United States Patent

Christian

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[54] POTENTIOMETRIC TITRATION PROCESS

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[21] Appl. No.: **878,312**

[52] **U.S. Cl.**.....**204/1 T,** 204/195

[51] **Int. Cl.**.....**G01n 27/40,** G01n 27/46

[58] **Field of Search**.....204/1 T, 195

[56] **References Cited**

UNITED STATES PATENTS

2,954,336 9/1960 Grutsch.....204/195

OTHER PUBLICATIONS

" Anal. Chim. Acta," Vol. 36 (1966), pp. 166–179

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[57] **ABSTRACT**

Potentiometric titration of a wide variety of reagents in solution can be conducted using an ion selective sensing device including a standard reference electrode, a reference electrolyte and a semipermeable polymeric membrane which separates the reference electrolyte from the solution containing the ion being titrated. The semipermeable polymeric membrane contains an ester of phthalic or isophthalic acid which serves to discriminate between the ion being titrated and other ions in the medium.

7 Claims, 8 Drawing Figures

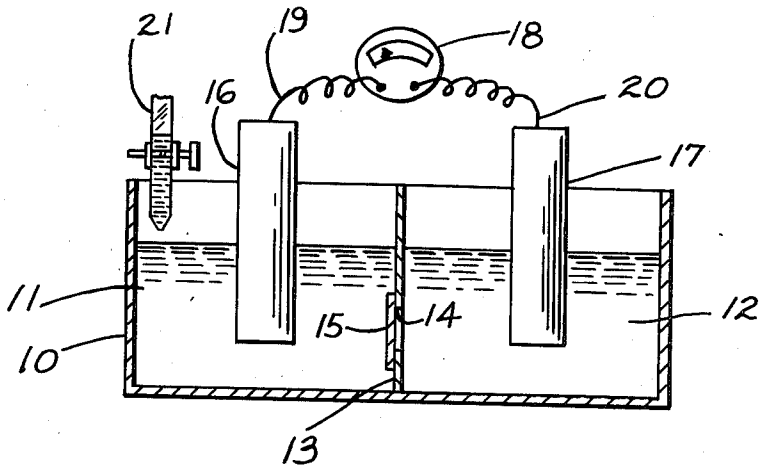
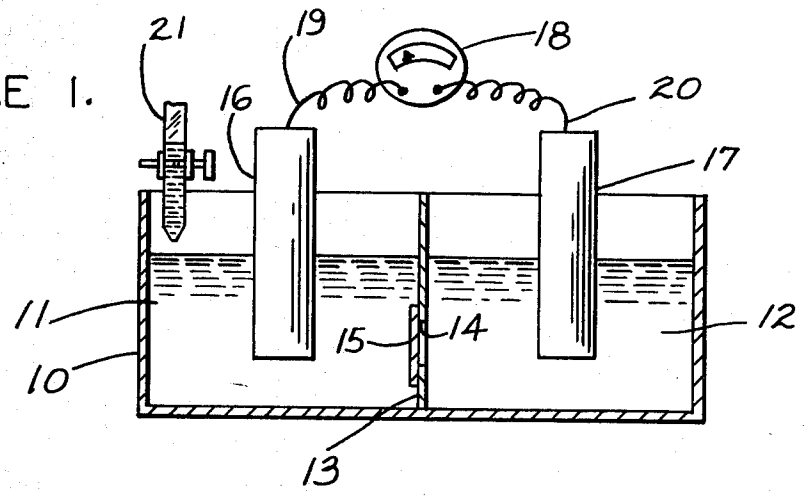


FIGURE 1.



