

THE USE OF MEMBRANE ELECTRODES MADE FROM ION EXCHANGE RESINS FOR POTENTIOMETRIC TITRATION

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During the last ten years a large number of papers have been published which have been devoted to the electrode properties of membranes made from ion exchange resins. It has been shown in these papers that membranes made from cation exchange or anion exchange resins can function as reversible electrodes. Hydrogen and metal functions have been studied in the case of cation exchange membranes [1-10] and also the chloride [11-15], bromide [16], fluoride [15] and other functions in the case of anion exchange membranes. The existence of the corresponding electrode functions in the membranes means that the latter can be used in potentiometric titration as indicator electrodes which are, in principle, reversible with respect to any ion e.g. to F^- , NO_3^- , CH_3COO^- , Li^+ , Rb^+ , Cs^+ , Mg^{2+} , Ba^{2+} ions etc, for which no reversible electrodes are known, or preparation of which involves considerable difficulty. In the work described here a study was made of membranes prepared from various Russian resins as indicated by the precipitation method.

Many authors have used membrane electrodes for potentiometric titration. Thus Sinkha [17], using electrodes made from IONAK S-200 sulfonated cation exchange resin, and resorcinol-formaldehyde resin, titrated hydrochloric acid with sodium hydroxide, while he used anion exchange electrodes made from the multifunctional anion exchange resin IONAK A-300 and the strongly basic anion exchange resin IRA-400 for some titrations based on precipitation. The curves he obtained did not have a clearly defined potential jump or break at the end point, and it is not clear with what accuracy such a titration can be carried out.

Results of the use of membrane electrodes for potentiometric titration based on precipitation are also given in Parson's article [18]. He used technical Amberplex C-1 cation exchange membranes and anion exchange membranes made from the strongly basic anion exchange resin IRA-400 as membrane electrodes, and titrated sulfuric acid and sodium sulfate with solutions of a barium salt. The authors evaluate the titration error as $\pm 0.4\%$.

Fischer and Bancroft [19] used electrodes made from inorganic materials for potentiometric titration. Thus they used a membrane made from barium sulfate for titrating sodium sulfate with barium chloride, and for titrating sulfuric acid with barium hydroxide. Sufficiently clearly defined potential changes were not obtained at the end points, however.

Bersier and Trueb [20] used an insoluble film of aluminum oxide for the potentiometric titration of halides. The error in establishing the end point was about 4%.

Experimental Technique. In order to study the behavior of ion exchange electrodes during potentiometric titration, the following ion exchange resins were used: the sulfo-cation exchange resins SBS and KU-2, the carboxyl cation exchange resin KB-4, the resorcinol-formaldehyde resin R, the anion exchange resins EDE-10 and AV-16 substituted to different extents with amino groups, the highly basic anion exchange resin AB-17 containing quaternary ammonium groups, and also the ion exchange membranes DKU-2 (ion exchange resin KU-2 cross-lined with polychloro vinyl).

Substitution of the mobile ions in the ionogenic groups of the resins by the requisite ions was carried out by treating the resin with appropriate solutions of acid or salt.

The electrodes were prepared by the technique adopted in the school of physical chemistry of Leningrad State University [7]. In accordance with this method some of the air-dry resin was ground in a ball mill and then sieved. The resin fraction chosen (about 200 mesh) was mixed in a definite proportion by weight with polystyrene dissolved in toluene. The mass while still unsolidified was transferred onto a foil, the toluene removed by evaporation, and the films obtained readily removed from the foil. Ten mm diameter discs were cut out of the films with a drill, the

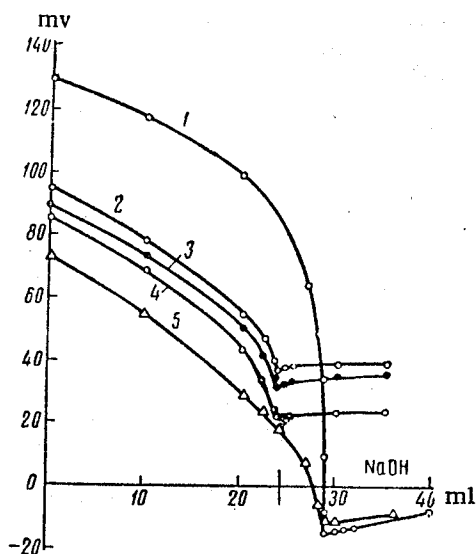


Fig. 1. Titration curves of 1 N hydrochloric acid (25 g) with 0.9572 N sodium hydroxide, using electrodes made from cation exchange resins R (curve 1), KB-4 (curve 5); titration curves of 0.964 N hydrochloric acid (25 g) with 0.9572 N sodium hydroxide using electrodes made from cation exchange resins SBS (curve 4), SDV-3 (curve 2), and Ku-2 (curve 3).

