

An Active Transport Mimetic System Based on Thioctic Acid as Carrier for Alkaline Earth Metal Ions

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(Received 5 July 2006, Accepted 11 October 2006)

Liquid membranes incorporating thioctic acid as a carrier to mimic an active transport system for alkaline earth metals has been described. A transport cell, operating on the same principle as the Schulman Bridge was used. It has been demonstrated that such a system is capable of transporting alkaline earth metals against a proton gradient, as driving force. The potential of thioctic acid to complex and transport these metal ions particularly Mg^{2+} , Ca^{2+} , and Ba^{2+} was verified. Furthermore, this transport phenomenon was extended to some different barium salts (Cl^- , Br^- , NO_3^- , and SCN^-) to determine the effect of nature of anion on the transport of the Ba^{2+} ions. The order of the transport rate was found to be $Ba^{2+} > Ca^{2+} > Mg^{2+}$ which is inconsistent with the stability of coordination to the carboxyl group. The rate of transport of Ba^{2+} ions were found to decrease with the anion type in the order $SCN^- > Br^- > NO_3^- > Cl^-$ which is related to the extent of hydration of the anions.

Keywords: Active transport, Liquid membrane, Alkaline earth, Thioctic acid, Anion type

INTRODUCTION

Amongst numerous different extraction processes, the spotlight on the separatory-membrane technology is increasingly being intensified [1]. A reason for this is that the technology has been reported to strongly limit the number of elementary procedures involved in traditional extraction and separation processes [1].

Trans-membrane transport systems using synthetically created membranes incorporating metal ion ionophores are biologically inspired in the sense that they mimic well known biological processes such as facilitated ion transport using ion-channels like Na^+ - K^+ ion pumps.

The ionophores are molecules that bind to a target analyte, transport it across a membrane and release it into another

solution phase. The improvement of selectivity of the trans-membrane transport has been the subject of many experimental attempts. Traditional methods have been aimed to the synthesis of porous inorganic or hybrid membrane of defined pore size, together with modification of surfaces with characteristic well known membrane [2].

Recent breakthrough in supramolecular chemistry has yielded sophisticated ionophores that are highly specific molecular or ionic complexing agents [1]. Great interest in ionophores began following the initial observation by Pedersen that a class of macrocyclic polyethers could efficiently complex with soluble metal cations and transport them across an organic phase [3].

In addition, advances in host guest recognition chemistry for the design and synthesis of host molecules to mimic bio-receptor functions have stimulated a number of research groups to develop novel types of sensing elements. In

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particular many successful application of acyclic as well as cyclic polyethers to liquid membrane type ion-selective electrodes for alkali and alkaline earth metals have been reported [2,4]. Some new type of liquid membrane ion-selective electrodes for organic guests and metal cyano complexes have been developed using polyamines [5-7], macrocyclic dioxopolyamines [8], a cytosine-pendant triamine [9], a calix (6) arene hexaester [10] as sensory elements. These ion selective electrodes exploit different modes of host-guest interaction for the potentiometric determination of various types of analytes.

Development of ion-channel sensors has also become a means of identifying receptor molecules for various analytes. A modified gold electrode based on thioctic acid as the receptor to mimic an ion-channel has been reported [11]. Further, the modified electrode has been used in the voltammetric determination of metal cations [12].

In this research, we wonder whether thioctic acid could be used as a carrier for the transport of metal ions particularly alkaline earth metals by ionophore translocation. It is also intended to investigate the effect of the associated anion on the rate of transport of the cation.

EXPERIMENTAL

Reagent

Magnesium nitrate hexahydrate (99%), calcium nitrate tetrahydrate (98%) barium nitrate (98%), barium chloride, barium Bromide (98%), barium thiocyanate (98%) were all laboratory reagent grade chemicals from BDH chemical Ltd., Poole, UK. Thioctic acid (98%) was from Wako, Japan, and reagent grade chloroform from Auro Avenda Export PVT Limited, India. Buffer tablets of pH 4 and pH 7.4 from Breckland Scientific Supplies, UK.

