Construction of 2-Aminoperimidinium Ion-Selective Electrode and Its Application to Potentiometric Titration of Sulfate

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A liquid membrane type 2-aminoperimidinium ion-selective electrode was constructed on the basis of the ion-pair extraction system. Nitrobenzene extract of 2-aminoperimidinium-tetraphenylborate ion-pair was used as the ion-exchange membrane. It was found that the ion-selective electrode shows a good Nernstian response to the object ion in the concentration range from 10^{-6} to 10^{-2} M. Potentials measured with 1 mM 2-aminoperimidinium test solutions were not affected by the change in pH from 2 to 6. The selectivity coefficients for various cations were evaluated by the mixed solution method. The electrode shows good selectivity with respect to most common metal cations, but poor selectivity for quaternary ammonium cations. The electrode shows quick response to object ion even in low concentration level. It was reported that 2-aminoperimidinium ion forms an ion-pair with sulfate of the mole ratio 2.3 : 1. The present electrode was successfully applied as the indicator electrode to the potentiometric precipitation titration of sulfate using standard 2-aminoperimidinium solution as the titrant.

1 Introduction

Recently, some ion-selective electrodes sensitive to sulfate ion¹⁻³⁾ were constructed and some of them were employed as the indicator electrode of potentiometric precipitation titration. On the other hand, a liquid membrane type ion-selective electrode⁴⁻⁷⁾ was constructed by using organic solution of quaternary ammonium cation-sulfate ion-pair as the ion sensing membrane. Generally, sulfate ion-selective electrode is not so sensitive and selective for the object anion and the slope of its calibration curve is less than 30 mV per activity decade, although sulfate ion is divalent anion.

Sulfate ion was potentiometrically titrated by using lead⁸⁻¹⁴⁾, iron^{15, 16)} and barium¹⁷⁻¹⁹⁾ ion-selective electrodes, because sulfate ion is precipitated by these metal ions. Sulfate ion was also titrated by the aid of glass electrode^{20, 21)} sensitive to divalent cations. However, the

potential change at the end-point is not so sharp because of its relatively high solubility product of metal-sulfate salts.

As well known, 2-aminoperimidinium bromide or chloride is the useful precipitant of sulfate ion. In this paper, a liquid membrane type ion-selective electrode sensitive to 2-aminoperimidinium cation was constructed and applied to the potentiometric titration.

2 Experimental

2.1 Reagent

2-aminoperimidinium·HBr (abbreviated as 2-Ap⁺Br⁻) was obtained from Dojindo Laboratories and a 10^{-2} M stock solution was prepared by dissolving 1.3206 g of reagent to 0.5 dm³ of water and stored in refrigerator. Purity of the reagent (99%) was determined by potentiometric titration against 10^{-2} M standard sodium tetraphenylborate solution by the aid of a tetraphenylborate ion-selective electrode²²⁾.

Sodium tetraphenylborate (abbreviated as Na⁺TPB⁻), the certified purity of which is more than 99.7% was obtained from Dojindo Laboratories. The stock solution of 10^{-2} M sodium tetraphenylborate was prepared by dissolving 3.4223 g of the reagent to 1 dm³ of water and stored in refrigerator. The pH of tetraphenylborate stock solution was kept to 8.5 by adding sodium hydroxide.

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Disodium ethylenediaminetetraacetate ($\text{Na}_2\text{H}_2\text{edta}$) solution (10^{-2}M) was prepared by dissolving 3.7225 g of the reagent, which was dried at 80°C for 3 h in dry oven, to 1 dm^3 of water.

Buffer solutions (pH 4 to 6) were prepared by mixing 0.2 M acetic acid and 0.2 M sodium acetate in the appropriate ratio. Other chemicals used were all of analytical reagent grade and used without further purification.

2.2 Potential measurement

All the potential measurements were carried out by means of a Takeda Riken Electrometer TR-8651, equipped with a Hitachi Recorder 056. A Horiba saturated calomel electrode 2535-05 T was used as an external reference electrode throughout the study. Composition of the present cell system including 2-amino-perimidinium ion-selective electrode is shown as follows.

