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SCIENCE DIRECT®

Talanta 64 (2004) 558–561

Talanta

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Short communication

The effect of magnetic field on the stability of (18-crown-6) complexes with potassium ion

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Received 22 November 2003; received in revised form 19 January 2004; accepted 10 February 2004

Abstract

Macrocyclic polyethers are ligands with selectivity for metal ions. In order to understand the interactions between ligand, ion and solvent we resorting to study of magnetic field effect on ion-macrocyclic complexes. Therefore, we studied the complexation between 18-crown-6 and potassium ion in water through the conductometry technique (in 25 + 0.05 °C) by a nonlinear least-square program (Genplot) under magnetic field.

We observed that stability constants of complexes in the presence of the magnetic field, were decreased. Like-wise, we observed that, magnetic field influenced on ion, solvent and ligand one by one.

Keywords: Macrocyclic polyether; 18-Crown-6; Metal ion; Magnetic field stability constant

1. Introduction

Macrocyclic polyethers (such as crown ethers) are multidentate ligands that exhibit selectivity for specific metal ions in solutions containing other chemically similar ions (Fig. 1). They have become model systems for understanding molecular recognition and ligand selectivity due to the enzyme-like specificity in their interactions with cations. Thus, a wide variety of data on these systems has been obtained and analyzed [1]. In many case, the observed selectivity has been rationalized by considering the relative sizes of the metal ions and the cavety of the macrocyclic ligand. However, even for simple homologous crown ethers, a more comprehensive model is required to explain all of the data [2]. This suggests the need for a more detailed understanding of noncovalent interactions between ions and neutral molecules and for accurate values of the critical parameters, to develop models of molecular recognition and biochemical systems with broad predictive capabilities.

Crown ethers are also interesting from a practical aspect of their potential utility in advanced chemical separation, and analytical methods [3].

Computational methods capable of predicting ligand selectivity in a variety of condensed-phase environments would be valuable tools for the advancement of separation technologies. Such methods, currently under development, require accurate models of the relevant noncovalent interactions and suitable experimental data to benchmark the calculations. One approach to achieve a detailed understanding of noncovalent interactions is the study of magnetic field effect on ion-macrocycle complexes. Measurements and calculations on these complexes allow separation of intrinsic interactions, from effects due to ion solvation and solvent-induced phenomena. Obtaining accurate data on complexes of cations with simple macrocyclic ligands and determining the formation constants of complexes required to accurately model these complexes are the first steps toward developing reliable models of the interaction between cations and more complex macrocycles.

Crown ethers, in particular 18-crown-6, have been the focus of a number of studies based on different methods. Complexes of crown ethers with alkali cations have also been studied previously [4,5] by conductometry in these

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doi:10.1016/j.talanta.2004.02.039

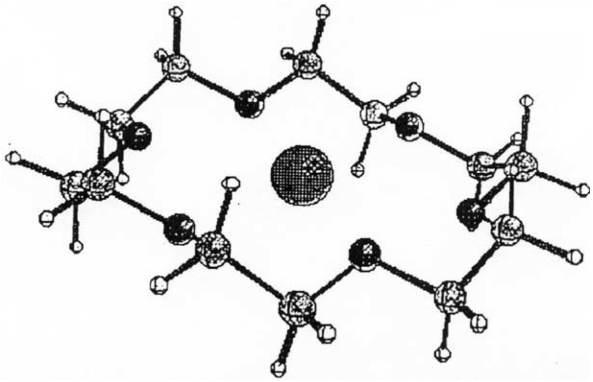

Fig. 1. Structure of metal/18-crown-6 complexes.

studies addition of the ligand to metal ion solution causes a continuous decrease in the molar conductance which begins to level off at mole ratios grater than one.

The solvation of the ligand and metal cation are influenced by the donor ability and dielectric constant of the solvents. As well as by the shape and size of the solvent molecules. However, as mentioned it has been shown that the donor ability of a solvent plays the most important role in the behavior of crown ether complexes with metal ions.