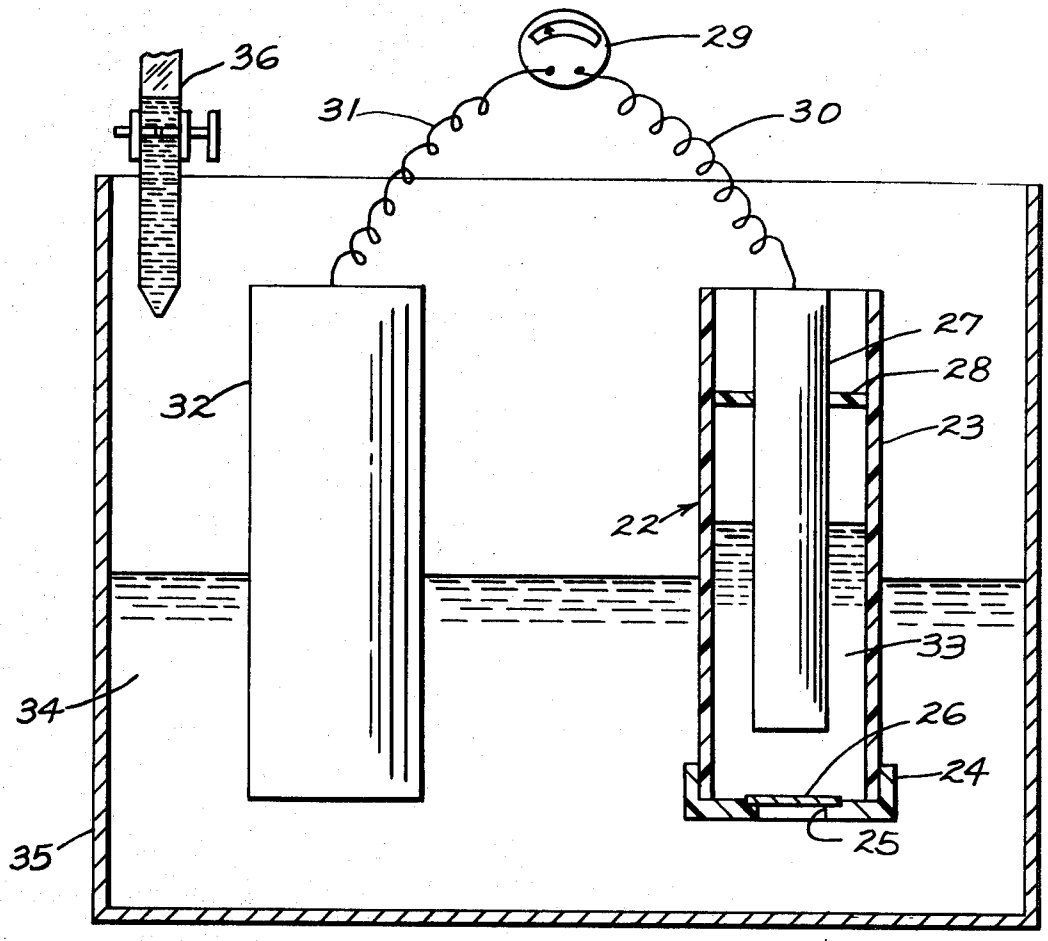


FIGURE 2.

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TITRATION OF HNO_3 WITH MEMBRANE CONTAINING DI-(2-ETHYLHEXYL) ISOPHTHALATE

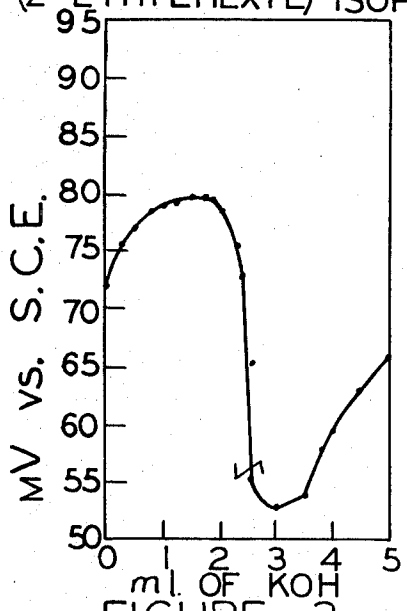


FIGURE 3.

TITRATION OF $Pb(NO_3)_2$ WITH MEMBRANE CONTAINING DI-(2-ETHYLHEXYL) ISOPHTHALATE

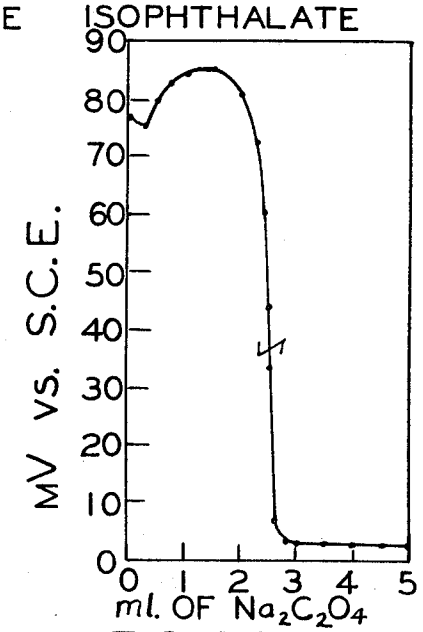


FIGURE 4.

