytic demineralization of the extract in the case of ion-exchange membranes. The observed strong difference in the manner in which the pH values of the retentate and the corresponding permeates vary in the course of electrodialysis indicates that the ionic composition of the solutions changes.

It is known that pyrophosphoric acid has ionization constants pK_2 2.36, pK_3 6.60, and pK_4 9.25 [4]. The ionic composition of the solution varies with the pyrophosphate concentration and pH value. A calculation demonstrated that, in accordance with the acid-base equilibrium laws [5], the solution pH is 11.12 at a 0.1 M concentration of pyrophosphate ions, whereas above this value, an excess amount of hydroxide ions is present in solution. At pH < 11.12, the solution composition is determined by hydrolysis of pyrophosphate ions contained in the solution at a concentration lower than 0.1 M or is a buffer mixture containing pyrophosphate and hydropyrophosphate ions. A decrease in pH to 7.92 results in that only pyrophosphate ions are present in solution, and upon further increase in acidity, a hydropyrophosphate–

dihydropyrophosphate buffer mixture is formed. Presence of only dihydropyrophosphate ions in solution is only possible at pH 4.48. These considerations underlie a calculation of the transport numbers of anions in membranes according to potentiometric titration data.

Figure 3 shows how anion transport numbers in the membranes vary in the course of electrodialysis. In the initial stage of the process, in electrodialysis with cellophane membranes (Fig. 3a), the excess of hydroxide ions is removed from the retentate (curve *1*) and the mass transfer is mostly by pyrophosphate ions (curve *2*). Further, as the pH of the retentate decreases (Fig. 2a, curve *1*), there occurs joint transfer of pyrophosphate and hydropyrophosphate ions (Fig. 3a, curves *2* and *3*). The sum of the transport numbers (Fig. 3a, curve *4*) at the beginning of the process is close to 0.5, in agreement with the nature of inert membranes. Further, however, this value decreases to become about 0.2 at the end of the process. The last value indicates that the inert membrane exhibits an electrochemical activity and acquires the properties of an ion-exchange membrane. This occurs because of the sorption interaction of humic acid salts present in the retentate, humates and fulvates, with the membrane. According to [1], humic acids contain functional carboxy and phenolic hydroxy groups, of which carboxy groups are almost completely deprotonated at the pH values obtained [6]. The humates and fulvates sorbed by the cellophane membrane form a modifying negatively charged layer on its surface, which hinders the anion mass transfer.

The fundamental aspects of the anion mass transfer from the retentate across anion-exchange membranes dramatically differ from those for cellophane membranes. The transfer of hydroxide ions is observed during the whole process, which corresponds to how the pH value varies (Fig. 2b), and gradually increases by its end. The transport numbers of pyrophosphate ions pass through a kind of maximum and then start to decrease (Fig. 3b, curves *2* and *2*') because a substantial degree of demineralization is reached. As also in the case of cellophane membranes, the reason for the considerable mass transfer of hydroxide ions is the sorption of humates and fulvates by the surface of anion-exchange membranes. In contrast to the case of inert membranes, the sorption occurs both because of electrostatic interactions with fixed ions of the membranes and via formation of sorbate–membrane and sorbate–sorbate hydrogen bonds. Because of the ion-exchange process, a modifying layer is formed in the early stage of electrodialysis. As a result, a bipolar layer is formed on the surface, and the enhanced dissociation of water generates hydroxide ions, which are transferred across the anion-exchange membrane, and hydrogen ions, which are delivered to the retentate and favor a stronger decrease in pH as compared with the data obtained for inert membranes (Fig. 2).

The results obtained demonstrate a strong difference in anion mass transfer between the MA-40 and MA-41 membranes. At the beginning of the process, the transport numbers of pyrophosphate ions across the MA-40 membrane (Fig. 3b, curve *2*) obviously exceed the same parameter for hydroxides ions (curve *1*), and only by the end of the process, their values become close. In the case of the MA-41 membrane, the transport numbers of pyrophosphate ions gradually decrease, and those of hydroxide ions, increase; however, their values differ only slightly (Fig. 3b, curves *1*' and *2*'). Noteworthy is the very large, >0.9 (Fig. 3b, curve *4*'), sum of the transport

