14. V. A. Koptyug, Zh. Vses. Khim. Obshch. im. D. I. Mendeleeva, 21, 247 (1976).
15. S. M. Shtein, Zh. Vses. Khim. Obshch. im. D. I. Mendeleeva, 21, 256 (1976).
16. G. G. Yakobson, Zh. Vses. Khim. Obshch. im. D. I. Mendeleeva, 21, 279 (1976).
17. H. Lankamp, W. Th. Nauta, and C. MacLean, Tetrahedron Lett., 249 (1968).

ANION-SELECTIVE ELECTRODES BASED ON LIQUID ION EXCHANGERS

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A review is given of the work done at the Chair of Physical Chemistry, Leningrad University, concerning the development and investigation of liquid and film-type anion-selective electrodes based on various liquid anion exchangers. The results obtained have shown that for all anion exchangers with noticeable dissociation the electrode's selectivity is practically the same, and for different anions it is determined by their extraction capability. In the instance of the nitrate electrode and nitric acid solutions it is shown that the emf can depend on acid absorption by the organic phase not due to exchange, and a method is proposed for finding the composition of the complex species in the organic media from the slope of the plot of emf vs log $a_{\pm HA}$ for an ion-selective electrode which is reversible to the anion A^-.

Systematic studies of the electrode properties of glasses and other ion-exchange materials have been conducted at Leningrad University over a period of more than 40 years. The first papers which provided a basis for the investigations in this direction appeared in the 1930s, when Nikol'skii suggested the thermodynamic ion-exchange theory of the glass electrode [1-3]. Later this theory was developed further in the work of Nikol'skii, Shul'ts, and co-workers [3-6], and also in the work of a number of American and European workers. Presently it is the basis of many investigations in the field of ion-selective membrane electrodes [7-9].

For a long time glass electrodes with univalent-cation function were studied. Attempts were also made to broaden the choice of electrodes by using other ion-exchange membranes, e.g., resin membranes, in addition to the glass membranes. But resin electrodes exhibiting marked selectivity to a certain ion could only be obtained in a few cases (NO_3^-, Ca^{2+}) [10, 11]. Accelerated research efforts concerning precipitate membranes also did not produce highly selective electrodes.

In the mid-1960s, American workers [7-9] suggested membranes of a new type based on liquid ion exchangers, and also membranes based on single- and polycrystalline materials. Progress in the fabrication of ion-selective electrodes with membranes prepared with crystalline salts is largely due to the fundamental work of Pungor [12, 13] and his school, who found a universal matrix for electrode membrane fabrication. In 1968 the investigation of liquid membranes was begun at Leningrad University. Electrodes for measuring the activity of a number of cations and anions were developed, studied, and improved during the past period [14-20]. Some of these results pertaining to electrodes with liquid and film-type anion-exchange membranes are presented in this paper.

Salts of quaternary ammonium bases differing in the radicals at the nitrogen atom (tetraoctyl-, tetranonyl-, tetradecyl-, tetralauryl-, methyltrioctyl-, methyltrinonyl-, and methyltrilaurylammonium), salts of phosphonium bases, and complex compounds of phenanthroline with Fe^{2+} and Ni^{2+} cations which were synthesized by us for these purposes were used as liquid ion exchangers.

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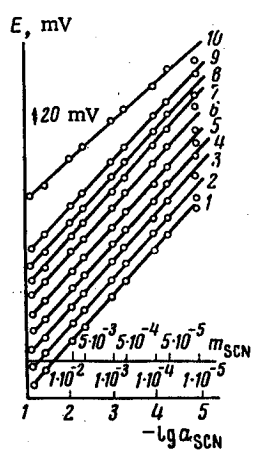

Fig. 1

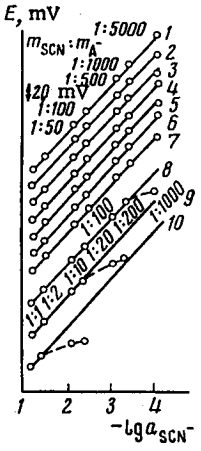

Fig. 2

Fig. 1. Calibration of thiocyanate electrodes based on the ion exchanger for the ClO_4^- electrode (Orion) (1), as well as on tetraoctylammonium (2), tetranonylammonium (3), tetradecylammonium (4), tetralaurylammonium (5), methyltrioctylammonium (6), methyltrinonylammonium (7), methyltrilaurylammonium (8), tetradecylphosphonium (9), and cetyltrimethylammonium (10).