TITRATION OF KCl WITH MEMBRANE CONTAINING DI-(2-ETHYLHEXYL) ISOPHTHALATE

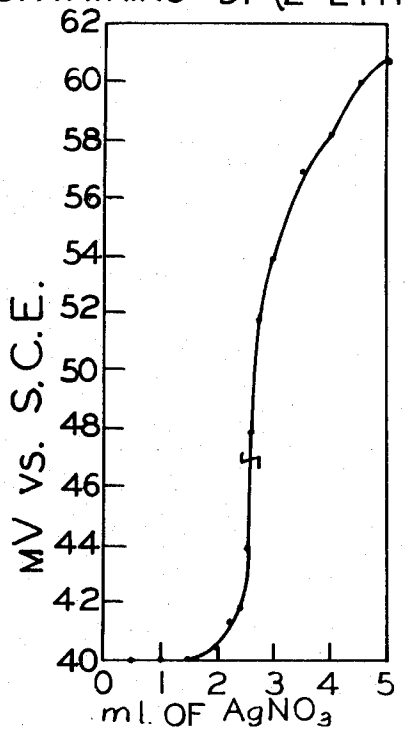


FIGURE 5.

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TITRATION OF HNO_3 WITH MEMBRANE CONTAINING DIPENTYL PHTHALATE

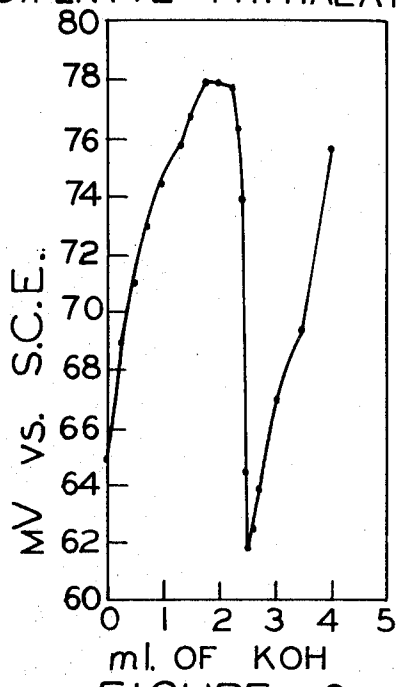


FIGURE 6.

TITRATION OF $Pb(NO_3)_2$ WITH MEMBRANE CONTAINING DIPENTYL PHTHALATE

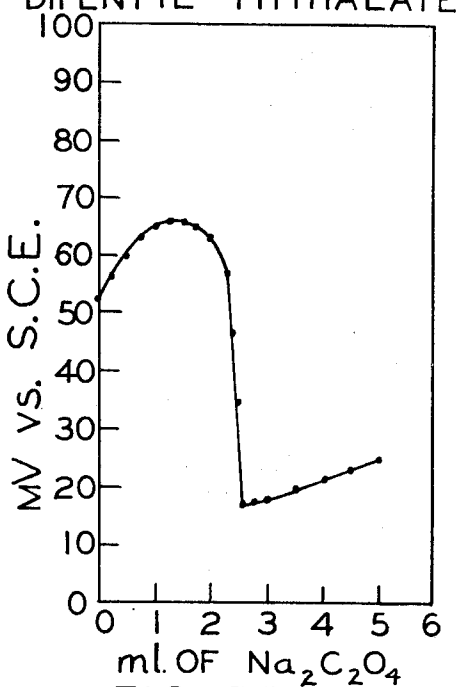


FIGURE 7.

TITRATION OF KCl WITH MEMBRANE CONTAINING DIPENTYL PHTHALATE

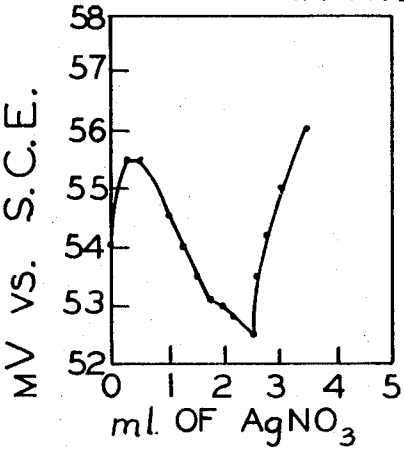


FIGURE 8.

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POTENTIOMETRIC TITRATION PROCESS

BACKGROUND OF THE INVENTION

This invention relates to potentiometric titrations. In one of its more particular aspects it relates to the detection and determination of ions in solutions also containing other ions which ordinarily interfere with the measurement of the particular ion to be detected by titration of the desired ion using an ion selective sensing device. For example, in the potentiometric titration of metallic ions other metallic ions than the ion being detected may be a source of interference.