Even for simple homologous crown ethers a more comprehensive model is required to explain all off the data. This suggest the need for a more detailed understanding of noncovalent interactions between ions, natural molecules and solvent, and for accurate values of the critical parameters. One approach to achieving a detailed understanding of these interactions is the study of magnetic field effect on ion–macrocyclic complexes.

Since 1980, the effect of a magnetic field on liquids has been studied. It has been found that water gives rise to many phenomena when exposed to a magnetic field, even if the magnetic flux density is not high and the treatment time is short [6]. Nevertheless, the experiments reported so far have been primarily qualitative and the results not reliable, the effect of a magnetic field on solution, therefore, need further study.

2. Experimental conditions

2.1. Reagents and solvent

18-Crown-6 (Merck) was recrystalized from acetonitrile (Merck) and, dried under vacuum for 72 h, at room temperature [5]. The potassium nitrate was purchased commercially from Merck and was recrystalized from dionized distilled water three times and, dried at 150 °C in an oven and then was kept in a vacuum desicator TMAP,$(Me_4N)_3PO_4$ was purchased commercially from Merck and used without any purification [5]. The solvent, water, distilled three times and dionized. The conductivity of the find product was less than 4×10^{-6} cm at 25 °C. The solution of tetramethyl ammonium phosphate (TMAP), 0.05 M has been used to keep pH's solvent (water) at 7.

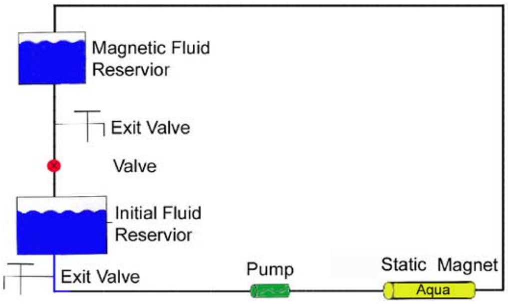

Fig. 2. The pilot of magnetic instrument.

2.2. Apparatus

The conductance measurement were performed by a "metrohm" conductometer, model AG 910 °C. The cell constant was $\theta = 0.4750\,\mathrm{cm}^{-1}$ at 25 °C.

The static magnetic field in a compact form, a unite called "AQUA CORRECT" was used. The equipment has a coaxial static magnetic system of 6000 G field strength, and was imported from Germany (H.P.S Co.) [DN = 20, 3/4 in., flow $2\,\mathrm{m}^3/\mathrm{h}$] for the experiments [7].

The equipment was connected from one end to the liquid pump and the other end to the pipelines of solvent reservoir. Solutions had to flow through a coaxial static magnetic gap, and came back to solvent reservoir. Therefore, solution could passed through the field for many times, in a closed cycle (Fig. 2).

3. Results and discussion

In the present study, the formation constant of $(18C6.K^+)$ complex in water, as solvent (at pH 7) under static magnetic fields was determined by conductometry. The K_{ML^+} values, obtained in this work, showed that the stability of complexes are affected by magnetic field in addition of various factors [4].

It is obvious from Table 1 and Fig. 3, in all cases, addition of the ligand to K^+ solution causes a continuous decrease in the molar conductance which begins to level off at mole ratios greater than one. The slope of the corresponding mole ratio plots changes sharply at the point where the ligand to cation mole ratio is one, indicating predomination or

Table 1
Formation constant of $(18C6.K^+)$ complex in water at the different magnetic field time exposure

A	B	C	D
$\log K_f$			
5.76 ± 0.09	4.99 ± 0.10	4.70 ± 0.08	4.61 ± 0.09

A: 0 min, B: 15 min, C: 1 h, D: 3 h.