Transport Process

All the experiments were conducted at room temperature of 27 ± 0.5 °C. Two similar transport glass cells obtained from the Glass Blowing Unit, Department of Chemistry, University of Cape Coast were used. Outline of these cells is as shown in Fig. 1 and is a modified form of Lamb *et al.* [13].

One cell served as control in which no carrier ligand (thioctic acid) was added to the chloroform membrane. In the

other cell, 35 ml of 1.0×10^{-2} M solution of thioctic acid in chloroform was put in the glass dish. Suspended 2 cm above the bottom of the dish was a glass cylinder. The cylinder opened at both ends with the lower part well below the level of the chloroform solution. This arrangement separated the upper part of the cell into inner and outer portions. On the top of the outer portion was carefully placed 10 ml of deionised water. This phase served as the receiving phase for the metal ions transported. In the inner portion of the cylinder and on top of the chloroform surface was placed 5 ml solution of the metal ions of a particular concentration and at pH of 7.4. This phase served as the source phase for the particular cation. The three phase system was then gently stirred with a magnetic stirrer for two hours in each case, before 4 ml sample of the receiving phase taken for the determination of the amount of cation transported.

Determination of the Amount of Cations Transported

The amount of Ba^{2+} transported in each experimental run was determined using a direct reading spectrophotometer DR/2000 from Hach Company, USA. This consisted of measuring 2.5 ml of the sample from receiving phase and diluting to 25 ml in a spectrophotometric cuvet. In the case of Ba^{2+} ions, a BariVer 4 barium reagent gel was added to the sample. The cuvet was then shaken to form a homogeneous solution. The reagent treated sample was placed in the direct reading spectrophotometer, and the absorbance was measured at a wavelength of 450 nm.

In the case of magnesium and calcium ions, however, the complexometric titration involving EDTA and Erichrome black T as indicator was used to determine their concentrations.

RESULTS AND DISCUSSION

Selection of pH for Transport Process

Binding of surface confined thioctic acid at pH of 7.4 to metal ions including the alkaline earth metal cations has been reported [12]. The negative charge on the dissociated acid caused these metal ions to electrostatically bind to the thioctic acid units. This suggests that at such a neutral pH, thioctic acid is capable of coordination to these metal ions in a bulk solution. This is because thioctic acid with pK_a of 5 is

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extensively deprotonated at pH of 7.4 to provide the requisite anionic receptor site. At pH 4, however, thioctic acid is protonated and thus can be generated from its metal salts. Therefore by a change in pH (ΔpH), complexation and de-complexation of thioctic acid to these metal ions can be achieved.

In this work, we used such a pH difference as a driving force in the transport of alkaline earth metal ions across a chloroform layer containing thioctic acid. The pH of each source and receiving phases were adjusted to 7.4 and 4.0, respectively, using either NaOH or HCl. We however believe that different pH settings for the source and receiving phases will have a significant effect on the rate of transport of these cations. Though an important factor, its contribution to the rate of transport was not assessed in this work.

Transport of the Alkaline Earth Metals

There was not any detectable movement of the cations across the chloroform membrane in the blank units. However, in the presence of the thioctic acid in the membrane phase, each of the cations was transported to give detectable amounts. The transport of the cations is principally due to their complexation with thioctic acid through its carboxylate end. The sulfur atoms of the acid are not likely to be involved in the complexation, since that will lead to the cations being held up in the chloroform membrane and thus no transport observed. Table 1 shows the amount of each cation transported within two hours when the source concentrations were set at 0.5 M and 1.0 M.