Pt-Pt electrode	Internal ref. soln., 1 mM $2\text{-Ap}^+\text{Br}^-$	Liquid ion-exchanger 1 mM $2\text{-Ap}^+\text{-TPB}^-$ in nitrobenzene	Sample soln. containing 2-Ap^+ , pH 5.0	SCE
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Electrode barrel used in this study was similar to that described elsewhere²³⁾. The EMF of present cell system in the presence of foreign ions is given by Nikolsky-Eisenman equation²⁴⁾.

$$E = E^\circ + \frac{2.303 RT}{F} \cdot \log(a_{2\text{-Ap}} + \sum_j K_{2\text{-Ap},j} \cdot a_j^{1/z_j}) \quad (1)$$

where E° is a constant, $a_{2\text{-Ap}}$ and a_j are the activities of object and j -th ion, respectively,

Fig. 1 Effect of $2\text{-Ap}^+\text{-TPB}^-$ ion-pair concentration in the ion-exchange membrane

Ion-pair concentration : $\blacktriangle$ — 0.01 mM, $\circ$ — 0.1 mM, $\bullet$ — 0.5 mM, $\triangle$ — 1.0 mM, Temp. 22.0°C

$K_{2\text{-Ap},j}$ is the selectivity coefficient and z_j is the absolute value of the charge on j -th ion.

3 Results and Discussion

3.1 Preparation of ion-exchange membrane

The liquid ion-exchange membrane was prepared as follows : to a 10 cm^3 of 1 mM 2-Ap^+ ion solution in a separatory funnel were added 10 cm^3 of 1 mM NaTPB solution and 10 cm^3 of nitrobenzene (NB). The mixture was shaken for 10 min and then let stand for about 20 min. Organic phase was separated and freed from water by the addition of anhydrous sodium sulfate. Concentration of $2\text{-Ap}^+\text{-TPB}^-$ ion-pair in ion-exchange membrane is 1 mM.

3.2 Selection of ion-pair concentration in ion-exchange membrane

The effect of ion-pair concentration in the

membrane was examined by making a calibration curve at several ion-pair concentration levels. As shown in Fig. 1, when the ion-pair concentration is 0.01 mM, the slope of the calibration curve (38 mV/activity decade) shows less than Nernstian value. The electrode of 0.5 mM concentration is not really suitable, because the potential of the electrode is unstable. The electrode constructed with 1 mM ion-pair concentration was acceptable, because the stability and reproducibility of the potential found to be the best.

Fig. 2 Response characteristics of the electrode 2-Ap^+ ion concentration change : A $10\text{ }\mu\text{M}$ to 0.1 mM , B $1\text{ }\mu\text{M}$ to $10\text{ }\mu\text{M}$

3.3 Response time

Concentration of the object ion was increased by the addition of appropriate amount of concentrated object ion solution. As shown in Fig. 2, the time required to reach the value equal to 90 and 95% of equilibrium potential value was 4 and 10 s, 15 and 25 s at the 2- Ap^+ ion concentration change from 10^{-5} to 10^{-4} M and 10^{-5} to 10^{-5} M, respectively.

3.4 Influence of pH

The change in electrode potential with pH of the test solution is shown in Fig. 3. The pH of the test solution containing 1 mM and 10 μM of 2- Ap^+ cation was adjusted by adding 0.1 M hydrochloric acid or 0.1 M sodium hydroxide containing the same concentration of object ion, the total ionic strength being kept to 0.1 M with sodium chloride. The potential of cell was independent of pH in the range from 2 to 6 at 1 mM 2- Ap^+ ion concentration. However, in the case of the cell consisting of 10 μM object ion concentration, the potential shifted to slightly negative value with increasing pH of the sample solution. At the pH higher than 6, the potential of the cell shifted to more negative as the pH increased because the concentration of 2- Ap^+ cation decreased by neutralization.