Various methods have been used for the detection and determination of ions in solution. Among these are colorimetric test methods which involve the preparation and use of chemical reagents, their addition to solutions containing the ion in question and observation of any color change occurring. Some of these colorimetric methods require the use of a spectrophotometer. Others rely upon visual colorimetric sensing and are subject to individual interpretation which can vary widely. Processes involving flame photometry or atomic absorption spectrophotometry have also been used but these methods are quite laborious. A convenient technique for determining ions in solution, particularly by the method of potentiometric titration, would have wide applicability, especially in laboratories staffed with relatively unskilled personnel or for use in the field.

PRIOR ART

Recently analytical methods involving the use of ion selective membranes have been devised. For example U.S. Pat. No. 3,398,066 to A. Ilani describes a method for determining potassium and sodium ions by means of an ion selective membrane. U.S. Pat. No. 3,450,631, to R. Bloch et al. describes the separation of metal ions using another membrane technique. Certain selective glass electrodes have also recently become commercially available. Such electrodes contain various special glass tips which are said to be useful for measuring concentrations of hydrogen, silver, potassium, ammonium, sodium and lithium ions, to mention but a few. U.S. Pat. No. 3,356,596, to G. Eisenman et al. describes such a glass electrode which is useful for measuring potassium ion concentrations. U.S. Pat. No. 3,450,604, to G. Eisenman describes a sodium ion electrode.

Each of the aforesaid methods suffers from certain disadvantages. The colorimetric methods are generally time consuming and complicated, involving the handling of chemical reagents and generally requiring the assistance of a skilled laboratory technician. The photometric and spectrophotometric methods are likewise cumbersome as well as expensive. The various electrometric methods involve the use of electrode devices which may be somewhat difficult to fabricate.

Previously available potentiometric titration devices utilizing ion selective membranes have shown only narrow utility as described in Ijsseling et al., Anal. Chim. Acta 36, 166 (1966), Anal. Chim. Acta 40, 421 (1968), Anal. Chim. Acta 43, 77 (1968) and Anal. Chim. Acta 45, 121 (1969).

SUMMARY OF THE INVENTION

This invention comprises a novel process for potentiometric titration of ions in solution. An ion selective sensing device useful in potentiometric titrations of various types comprises a reference electrode and a semipermeable polymeric membrane having interposed between them a reference electrolyte containing a known concentration of ions to which the membrane is selectively permeable. This sensing device, when used as one electrode in an electrochemical cell, the other electrode being a standard reference electrode, results in the development of a potential difference across the membrane. This developed potential difference is a function of the concentration of ions to which the membrane is selectively permeable and can be used to follow the course of a titration by plotting values thereof against the volume of titrant used. The result is a conveniently obtained titration curve.

The semipermeable polymeric membrane of the ion selective sensing device in effect constitutes an immobilized discriminating agent. The agent is conveniently immobilized and thereby made available for use in the solid phase by incorporation with a semipermeable polymeric matrix. One convenient way of accomplishing such immobilization is by incorporating the discriminating agent into a suitable polymer and casting a membrane from a solution of the polymer and discriminating agent in a suitable solvent.

Materials which can be used as the polymeric matrix include ethyl cellulose, polyvinyl chloride, cellulose acetate and collodion. Such materials are known to be permeable to small particles, such as water and metallic ions, and impermeable to larger molecules such as polymeric species. Incorporated with a discriminating agent in accordance with the instant invention the permeability becomes selective.

As discriminating agent there can be used an ester of phthalic or isophthalic acid such as dibutyl phthalate, dipentyl phthalate, di-n-octyl phthalate, dimethyoxyethyl phthalate, diphenyl phthalate or di-(2-ethylhexyl) isophthalate. The discriminating agent may also serve the function of plasticizer for the polymeric matrix.

In order to prepare the membranes of this invention the polymeric matrix material, solvent and discriminating agent are mixed together and cast upon a suitable, relatively impervious surface such as a glass, wood, plastic or metal plate. Upon drying, usually at a temperature of about from 40° to 105° C. for a period of time of about from 5 minutes to 1 hour, the film of polymeric matrix material containing discriminating agent is available in the form of a polymeric membrane which can be used with a paper, glass, plastic or other suitable backing or without such backing as desired.