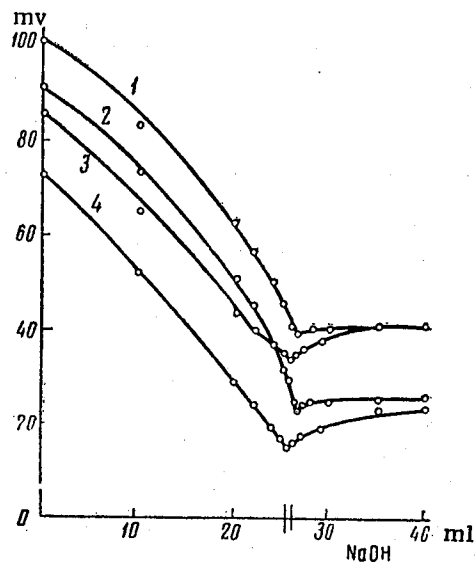


Fig. 2. Titration curves of 1.0858 N nitric acid (25 g) (curves 1 and 2) and of 0.5188 M sulfuric acid (25 g) (curves 3 and 4) with 0.9698 N sodium hydroxide using electrodes made from cation exchange resins SBS (curves 2, 4) and KU-2 (curves 1, 3).

discs were glued with polystyrene glue (a solution of polystyrene in toluene) to polystyrene tubes. The ion exchange resin content of membranes made from the cation exchange resins was

50%, while in the case of membranes made from the anion exchange resins it was 25%.

Before the ion exchange electrodes were used for potentiometric titration, they were calibrated by measuring their potentials in suitable solutions of electrolytes of varying concentration. In these experiments a silver chloride electrode was used as the reference electrode in chloride solutions, and a glass electrode in sulfuric acid solutions. The electrodes chosen were those for which the deviation of the experimental emf from the calculated value was within the limits 1-2 mv.

Potentiometric titration was carried out in a cell with 3-5 membrane electrodes whose potentials were measured with respect to a calomel electrode. The solution being titrated was measured out by weight. The 5-6 electrodes tested for each resin, as a rule, gave coincident results.

Results of Potentiometric Titration of Acids. Electrodes in the hydrogen form, made from resins differing in chemical nature, were used for titrating acids (hydrochloric, sulfuric, and nitric).

Potentiometric titration curves of 1 N hydrochloric acid using different membrane electrodes are shown in Fig. 1. The amount in ml of alkali which corresponds to the equivalent point according to titration results obtained with an indicator is marked on the abscissa. Fig. 1 shows that the shape of the curve obtained depends on the type of ion exchange resin used for preparing the membranes. The curve obtained with membranes prepared from the hydroxyl resin R (Fig. 1, Curve 1) approximates the usual potentiometric titration curve obtained with a hydrogen electrode. An appreciable potential jump is observed at the end point in this case. There is a sharp change in potential near the end point in the case of the membrane made from the carboxyl resin KB-4 (Curve 5), but there is still not a jump. The potential change near the end point is small in the case of electrodes made from the sulfo resins; the change can be established on the basis of the minimum on the curve.

Titration curves of 0.5 M sulfuric acid and 1 N nitric acid obtained on using electrodes made from the sulfo resins (SBS and KU-2) are shown in Fig. 2. The curves exhibit a clearly defined minimum at the end point, the minimum coinciding with the results of an indicator titration to an accuracy of 0.02 ml.