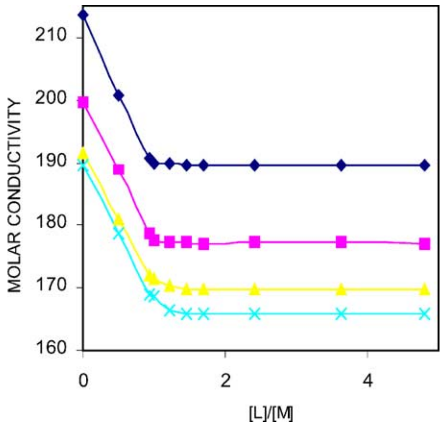

Fig. 3. Molar conductance-mole ratio plots for (18C6.K^+) complex in water at different time exposures at 25 °C: (A) 0 min, (B) 15 min, (C) 1 h (D) 3 h.

relatively stable 1:1 complex. Moreover, we obtained that, when the solvent, ion or ligand solutions passed through the magnetic field, before the complexation reaction, the stability of complexes decreased (Table 1).

At first, we must explain the mechanism of magnetic field treatment on complexation of crown ethers with metal ions. The magnetic technology has been cited in the literature and investigated by many other researcher such as Ueno [8]. The general operating principle for the magnetic technology is a result of the physics of interaction between a magnetic field and moving electric charge, in this case in the form of an ion (Table 2).

When ions pass through the magnetic field, a force is exerted on each ion. The forces on ions of opposite charges are in opposite directions (Fig. 4).

The redirection of the charged particles tends to increase the frequency with which ions of opposite charge collide and combine to form a mineral precipitate, or insoluble compound [9].

The magnetic technology is generally not applicable in situations where the water contains appreciable concentration of paramagnetic ions such as iron. The reason for this precaution is that the action of the magnetic field on the ions such as K^+ is weak. Conversely, the action of the paramagnetic ions is very strong, which interferes with the water conditioning action [10,11] (Fig. 5).

Table 2
Molar conductance data for various [18C6]/[K^+] ratios in H_2O at different magnetic field time exposure

A		B		C		D	
MR	Λ	MR	Λ	MR	Λ	MR	Λ
0	213.740	0	199.700	0	191.610	0	189.710
0.49	202.911	0.49	188.871	0.49	180.890	0.49	175.937
0.94	192.710	0.97	178.670	0.97	170.744	0.97	165.818
1	192.510	1	178.510	1	170.592	1	165.670
1.22	191.910	1.22	177.901	1.22	169.962	1.22	165.030
1.46	191.740	1.46	177.292	1.46	169.710	1.46	164.757
1.70	191.761	1.70	177.082	1.70	169.712	1.70	164.759
2.42	191.750	2.42	177.103	2.42	169.711	2.42	164.756
3.62	191.741	3.62	177.092	3.62	169.710	3.62	164.758
4.81	191.739	4.81	177.083	4.81	169.709	4.81	164.757

A: 0 min, B: 15 min, C: 1 h, D: 3 h. Units: Λ, $S\,cm^{-2}\,mol^{-1}$; [K^+] = 5×10^{-4} M.

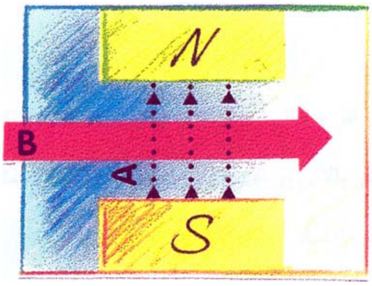

Fig. 4. Effective factors in the magnetic field. A: Lines of magnetic field; B: fluid current; Q: number of charged particles, which are dissolving in the fluid; θ: the angle between magnetic field and fluid direction, which is always vertically; F: magnetic field's force. $F = |A||B|Q \sin\theta$. The maximum of magnetic. field's force is obtained when $\theta = 90°$ C. $F = |A||B|Q$.