When the resulting membrane is incorporated into an ion selective sensing device as described above and used as one electrode in an electrochemical cell in which the other electrode is a standard reference electrode, the resulting system can be used in electrochemically sensing the change in potential produced in such cell upon various chemical reactions occurring within the cell. In this way the system can be used to follow the course of a titration and detect the end-point thereof. Titrations of the precipitation, oxidation-reduction, compleximetric or acid-base type can thus be performed. Titrations can be conducted in aqueous or nonaqueous systems.

DESCRIPTION OF THE DRAWING

FIG. 1 is a semi-diagrammatic vertical sectional view of a concentration cell which can be used in the potentiometric titration process of this invention. The numeral **10** represents a container separated into two compartments **11** and **12** by a liquid impermeable divider **13** which is formed with at least one opening **14** which is covered by a semipermeable membrane **15**. Membrane **15** is secured to divider **13** in a known manner and can be a semipermeable polymeric membrane of the type described above. It will be apparent that container **10** and divider **13** should be constructed of electrically insulating material. Electrodes **16** and **17** are placed on opposite sides of the membrane in compartments **11** and **12**, respectively. Electrodes **16** and **17** may be any standard reference electrode, for example, saturated calomel or silver-silver chloride electrodes. Within compartment **12** is placed a reference electrolyte containing a known concentration of ions to which membrane **15** is selectively permeable. Within compartment **11** is placed the solution in which the concentration of a particular ion is to be determined, that is, the solution to be titrated. A means **18**, such as a millivoltmeter, for measuring a difference in electrical potential between electrodes **16** and **17** is connected to electrodes **16** and **17** through wires **19** and **20**. Buret **21** is used to titrate the solution in compartment **11**.

FIG. 2 is a semi-diagrammatic vertical sectional view of a preferred experimental set-up for conducting potentiometric titrations according to the process of this invention. Electrode

assembly 22 comprises a tubular fluid impermeable body 23 which is closed at one end by means of a cap 24 having a central opening 25 which is covered by a semipermeable membrane 26 which is secured to cap 24 in a known manner. A standard reference electrode 27 is maintained in position coaxially within body 23 as shown by means of a mounting ring 28 positioned within body 23 at a point remote from cap 24. Electrode 27 is connected to a potential measuring device 29, such as a millivoltmeter by means of wire 30. Wire 31 connects the potential measuring device 29 to a standard reference electrode 32 which may be the same as or different from standard reference electrode 27. Electrode assembly 22 contains reference electrolyte 33 into which the standard reference electrode 27 is immersed. Both electrode assembly 22 and standard reference electrode 32 are immersed in an unknown solution 34 to be tested, which solution is contained within vessel 35. Buret 36 is used to titrate the unknown solution 34.

It is apparent that body 23, cap 24, mounting ring 28 and vessel 35 should be constructed of electrically insulating material.

For example, standard reference electrode 27 can be a saturated calomel electrode and standard reference electrode 32 a silver-silver chloride electrode. When reference electrolyte 33 is a 0.001 M lead nitrate solution, for example, the potential measuring device records a potential difference of 23 millivolts if the unknown solution 34 contains a concentration of silver ions of 0.001 M and a potential difference of 59 millivolts if the unknown solution contains a concentration of silver ions of 0.01 M. Other typical potential responses using a membrane containing dipentyl phthalate are shown in Table 1.

TABLE 1

Membrane Response to Various Cations

Cation	Potential 10^{-3}M	10^{-2}M	AE,mV
Ag^+	23	59	36
H^+	144	261	117
Na^+	22	21	−1
K^+	30	73	43
Pb^{++}	43	79	36
Ca^{++}	12	20	8

In addition a plot of potential difference against volume of titrant added would result in a typical S-shaped titration curve.

EXAMPLE 1

To 0.25 g. of polyvinyl chloride and 0.75 ml. of dipentyl phthalate was added enough cyclohexanone to produce a 5 ml. fluid mixture.

The resulting fluid mixture was then poured upon glass microscope slides and allowed to dry in air at room temperature for 12 hours to yield a colorless, translucent, stable membrane.

EXAMPLE 2

The procedure of Example 1 was repeated using 0.75 ml. of di-(2-ethylhexyl) isophthalate instead of dipentyl phthalate. The resulting membrane was colorless, translucent and stable.

EXAMPLE 3

The procedure of Example 1 was repeated except that dibutyl phthalate was used in place of dipentyl phthalate.

EXAMPLE 4

The procedure of Example 1 was repeated except that di-n-octyl phthalate was used in place of dipentyl phthalate.