As indicated in Table 1, the amount transported increases in the order $\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$. This order is inconsistent with the stability of the coordination of the carboxylate group with the metal ions in which Mg^{2+} is known to have higher stability than the other cations, a quality that decreases in the order $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$. Although we have no clear explanation at the present stage, the following may account for the discrepancy between the amount transported and the complex stability. The observed order is consistent with the order of the water exchange rate between the inner hydration shells [14]. The slower dehydration of the inner shell may bring about the lower coordination stability of the terminal carboxylate units. In this context, dehydration of the Mg^{2+} inner shell is believed to hinder its complexation to thioctic

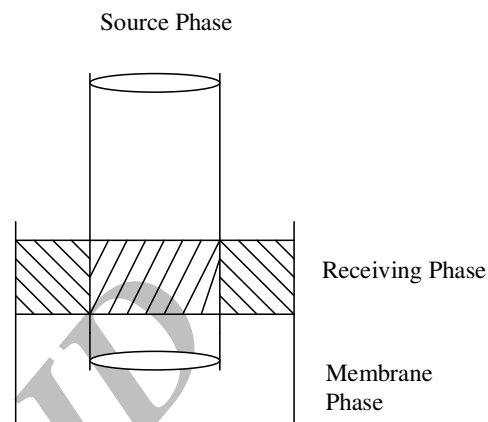


Fig. 1. Schematic diagram of the transport cell.

Table 1. Amount of Cation Transported at Source Phase Concentrations of 0.5 M and 1.0 M

| Cation | Amount transported $\times 10^7$ M | |
|------------------|------------------------------------|--------------------|
| | 0.5 M cation in SP | 1.0 M cation in SP |
| Mg^{2+} | 4.86 | 7.45 |
| Ca^{2+} | 61.0 | 285 |
| Ba^{2+} | 410 | 730 |

Table 2. Amount of Barium Ions Transported with Different Anions at Source Phase Concentrations of 0.01 M and 0.02 M

| Anion | Amount transported $\times 10^7$ M | |
|-----------------|------------------------------------|-------------------|
| | 0.01 M salt in SP | 0.02 M salt in SP |
| Cl^- | 1.16 | 1.31 |
| NO_3^- | 1.24 | 1.43 |
| Br^- | 1.75 | 3.37 |
| SCN^- | 1.97 | 3.73 |

acid and its subsequent transport.

Additionally, one significant observation is that, as the source phase concentration of the cation is increased, the amount transported also increases. This is expected on the basis that increased concentration of the cation increases the

frequency of interaction with carrier ligand (thioctic acid) and, hence, increases the extent of complexation of the ions. This eventually increases the final rate of transport.

A feature that is eminent in Table 1 is that the barium ions are transported about hundred times more than the magnesium ions. This suggests that the barium ions can be selectively extracted from a sample matrices containing both barium and magnesium ions to an appreciable extent, using this system. Alternatively, if thioctic acid is used as a sensory element, it should be able to respond discriminatively between magnesium and barium ions. This agrees with an earlier report that a modified gold electrode based on thioctic acid as receptor, a voltammetric sensor, responded appreciably better to barium ions than magnesium ions [12].

Effect of Anion Type on the Transport Rate

The nature of the anion is a factor that determines the rate of cation transport. The mobility of the cation-carrier-anion complex depends on the characteristics of the anion. Table 3 shows the influence of some counter anions on the transport of barium ions

As it is obvious from Table 2, the amount of barium transported varies with the type of anion even at the same source phase concentration of the cation. The amount of barium transported increases in the anion order $\text{Cl}^- < \text{NO}_3^- < \text{Br}^- < \text{SCN}^-$. This ordering of anions is quite consistent with charge to size considerations of the anions. That is, anions with smaller Gibb's free energy of hydration allow faster cation transport. The ordering here agrees with an earlier report [15] that among the halides, for every cation-carrier complex, the iodide salts always transport rapidly and the transport rate decreases in the order iodide > bromide > chloride an > fluoride.

CONCLUSIONS

Thioctic acid has been shown to be a suitable carrier for bulk liquid membrane transport of alkaline earth metal ions. The efficiency of transport of these metal cations is in the order $\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$, which is consistent with the order of

the water exchange rate between the inner hydration sphere. Also it has been shown that the associated anions to the cation-carrier-complex influences the transport rate and the ordering can be related to the charge to size ratio of the anion.

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