Fig. 2. The effect of foreign ions on the SCN^- function of an electrode based on tetradecylammonium. The base electrolyte was 0.5 M for the foreign ions SO_4^{2-} (1), CO_3^{2-} (2), Cl^- (3), F^- (4), CH_3COO^- (5), $H_2PO_4^-$ (6), and HCO_3^- (7); the base electrolyte was 0.1 N for the foreign ions Br^- (8), NO_3^- (9), and I^- (10).

Chlorobenzene, nitrobenzene, and a number of esters of different acids, among them dibutyl phthalate, served as the solvents. Liquid membrane electrodes based on these compounds were fabricated in fluoroplast [PTFE] tubes closed off with cellophane as an inert, porous diaphragm, or in the housing of an Orion liquid electrode. But the most promising shape of membrane electrodes based on liquid ion exchangers proved to be that of a film, and they were used in preference. They were realized with a polyvinyl chloride matrix impregnated with organic solutions of the liquid anion-exchange materials listed above.

Such plasticized membranes are not fundamentally different from the liquid membranes where the functioning mechanism is concerned. But by enclosing the liquid ion exchanger into the polymer matrix one obtains a better defined boundary between the phases (membrane/aqueous solution), and also more constant operation of the film-type membrane and longer service life.

Dibutylphthalate-plasticized film-type polyvinyl chloride membranes for electrodes selective toward Cl^-, Br^-, I^-, NO_3, BF_4^-, CNS^-, and ClO_4 ions were made and studied in detail [14-20]. These electrodes were fabricated by gluing membrane disks of 12.5 mm diameter to the end of polyvinyl chloride tubes. In most cases a silver–silver chloride electrode was used as the internal electrode. The limits of functioning of the electrodes were determined by calibrating them in pure solutions of the corresponding electrolytes using the following galvanic cell:

$$\underset{\text{membrane electrode}}{\text{Ag}\,|\,\text{AgCl}\,\underset{0.1m}{\text{NaA}}\,|\,\text{membrane}\,|}\;\underset{\text{variable m}}{\text{NaA test solution of}}\;|\;\underset{\text{(sat.)}}{\text{KCl, AgCl}}\;|\;\text{Ag} \qquad \text{(I)}$$

Results obtained for the thiocyanate electrode are presented as an example in Fig. 1 [20]. It can be seen that these electrodes, with all the ion exchangers studied, exhibit the thiocyanate function over a wide range of

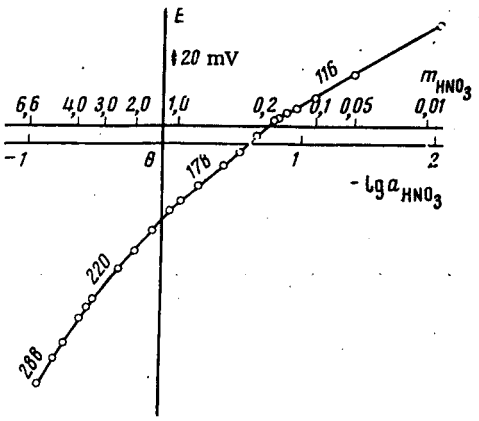

Fig. 3. The emf of galvanic cell (I) as a function of $-\log a_{HNO_3}$. The numbers at the curve are the slopes in mV.