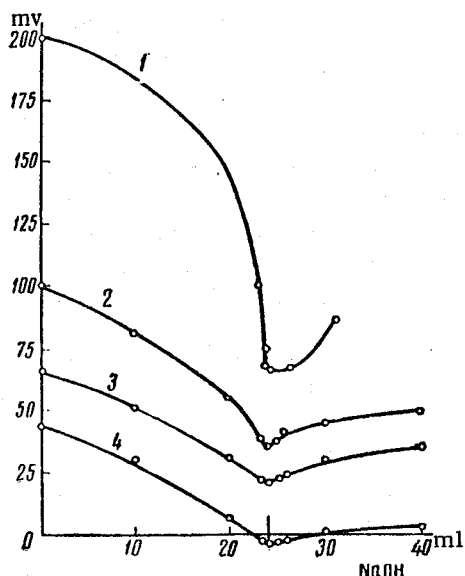


Fig. 3. Titration curves of 0.1 N hydrochloric acid (25 g) with 0.1046 N sodium hydroxide, using electrodes made from cation exchange resins R (curve 1), SBS (curve 2), KU-2 (curve 3), and DKU-2 (curve 4).

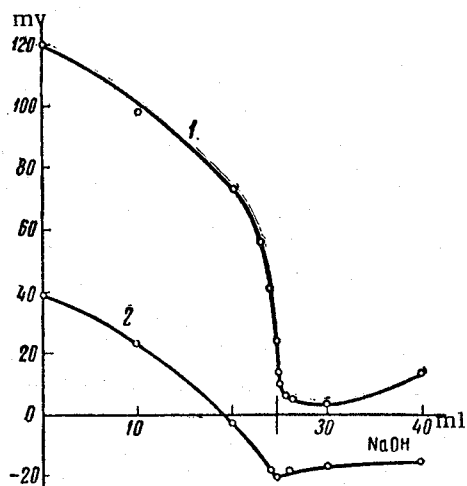


Fig. 4. Titration curves of 0.01 N hydrochloric acid (25 g) with 0.0101 N sodium hydroxide, using electrodes made from cation exchange resins R (curve 1) and SBS (curve 2).

During titration of 1 N solutions of acids, membranes in the hydrogen form were used with 0.1 N hydrochloric acid as an internal solution

Under these conditions, however, high results were obtained for 0.1 and 0.01 N hydrochloric acid when electrodes made from sulfo resins were used. The reason for the appearance of additional acidity in the solution may be the exchange of hydrogen ions from the membrane for sodium ions from the solution, which occurs during titration. In order to eliminate this effect, during titration of dilute solutions of acids electrodes made from sulfo resins were used in sodium form, while 0.1 M sodium chloride was used as the internal solution. When electrodes made from weakly acid resins are used during titration of dilute acid solution acidification of the solution following from exchange of hydrogen ions does not occur, and these membranes can be used in the hydrogen form.

Titration curves of 0.1 N hydrochloric acid using membrane electrodes made from sulfo resins in the sodium form are shown in Fig. 3. In this case the end points obtained from the potentiometric curves agree with the results obtained during titration with an indicator, while the character of the curve, as in the case of 1 N solutions, is determined by the type of resin from which the electrode is prepared.

Similar results were obtained for 0.01 N solutions of hydrochloric acid (Fig. 4). The accuracy of titration with membrane electrodes is a few tenths of a percent for all the concentrations studied.

Thus the experimental results show that membrane electrodes made from cation exchange resins in the hydrogen form can be successfully used for potentiometric titration of various acids (1-0.01 N) with alkali solutions. The character of the changes in emf during titration is determined by the acid strength of the active groups of the resin from which the membrane electrode is made. In the case of resins with weakly acid groups (the hydroxyl resin R and the carboxyl resin KB-4) there is a sufficiently sharp change in emf at the end point, corresponding to an appreciable change in pH at the titration end point (curve 1 in Figs. 1, 3, 4). The emf change from the beginning of a titration to the end point is 120-140 mv for electrodes prepared from resin R, the potential jump being 60-70 mv. For electrodes made from the carboxyl resin KB-4 the emf change up to the end point is about 90 mv (curve 5, Fig. 1). Such behavior on the part of electrodes made from weakly acid resins can be explained by the larger selectivity of these resins for hydrogen ions than for sodium ions. The transition region from a hydrogen function to a sodium function, according to our results, lies within the pH range 4-7 for resin R and within the pH range 3-6 for the carboxyl resin.

The change in emf with addition of alkali in the case of electrodes made from the sulfo resins can be explained as follows. At the beginning of titration the membrane is in the hydrogen form, and its potential is determined by the hydrogen ion concentration.