3.5 Selectivity

The selectivity coefficients for diverse ions were evaluated by the mixed solution method²⁵⁾, i.e., by measuring the potential while varying the concentration of 2- Ap^+ cation from 10^{-4} to

Table 1 Selectivity coefficient of 2-aminoperimidinium ion-selective electrode (mixed solution method)

Cation	Added as	Concn.	$-\log K_{2-\text{Ap},j}$
Na^+	NaCl	10 mM	3.56
K^+	KCl	10 mM	3.17
NH_4^+	NH_4Cl	10 mM	3.01
Cu^{2+}	CuCl_2	10 mM	4.54
Ca^{2+}	CaCl_2	10 mM	4.25
Mg^{2+}	MgCl_2	5 mM	3.81
$(\text{CH}_3)_4\text{N}^+$	$(\text{CH}_3)_4\text{NCl}$	1 mM	1.84
$[(\text{C}_2\text{H}_5)_3\text{NH}]^+$	$[(\text{C}_2\text{H}_5)_3\text{NH}]\text{Cl}$	1 mM	1.48
$[(\text{C}_3\text{H}_7)_4\text{N}]^+$	$[(\text{C}_3\text{H}_7)_4\text{N}]\text{Cl}$	1 μM	-0.93
$[(\text{C}_{12}\text{H}_{25})\text{N}(\text{CH}_3)_3]^+$	$[(\text{C}_{12}\text{H}_{25})\text{N}(\text{CH}_3)_3]\text{Cl}$	1 μM	-1.00
$[(\text{C}_{16}\text{H}_{33})\text{N}(\text{CH}_3)_3]^+$	$[(\text{C}_{16}\text{H}_{33})\text{N}(\text{CH}_3)_3]\text{Cl}$	1 μM	-0.68
Zeph $^+$	ZephCl	1 μM	-0.53

Concentration range of 2- Ap^+ : 0.1 mM–10 μM , Zeph $^+$: Benzyl-dimethyltetradecylammonium cation

10^{-5} M at a high concentration of diverse ion. The activity coefficient table of Kielland²⁶⁾ was used for the conversion of ionic concentration to activity. As shown in Table 1, the present electrode shows a good selectivity with respect to the common metal ion, as well as ammonium ion. The electrode, however, shows no selectivity to quaternary ammonium cations. In general, the selectivity coefficient increased with increasing molecular weight of the quaternary ammonium cation.

3.6 Standardization of 2-aminoperimidinium solution by the aid of the present electrode

Stock solution of 2-aminoperidine·HBr was standardized potentiometrically by use of the present ion-selective electrode as an indicator

Fig. 3 Electrode response as a function of pH
2- Ap^+ ion concentration: —○— 1 mM, —●— 10 μM ,
Ionic strength: 0.1 M with NaCl

Fig. 4 Potentiometric titration curves of
2- Ap^+Br^- solution with standard NaTPB
solution

ca. 1 mM 2- Ap^+Br^- solution taken: —○— 5
 cm^3 —●— 10 cm^3 , —△— 15 cm^3

electrode against standard sodium tetraphenylborate solution. Figure 4 shows the typical potentiometric titration curves, and the potential jump in the vicinity of end-point is about 120 mV. The concentration of 2- Ap^+ solution obtained from this method shows a good agreement with that of argentimetric titration method.

3.7 Potentiometric titration of sulfate ion

Since 2-aminoperimidinium ion is used as a good precipitant of sulfate ion, the present ion-selective electrode has been successfully applied to potentiometric titration. Figure 5 shows the potentiometric precipitation titration of 20 cm^3 of ca. 10 mM 2- Ap^+Br^- standard solution with 10 mM sulfuric acid, copper sulfate, zinc sulfate and magnesium sulfate. Almost the same shape of titration curves was obtained, because hydrogen, copper, zinc and magnesium ions do not affect the potential of the present electrode. Stephan²⁷⁾ reported that the mole ratio of ion-pair of 2- Ap^+ and SO_4^{2-} be 2.3 : 1. We titrated several kinds of sulfate solution and the mean of the mole ratio of 2.305 : 1 quite well agreed with that of the above value. Five kinds of sulfate solutions are titrated and the mole ratio and factors of 10 mM sulfate sample solution are tabulated in Table 2. Factors of the sulfate solution at the present titration were compared with that of conventional method, i.e., acid-base titration,

Table 2 Comparison of the results obtained by conventional and present method

Sample solution ^{a)}	H_2SO_4	CuSO_4	ZnSO_4	MgSO_4	Na_2SO_4
Titrant	$\text{NaOH}^{\text{b)}$	edta	edta	edta	$\text{BaCl}_2^{\text{c)}$
Mole ratio ^{d)}	2.2970	2.2740	2.3470	2.3290	2.2790
Factor (conventional method)	0.9973	0.9939	0.9941	1.0060	0.9816
Factor (present method)	0.9976	1.0110	0.9795	0.9946	1.0040
Difference (%)	+0.03	+1.76	-1.47	-1.13	+2.32

a) Concentration of sample solution : ca. 10 mM,

b) Acid-base titration method, c) Gravimetry,

d) Mole ratio of 2- Ap^+ to SO_4^{2-} (mean 2.305)

chelatometric titration and gravimetry with barium chloride. The differences of both methods are within 2.5%, a good agreement being observed.