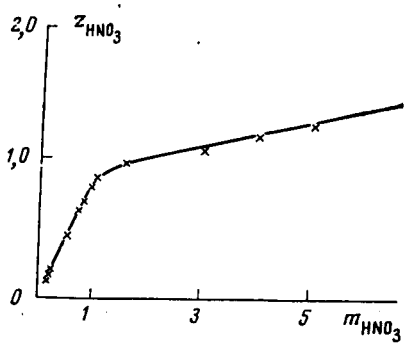

Fig. 4. Dependence of z_{HNO_3} on nitric acid concentration in aqueous solution for the extraction of HNO_3 with a 0.05 M tetradecylammonium NO_3 solution in chlorobenzene.

concentrations (10^{-1} to $5 \cdot 10^{-5}$ M SCN^-; the dependence of E on $-\log a_{SCN^-}$ is linear; the slope is 57 to 58 mV). To estimate the selectivity toward SCN^- ion we studied the influence of a number of foreign ions on the electrode function: SO_4^{2-}, CO_3^{2-}, Cl^-, F^-, CH_3COO^-, $H_2PO_4^-$, HCO_3^-, Br^-, I^-, NO_3^-, and ClO_4^-. For these purposes we measured the emf of cell (I) when this contained mixed solutions with a variable concentration of the basic ion and constant concentration of the foreign ion. Figure 2 shows the results only for the electrode based on tetradecylammonium, since for electrodes with other ion exchangers perfectly identical behavior was found, i.e., the thiocyanate function is preserved when the solution contains a 5000-fold excess of SO_4^{2-}, F^-, or $H_2PO_4^-$ ions, a 1000-fold excess of CO_3^{2-}, HCO_3^-, CH_3COO^-, or Cl^- ions, a 200-fold excess of Br^- ions, or a 10-fold excess of NO_3^- ions.

Thus, varying the radical from octyl to lauryl in the salts of symmetric or unsymmetric bases, or replacing the ammonium base by phosphonium base does not alter the sensitivity of the electrodes (the lower limit of functioning) or their selectivity. Similar behavior was found when studying electrodes which were reversible with respect to other anions (BF_4^-, NO_3^-, Br^-, and others). Thus, the results obtained indicate that the electrodic selectivity of liquid membranes with noticeable dissociation is substantially independent of the nature of the anion exchanger. Equally important is a conclusion drawn after systematic investigation of electrode systems based on liquid ion exchangers: There is a clear correlation between electrodic selectivity and the extraction capability of the systems.

In the selection of the salts of tetraalkylammonium bases as electrode-active materials we proceeded from data on the extraction capability of these compounds available in the literature. Thus, for tetraoctylammonium the extraction exchange constants were determined by Gindin and co-workers [21] for the exchange between hydroxyl and a number of anions, and the following extraction series was established for the anions:

$ClO_4^- > I^- > NO_3^- > Br^- > Cl^- > Ac^- > F^- > OH^-$; this is in accordance with the anion series for the energies of hydration. We found that the selectivity coefficients of the thiocyanate and other anion electrodes based on tetraalkylammonium correlate well with the exchange constants. Available data on the properties of liquid electrodes and the large amount of information on the behavior of these electrodes which has accumulated to the present in the literature allow us to assume that for most liquid membranes the selectivity coefficients are determined chiefly by the equilibrium factor, i.e., by the exchange constant. This is the chief distinguishing feature between liquid and solid membranes. The ionogenic groups in the liquid membranes are mobile rather than fixed; therefore high affinity of the ionogenic group to the counter ion has essentially no effect on the mobility of the current carriers.

Of great interest is the behavior of liquid and film-type electrodes in strongly acidic media. It is known that all the nitrate-selective electrodes developed in recent years on the basis of liquid ion exchangers exhibit the full nitrate function in aqueous solutions at pH > 1-2. The development of a nitrate electrode capable of functioning in strongly acidic media (pH < 1) is one of the important tasks of ionometry.