As alkali is added the membrane is gradually converted into the sodium form and reacts both to decreases in hydrogen ion concentration and to increases in sodium ion concentration. The nature of the curve obtained agrees with the ion exchange properties of sulfo resins, which do not exhibit selectivity toward hydrogen and other cations.

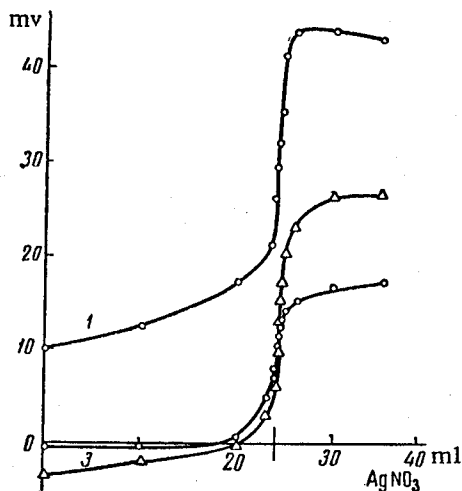


Fig. 5. Titration curves of 0.1 M sodium chloride (25 g) with 0.1014 N silver nitrate, using electrodes made from anion exchange resins AV-16 (curve 1), and AV-17 (curve 2, 3).

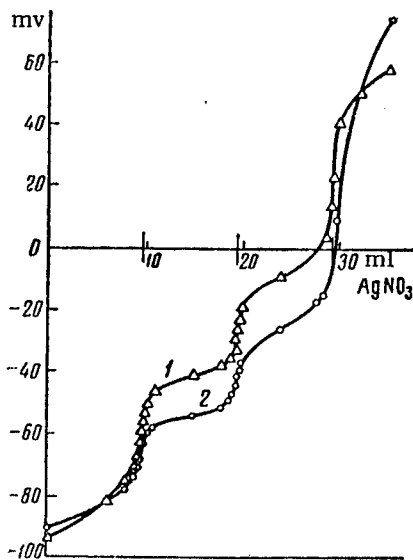


Fig. 6. Titration curves of chloride, bromide iodide (10 g of 0.1 M NaCl + 10 g 0.1 M NaBr + 10 g 0.1 M KI) with 0.1014 N silver nitrate, using electrodes made from anion exchange resins EDE-10 (Curve 1) and AV-16 (curve 2).

The transition range from hydrogen function to a sodium function lies within the pH range 1.5-3.5 [7] for electrodes made from sulfo resins. After the end point the emf is a function of the sodium ion concentration only and slowly increases as the latter increases (excess alkali).

Results of Potentiometric Titration by a Precipitation Method.

Membranes made from the anion exchange resins AV-17, AV-16, and EDE-10 were used for titrating halides with a silver nitrate solution. Preliminary experiments showed that an electrolyte not containing the anion of the solution being titrated should be used as the internal solution. In the main experiments a solution of 0.05 M sulfuric acid was poured inside the membranes while a micro calomel electrode served as the internal electrode. Results of titration of 0.1 M sodium chloride with silver nitrate solution are shown in Fig. 5, from which it is clear that there is a sharp potential jump at the end point, while the position of this jump coincides with the end point determined by titration with an indicator.

The titration curves obtained with anion exchange membranes are similar in character to the curve obtained with a silver chloride electrode. The value of the potential jump at the end point in the case where membrane electrodes are used, is however, less than that obtained when a silver chloride electrode is used. In this case the change in emf up to the end point is determined mainly by the concentration of chloride ions, and not by that of NO_3^- ions, since the exchange process proceeds at a comparatively slower rate on anion exchange membranes. The chloride ion concentration changes most sharply near the end point, and the result is a sharp change in potential. After the end point only NO_3^- ions are present in solution, but the transition to the new function proceeds slowly, and, accordingly, the emf remains almost constant.

The results obtained during titration of sodium chloride with silver nitrate solution indicate that it should be possible to use anion exchange membranes for titrating mixtures of halides. The titration curves shown in Fig. 6, show that at the end points corresponding to complete precipitation of the corresponding halide, there are clearly defined jumps which correspond to the end points obtained during titration with indicators.