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Fig. 5 Potentiometric titration curves of 2- Ap^+Br^- standard solution with sulfate ion. 20 cm^3 of 10.0 mM 2- Ap^+Br^- solution was titrated with ca. 10 mM solution of : —○— H_2SO_4 , —●— CuSO_4 , —△— ZnSO_4 , —▲— MgSO_4 . Arrows show the beginning of titration

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会員のページ

キール大学へ留学

1980年10月から3年間にわたって西ドイツ政府の奨学金を受け、Kiel大学において博士課程の学生(Doktorand)として研究する機会を得た。ここに簡単にKiel大学および研究所を紹介したいと思う。大学の起源は1665年、当時のこの地方の領主Albrechtの命により神学校として発足したときである。ドイツの他の大学がそうであるように、Kiel大学は正式にはその創設者の名前をとってChristian-Albrecht-Universität(CAU)と呼ばれる。19世紀中頃までは神学が中心だったが、それ以後種々な分野が設けられ、今日のような総合大学として成長してきた。戦争中ドイツの誇る軍港を控えていたのが災いして、街のかかなりの部分が爆撃により破壊されてしまった。戦後、医学系とその付属病院だけを街の中心に残して、街の北西部約80haの敷地の中に大学は新しく建て換えられた。KielはMax Plankの生まれたところで、彼はこの大学でも一時教えていた。

ドイツの大学は大きく専攻科で分けられ、研究所を単位として成り立っている。たとえばKiel大学には化学系として、有機化学、無機化学、物理化学、生物化学等の研究所があり、化学を専攻する学生はこれらのどの研究所で行なわれている講義、学生実験等に原則的に自由に参加できる。ただし卒業試験は難しく、実験研究まで終えて卒業するDiplom(年令的に日本の修士に対応させている)の資格まで取れるのは大学入学者の2割にも満たない。私が所属していた物理化学研究所を参考にその構成、研究活動に関して若干話そう。5人いる教授はおの物理化学の中でさらに専門の分野を担当する。私のついたProf. Schindlerは電気化学と反応速度論を受けもっていた。研究室によって若干異なるが、一人の教授の下には一つの分野ごとに数名のDoktor, 5~6名の

Doktrand それにたまにDiplomand(修論生+卒論生)がおり、おのおのが直接教授とcontactをとって研究を進めている。若干名の研究補助員もいる。したがって日本の助教授、助手に相当するポストはなく、しいて挙げるとすれば教授になる資格(Habilitation)を持った者が空きを待って大学に残っているぐらいのものである。学部学生に対する実験指導、問題演習等はすべての責任をDoktrandもしくはDoktorが行なうことになり、それに対しては当然かなりの報酬がある。したがって研究室にいる者はほとんどが何らかの形で、大学もしくは国から十分な収入を約束されており、その地位も認められている。ただしこれらはすべて契約制なので、その期限が切れて延長できなくなると大学から出てゆかなければならない。私も学生実験を担当したが、女子学生も多くいたので実に楽しく、多に勉強になった。

研究費はおもに国の研究助成機関からくるが、定まった国の予算の中からいくらか獲得できるかはひとえに教授の政治的手腕によるところが大きいと聞く。獲得額によっては当然研究室の活性度も変わってくる。私のいたところは、研究費の面ではかなり恵まれた方であつたらしく、新しい高価な器械を次々と使わせてもらえた。隠れた研究費として研究所に付属していた工作所(Werkstatt)の存在も見逃せない。そこには数人のスタッフがおり、単純なものから、かなり高度な技術を要するものまで、実験装置の製作、組み立て、修理をすぐにやってもらえた。その存在は大いに価値のあるものであった。また広く、よく清浄された部屋での実験や一人一部屋主義の環境は、研究者にとって非常に恵まれていると言えよう。

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(東京大学工学部 中尾 正史)