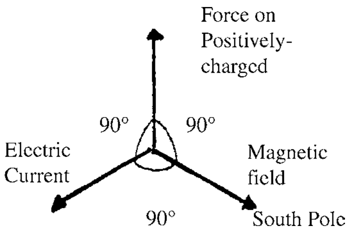

Fig. 5. Diagram showing positioning of field and force on positively charged.

The result of these forces on the ions is that, in general, positively ions (first potassium ion) and negatively charged ions are directed toward each other with increased velocity. The increased velocity should result in an increase in the number of insoluble particular matter and decrease in the solvation of each ions and thus complexation with crown ethers, subsequently (see Fig. 6). Magnetic treatment should have no direct effect water chemistry (unless the magnets are in contact with the water), yet it is claimed to alter the morphology and adhesion of soluble ions. We have established that a magnetic field effect exists [12]. A simple hydrodynamic model, using the Navier–Stoke's and Maxwell

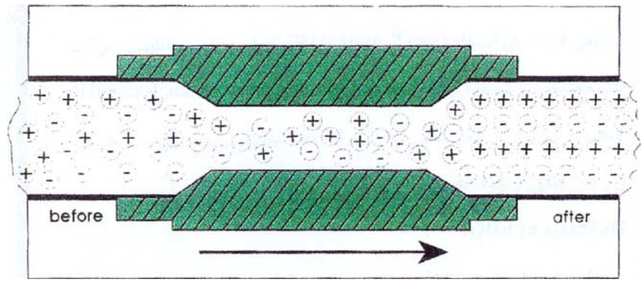

Fig. 6. Configuration of ions in magnetic field.

equations, predicts that there is a strong energy coupling and transfer between the kind of energy turbulent flow and the magnetic field which can be amplified [13]. The main theoretical issues which have to be addressed are coupling and transfer of magnetic energy between the molecules and the magnetic field. As water is an essential material in the living body, the understanding of the behaviour of water under magnetic fields provided information to discuss the effects of magnetic field on living systems. The so called (Moses) effect, can be explained by the diamagnetic property of water. Since water is diamagnetic, when a magnetic force acting on water reaches a high enough value, it presses back the water.

Also, it is important to understand the mechanism of the interaction of magnetic fields with organic (crown ether) and water molecules.

A diamagnetic macromolecule such as crown ethers is a good model for studying biomagnetic effects because crown ethers are oriented parallel to the direction of magnetic fields. Compared to paramagnetic inorganic materials, solutions of biological materials such as antibiotics (crown ethers are models for some of antibiotics) are mostly diamagnetic, and their magnetic susceptibility is small.

We reported in this study, the effect of magnetic fields on biological compounds, such as 18-crown-6 using an electrochemical technique (conductometry). We observed that conductivity of 18C6 decreased by 10–20% after a magnetic field exposure for 1 min to 3 h. Also, it is important to investigate the effects of dissolved oxygen concentration on the properties of aqueous solution.

Many researchers have showed that the field-induced changes in water structure and magnetic moment interaction will strongly affect the hydrogen bond distribution and the internal energy of water. The external magnetic field can weaken or even partly break a hydrogen bond and increase the number of monomer water molecules which may be result in some biological effects. Note that, were reported when the magnetic field is switched off within the time, an increase in the resistance grows during the time of inertia (∼200 h) and, after attaining a maximum, it returns to its initial value [14]. Thus, by measuring the relative change in water conductivity, we observed the effect of initiating slow physic chemical processes when low magnetic fields are applied.

The effect can be attributed to the bulk of water, probably because of the modified water structure. Nevertheless, the experiments reported so far have been primarily qualitative and the effect of a magnetic field on complexation of crown ethers with metal ions are of interest, because crown ethers are models for antibiotics and some other drugs treatment in biological systems [15].

Acknowledgements

The authors are grateful for partial support of this work by Sabzevar Teacher Training and Fariman Payam-e-Noor Universities Research Concils.

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