We studied the behavior of film-type NO_3^- electrodes in HNO_3 solutions over the concentration range from $5 \cdot 10^{-4}$ to 6 M in cells without and with transference [22]. It can be seen from Fig. 3 that the relation between E and $-\log a_{HNO_3}$ (for cells without transference) can be visualized as the sequence of several linear sections. The first of these, in the concentration range from $5 \cdot 10^{-4}$ to $2 \cdot 10^{-1}$ M HNO_3, corresponds to the theoretical NO_3^- function with the slope $\alpha = 116 \pm 1$ mV. The second linear section, with $\alpha = 178$ mV, corresponds to the concentration range from 0.2 to 1.0 M HNO_3; the third, with $\alpha = 220$ mV, covers the concentration range from 1.0 to 3.5 M; and the fourth, with $\alpha = 288$ mV, corresponds to the range from 3.5 to 6.6 M HNO_3. We have suggested that this complicated relation between E and $-\log a_{HNO_3}$ is caused by superequivalent sorption of nitric acid by the organic phase of the membrane, which yields compounds of the type of $R_4NNO_3 \cdot nHNO_3$. To establish the correlation between the change in electrode potential in acidic media and the superequivalent absorption of nitric acid we studied the equilibrium distribution of nitric acid between tetradecylammonium (TDA) nitrate solutions in chlorobenzene and aqueous HNO_3 solutions. The data obtained (Fig. 4) indicate that the superequivalent absorption of nitric acid begins from 0.2 M solution, i.e., at the concentration which corresponds to the change in the slope of the E vs log a_{HNO_3} curve. Over the range from 1 to 3 M HNO_3 the value of n is close to one, i.e., the compound $R_4NNO_3 \cdot HNO_3$ is dominating, where 1 mole of the salt of quaternary ammonium base is associated with 1 mole of acid. When species $[NO_3 \cdot HNO_3]^-$ becomes responsible for the charge transport in the membrane phase, then the emf of the call without transference will be given by the equation: $E = E^\circ + 23 \log a^2 HNO_2$, and on the curve displaying the $E = f(-\log a_{HNO_3})$ relation there must be a section with a slope of 232 mV. A similar value was obtained experimentally ($\alpha = 220$ mV). It follows that by analysis of the relation between E and $-\log a_{HA}$ in the case where solvates or other, complicated complex species are formed in the organic phase of the membrane, the composition of these species can be determined from the slope of the emf curve (from the factor by which it exceeds the quantity $\vartheta = 58$ mV).

We used this method to study the composition of the complex species forming during the interaction between amines and saturated carboxylic acids. It was found, in particular, for acetic acid and using a film-type ion-selective acetate electrode, that the compound $R_4NAc \cdot 3HAc$ is formed in the organic phase. According to literature data, the same composition was found for this sort of system of extraction [23].

Thus, a new method can be suggested for finding the composition of complex species in organic media from the slope of the relation between E and log a_{A^-} for an ion-selective electrode which is reversible with respect to anion A^-.

LITERATURE CITED

1. B. P. Nikol'skii, Zh. Fiz. Khim., 10, 495 (1937).
2. B. P. Nikol'skii, Zh. Fiz. Khim., 10, 504 (1937).
3. B. P. Nikol'skii, Zh. Fiz. Khim., 27, 724 (1953).
4. B. P. Nikol'skii and E. A. Materova, Zh. Fiz. Khim., 25, 1335 (1951).
5. B. P. Nikol'skii and M. M. Shul'ts, Vestn. Leningrad. Un-ta, No. 4, 73 (1963).
6. O. K. Stefanova, M. M. Shul'ts, E. A. Materova, and B. P. Nikol'skii, Vestn. Leningrad. Un-ta, No. 4, 314 (1963).
7. R. A. Durst (editor), Ion-Selective Electrodes, National Bureau of Standards Special Publication No. 314 (1969) [Russian translation: Mir, Moscow (1972)].
8. G. J. Moody and J. D. R. Thomas, Selective Ion-Sensitive Electrodes, Merrow Publ. Co., Newcastle-upon-Tyne, England (1971).