Anion exchange membrane electrodes in the sulfate form were used for titrating sulfuric acid and sodium sulfate with barium chloride and barium acetate solution. Titration curves of sulfuric acid with barium acetate using membrane electrodes made from anion exchange resins AV-16 and AV-17 are shown in Fig. 7. The curves obtained have a clearly defined peak which coincides with an accuracy of a few tenths of a percent with the end point obtained during indicator titration. Up to the end point the emf is determined mainly by the SO_4^{2-} concentration, which changes most sharply at

the titration end point; acetate ions hardly play any part because of the low dissociation of acetic acid. In order to compare the behavior of anion exchange membranes with cation exchange membranes during titration of sulfuric acid with a barium acetate solution, cation exchange membranes in the hydrogen form made from resin KU-2 (Fig. 7, curve 3) were used. At the end point the potential of the cation exchange membrane gives a sharp minimum, the presence of which is explained by the fact that during titration the hydrogen ion concentration decreases up to the end point as a result of the formation of the sparingly dissociated acid, and the emf decreases; after the end point the emf is determined by the barium ions, and the potential increases as the barium concentration increases.

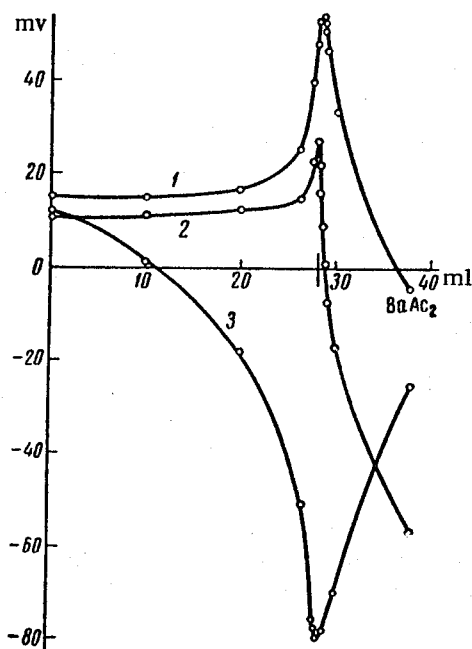


Fig. 7. Titration curves of 0.05 M sulfuric acid (50 g) with 0.1766 N barium acetate, using electrodes made from anion exchange resins EDE-10 (curve 1), AV-17 (curve 2), and cation exchange resin KU-2 (curve 3).

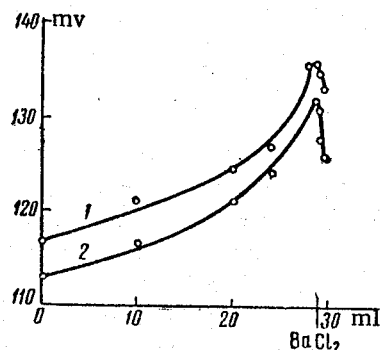


Fig. 8. Titration curves of 0.1 M sodium sulfate (25 g) with 0.1688 N barium chloride, using electrodes made from the anion exchange resin EDE-10 (curves 1, 2).

A most interesting case is titration of sodium sulfate with barium chloride solution (Fig. 8). Titration was carried out using anion exchange electrodes in the sulfate form; these electrodes react to changes in sulfate ion concentration, as a result of which there is a fairly sharp maximum peak at the end point.

SUMMARY

Membranes made from the sulfo cation exchange resins SBS, KU-2 and SDV-3, and from the carboxyl cation exchange resin KB-4 and the hydroxyl resin R, have been used as indicator electrodes for the potentiometric titration of acids. An explanation is given of the nature of the curves obtained during acid - alkali titration when membrane electrodes made from resins containing active groups differing in their chemical nature are used.

It has been established that membranes in the hydrogen form can be used for titrating concentrated acids. For titration of dilute acid solution, membranes made from the sodium form of strongly acidic resins and from the hydrogen form of weakly acidic resins should be used.

A study has been made of anion exchange membrane electrodes made from the resins AV-16, AV-17, and EDE-10 as indicator electrodes for potentiometric titration of halide and sulfate ions by precipitation methods. The curves obtained during titration of halides are similar in character to those obtained during titration with the usual electrodes which are reversible with respect to these ions. The titration curve obtained during titration of sulfate ions has a peak maximum at the end point.

The use of membranes as indicator electrodes opens up possibilities of potentiometric titration by precipitation methods.

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