EXAMPLE 5

The procedure of Example 1 was repeated except that dimethoxyethyl phthalate was used in place of dipentyl phthalate.

EXAMPLE 6

The procedure of Example 1 was repeated except that diphenyl phthalate was used in place of dipentyl phthalate.

EXAMPLE 7

The experimental set-up of FIG. 2 was used utilizing a saturated calomel electrode for both electrodes 27 and 32, electrode 32 being of the sleeve type. Solution 33 was a 0.001 M lead nitrate solution. Membrane 26 was a membrane containing di -(2-ethylhexyl) isophthalate prepared according to the procedure of Example 2. It was circularly cut and mounted in an electrode assembly made of polytetrafluoroethylene. The diameter of the exposed membrane was 8 mm. Solutions were prepared of reagent grade materials and deionized distilled water was used for their preparation. During titration a polytetrafluoroethylene coated magnetic bar was used to stir the solution being tested. The potential measuring device was a Keithley 610–B Electrometer. All cables were shielded and the cell assembly was placed in a copper gauze cage in order to insure stable reading and adequate grounding. In addition to the elements shown in FIG. 2 a saturated ammonium nitrate agar salt bridge was used in the electrochemical cells. The resulting cell had the following configuration:

S.C.E.; 10^{-3}M $Pb(NO_3)_2$; Membrane; Sample Solution; Sat'd. NH_4NO_3, Agar Salt Bridge; Sat'd. KCl; S.C.E.

Electrode assembly 22 was stored in the open for 48 hours for preconditioning of membrane 26. Potential readings were recorded after an interval of 1 to 2 minutes. Twenty-five ml. of 0.01 M nitric acid solution was titrated with 0.1 M potassium hydroxide solution. The resulting titration curve was in the inverse sense to the typical well defined S-shaped titration curve and is shown in FIG. 3.

EXAMPLE 8

Using the procedure of Example 7, 25 ml. of 0.01 M lead nitrate solution was titrated with 0.1 M sodium oxalate solution. The titration curve obtained is shown in FIG. 4.

EXAMPLE 9

Using the procedure of Example 7, 25 ml. of 0.01 M potassium chloride solution was titrated with 0.1 M silver nitrate solution. A typical well defined S-shaped curve was obtained and is shown in FIG. 5.

EXAMPLE 10

The procedure of Example 7 was repeated except that the membrane used, which contained dipentyl phthalate, was prepared according to the procedure of Example 1. The titration curve obtained, which was of the first derivative type, is shown in FIG. 6.

EXAMPLE 11

The procedure of Example 8 was repeated except that the membrane used, which contained dipentyl phthalate, was prepared according to the procedure of Example 1. The titration curve obtained is shown in FIG. 7.

EXAMPLE 12

The procedure of Example 9 was repeated except that the membrane used, which contained dipentyl phthalate, was prepared according to the procedure of Example 1. The titration curve obtained is shown in FIG. 8.

I claim:

1. In a process for conducting potentiometric titrations which comprises adding to a solution containing a first ion, the concentration of which is to be determined, a solution containing a second ion reactable with said first ion, whereby the concentration of said first ion changes in a predictable manner as said second ion is added, measuring the electrical potential between the resulting solution and a reference electrolyte, and plotting the electrical potential throughout the course of addition of said second ion, thereby obtaining a titration curve for said reaction, the improvement which comprises measuring said electrical potential while said resulting solution and said reference electrolyte are in contact with opposite sides of and separated by a membrane comprising a semipermeable polymeric matrix selected from the group consisting of ethyl cellulose, polyvinyl chloride, cellulose acetate and collodion, said matrix having an ester of phthalic or isophthalic acid incorporated therewith.

2. A process according to claim 1 wherein the ester is selected from the group consisting of dibutyl phthalate, dipentyl phthalate, di-n-octyl phthalate, dimethoxyethyl phthalate, diphenyl phthalate and di-(2-ethylhexyl) isophthalate.

3. A process according to claim 1 wherein the reference electrolyte is a solution containing ions to which said membrane is selectively permeable.

4. A process according to claim 1 wherein the reference electrolyte is a solution containing lead ions.

5. A process according to claim 1 wherein the reference electrolyte is a lead nitrate solution.

6. A process according to claim 1 wherein the titration is of an acid-base, precipitation, oxidation-reduction or compleximetric reaction.

7. A process according to claim 1 wherein the titration is conducted in a non-aqueous medium.

* * * * *