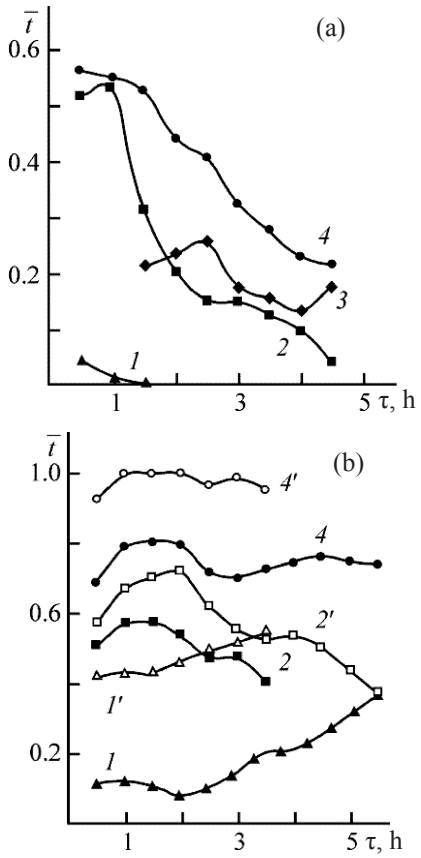

Fig. 3. Transport numbers $\bar{t}$– vs. the duration τ of electrodialysis with (a) cellophane and (b) ion-exchange membranes. Ionexchange membrane: (*1, 2, 4*) MA-40 and (*1*', *2*', *4*') MA-41. Anion: (*1, 1*') hydroxide, (*2, 2*') pyrophosphate, (*3, 3*') hydropyrophosphate, and (*4, 4*') $\Sigma\bar{t}$.

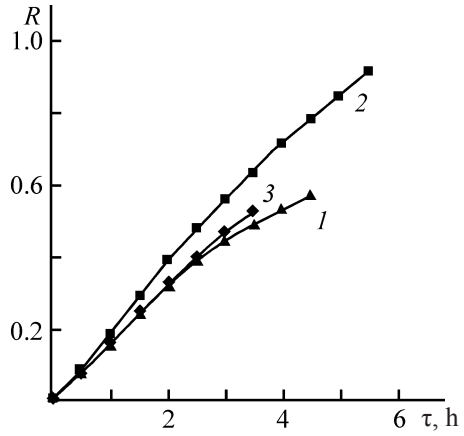

Fig. 4. Degree of demineralization, R, of an alkaline extract vs. the duration τ of electrodialysis with ion transfer across (*1*) cellophane membranes and anion-exchange membranes (*2*) MA-40 and (*3*) MA-41).

numbers of anions across the MA-41 membrane, to which a substantial contribution is made by hydroxide ions, whereas for MA-40, this value is 0.7–0.8 (curve *4*). The reason for this difference consists in the following. The structure of humic substances is based on chains of phenylcarboxylic acids [1]. Therefore, the nonexchange sorption of humates and fulvates by MA-41 membranes is more intense because of the aromatic nature of both the sorbent and sorbate. As a result, the modifying layer on an MA-41 membrane is more pronounced than that on MA-40, which has an aliphatic matrix. At the same time, the transfer numbers of hydroxide ions increase in the course of the process for both membranes and the pH values of the retentates sharply decrease (Fig. 2b) because the limiting diffusion current is reached upon a decrease in the electrolyte concentration. The differences in the concentrations at which the limiting current is reached is in agreement with the results of [7] and is presumably due to the dissimilar states of the membrane surfaces.

The efficiency of mass transfer across each of the membranes studied was evaluated by the degree of demineralization of the retentate to remove hydroxide and phosphorus-containing ions. According to the data in Figs. 2 and 3, the excess amount of hydroxide ions remaining in solution upon an interaction with the soil was completely removed, i.e., a full demineralization was achieved. The results of demineralization of extracts to remove phosphorus-containing ions are shown in Fig. 4. Comparison of the results shows that the demineralization is the most efficient with the MA-40 membrane because of the higher transport number of phosphorus-containing ions in this membrane (Fig. 3b). At the same time, the desalting of the extracts with cellophane and MA-41 anion-exchange membranes occurs with close intensities.

The possibility of transfer of humates and fulvates across a membrane was assessed on the basis of the light absorption by the permeates. Solutions of humates and fulvates are colored and absorb electromagnetic radiation in the visible spectral range [1]. According to the results obtained by measuring the light absorption by the permeates with a KFK-2 photocolorimeter at wavelengths of 465 and 665 nm, all the solutions were optically transparent, which confirmed that they contain no humic substances.

The purity of the humic acid preparations obtained was evaluated by the amount of the calcination residue formed when drying the samples in a muffle furnace at 600°C. This amount was 13.4% for the preparation isolated from the alkaline extract by the standard method of acidification with hydrochloric acid, and 4.0, 6.6, and 2.5%, respectively, for the preparations obtained with a preliminary electromembrane demineralization with cellophane, MA-40, and MA-41 membranes.

CONCLUSIONS

(1) The method of electrodialysis with ion-exchange membranes makes it possible to perform demineralization with a sufficiently high efficiency and to obtain humic acid preparations with increased purity. The optimal way is to combine cation-exchange membranes with MA-40 anion-exchange membranes of aliphatic nature, compared with the MA-41 having an aromatic matrix.

(2) As a result of sorption of humates and fulvates in the course of electrodialysis, the inert cellophane membrane acquires properties of a cation-exchange membrane.

(3) An enhanced mass transfer of hydroxide ions across the MA-41 membrane is due to an additional dissociation of water in the bipolar layer.

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