9. U. E. Morf, D. Ammon, E. Pretsch, and W. Simon, Pure Appl. Chem., 36, 421 (1973).
10. F. A. Belinskaya, E. A. Materova, L. A. Karmanova, and V. I. Kozyreva, Élektrokhimiya, 7, 214 (1971).
11. E. A. Materova, Z. S. Alagova, and I. N. Kuznetsova, in: Investigation of the Properties of Ion-Exchange Materials [in Russian], Nauka, Moscow (1964), p. 192.
12. E. Pungor, Anal. Chem., 39, 28 A (1967).
13. E. Pungor and K. Toth, Pure Appl. Chem., 36, 441 (1973).
14. A. L. Grekovich, E. A. Materova, and F. A. Belinskaya, Élektrokhimiya, 6, 1036 (1970).
15. E. A. Materova, A. L. Grekovich, and S. E. Didina, Élektrokhimiya, 8, 1829 (1972).
16. B. P. Nikol'skii, E. A. Materova, A. L. Grekovich, and V. E. Yurinskaya, Zh. Anal. Khim., 29, 205 (1974).
17. A. L. Grekovich, E. A. Materova, and G. I. Shekina, Élektrokhimiya, 10, 342 (1974).
18. E. A. Materova, V. V. Muchovikov, and M. G. Grigor'eva (Grigorjeva), Anal. Lett., 8, 167 (1975).
19. A. L. Grekovich, E. A. Materova, and N. V. Garbuzova, Zh. Anal. Khim., 28, 1206 (1973).
20. A. L. Grekovich, E. A. Materova, S. E. Didina, and S. N. Silin, Élektrokhimiya, 12, 723 (1976).
21. I. M. Ivanova, L. M. Gindin, and G. I. Chichagova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., 7, No. 3, 100 (1967).
22. E. A. Materova, Z. S. Alagova, and V. P. Zhes'ko, Élektrokhimiya, 10, 1568 (1974).
23. L. A. Chaikhorskii, B. P. Nikol'skii, and B. A. Mikhailov, Radiokhimiya, 8, 2 (1966).

ZERO-FREE-CHARGE POTENTIALS OF PLATINUM AS A FUNCTION OF SALT CONCENTRATION

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The potentials of zero free charge (p.z.f.c.) of the platinized platinum electrode were determined in the solutions: $3 \cdot 10^{-3}$ N HCl + xN KCl (I), $3 \cdot 10^{-3}$ N HBr + xN KBr (II), $3 \cdot 10^{-3}$ N KOH + xN KBr (III), and $3 \cdot 10^{-3}$ N KOH + xN KI (IV), where $x = 10^{-2}$, 10^{-1}, and 1. For an increase in salt concentration by one order of magnitude, the p.z.f.c. was found to shift in the negative direction: by 27 ± 5 mV in systems I and II, by 32 ± 10 mV in system III, and by 24 ± 5 mV in system IV. The data obtained are discussed in terms of the equations of the thermodynamic theory of the platinum electrode. It is concluded that the small p.z.f.c. shifts found when the salt concentration is varied are due to decreasing cation adsorption as the potential is shifted anodically, and to displacement of adsorbed hydrogen when salt with a surface-active anion is added near the p.z.f.c.

In the work of Frumkin and co-workers [1], a concept of electrode charge was formulated from which it follows that for the platinum metals, potentials of zero total and zero free charge must exist. Methods suitable for determining these quantities, and thermodynamic relationships characterizing them as a function of pH and solution concentration, have been discussed in [2, 3], where tables of the zero-charge potentials of the platinum metals are provided as well. Little attention was given to the experimental determination of the potential of zero free charge (p.z.f.c.) as a function of neutral-salt concentration. Such data have only been reported in [4], and refer to acidified and alkalized sodium bromide solutions. The p.z.f.c. was found to shift in the negative direction as the salt concentration c is made larger. The shift was about 50 mV for solutions of pH 3, and about 60 mV for solutions of pH 12, when the concentration was changed by an order of magnitude within the range of 10^{-3} to 10^{-1} N. No shift of the p.z.f.c. with increasing c was found at $c > 0.1$ N. The p.z.f.c. in the dilute salt solutions were determined by a radiotracer technique; those in the more concentrated solutions were determined from the change in H^+ ion concentration in the solution.

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