Stability of Ag$^+$ Complexes with Cryptand 222 in Ionic Liquids

A. LEWANDOWSKI[*], M. OSIÑSKA and I. STĘPNIAK
Faculty of Chemical Technology, Poznañ University of Technology, PL-60 965 Poznañ, Poland

Abstract

Stability constants of silver(I) complexes with cryptand 222 were measured in a number of ionic liquids, applying potentiometric titration. The ionic liquids were based on 1-butyl-3-methylimidazolium, 1-ethyl-3-methylimidazolium, 1-butyl-1-methyl-pyrrolidinium and 1-methyl-1-propyl-pyrrolidinium cations, as well as on tetrafluoroborate, triflate and bis(trifluoromethane sulfonyl) imide. The stability constants, expressed in log K scale, were within the broad range of 8.4–17.2. The formation of the Ag$^+$222 cryptates was not detected in ionic liquids based on halide anions. Free enthalpy of silver(I) transfer from dimethylsulfoxide as a reference molecular solvent to ionic liquids was calculated applying the cryptate assumption. The results were discussed in terms of the competition between silver(I) complexation by ion forming ionic liquid and its complexation by cryptand 222.

Introduction

The complexation properties of macrocyclic ligands, such as crown ethers and cryptands, in pure and mixed solvents, have been studied extensively during the last three decades [1–3]. Cryptands (Cry) encapsulate a metal ion (M) in their three-dimensional cavity, to form stable [M]/[Cry] = 1:1 inclusion complexes. However, in a few cases 1:2 or 2:1 complexes have been reported [1–3]. To date our understanding of the cryptates solution chemistry has been based on their behavior in molecular solvents (molecular solvents, ML), such as water, methanol, acetonitrile propylene carbonate etc. The role of the solvent is very important, as the cation complexation competes with its solvation by solvent molecules. Stability constants of silver (I) complexes with cryptands, especially with cryptand 222, were determined in a number of solvents [4–22].

During the last decade there has been a growing interest in room temperature ionic liquids, which can be regarded as a new class of liquid media [23–25]. Ionic liquids (or molten salts) consist entirely of ionic species. Both thermodynamics and kinetics of processes carried out in ionic liquids (IL) may differ considerably from those in conventional molecular liquids. Chloroaluminate ionic liquids seem to be the first to have been extensively examined over the past two decades. However, chloroaluminate ionic liquids are moisture sensitive, which limits their possible application. More recently numerous non-chloroaluminate room-tempera-ture ionic liquids have been synthesized [23–25]. Most consist of unsymmetrical quaternary ammonium cations and various anions. Both the thermodynamic properties of cations as well as their complexation in a molten salt medium to our knowledge are unknown. The general aim of this work was to study the complexation of silver(I) cation by cryptand 222 in a number of ionic liquids.

Experimental

Chemicals

Silver triflate (AgCF$_3$SO$_3$) and cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexac-osane) were used as received from Merck. Bromoe-thane (Aldrich) and 1-methylimidazole (Fluka) were purified by distillation under atmospheric pressure. Dimethyl sulfoxide (DMSO, Fluka) was distilled under reduced pressure. Silver tetrafluoroborate (AgBF$_4$) was synthesized from silver oxide (Ag$_2$O, P.O.Ch., Gliwice) and tetrafluoroboric acid (HBF$_4$, 48% aqueous solution, Fluka). Salts: 1-ethyl-3-methy-limidazolium bromide (EMImBr) and 1-butyl-3-methy-limidazolium bromide (BMImBr) were prepared from 1-methylimidazole and freshly distilled bromoethane and bromobutane, respectively, in chloroform [26]. The ionic liquids 1-ethyl-3-methylimidazolium tetraflu-oroborate (EMImBF$_4$) as well as 1-butyl-3-methylim-idazolium tetrafluoroborate (BMImBF$_4$) were obtained by reacting EMImBr or BMImBr, respectively, with

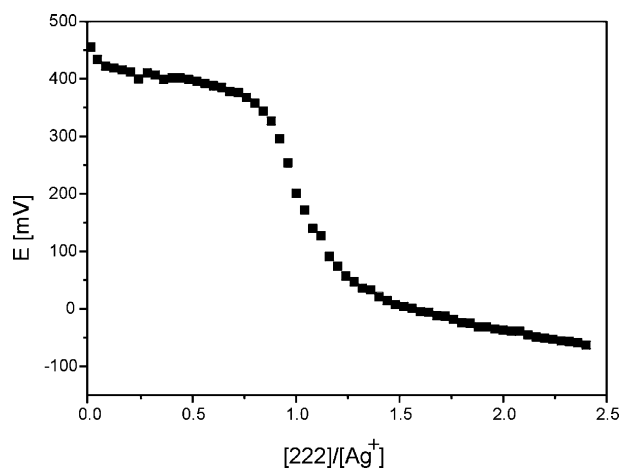* Author for correspondence. E-mail: andrzej.lewandowski@put.
poznan.pl

Figure 1. Potentiometric titration of 0.5 ml Ag$^+$ 0.01 mol/dm^3 with 222 0.02 mol/dm^3 in BMIm N(CF$_3$SO$_2$)$_2$. $T = 25$ °C.

AgBF$_4$ in aqueous solution and dried in a vacuum at 70 °C [26].

Ionic liquids: 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl) imide (EMIm N(CF$_3$SO$_2$)$_2$) and 1-butyl-3-methylimidazolium bis(trifluoromethane sulfonyl) imide (BMIm N(CF$_3$SO$_2$)$_2$) were synthesized from the respective bromides (EMImBr or BMImBr) and lithium bis(trifluoromethanesulfonyl) imide (Fluka) [27]. Salts: 1-butyl-1-methylpyrrolidinium iodide (BMPyrI) and 1-methyl-1-propylpyrrolidinium iodide (MPPyrI) were synthesized by reacting 1-methylpyrrolidine (Fluka, >99%) with 1-iodobutane (Fluka) or 1-iodopropane (Fluka), respectively [28]. Ionic liquids: 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethanesulfonyl) imide (BMPyrN(CF$_3$SO$_2$)$_2$) and 1-methyl-1-propyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (MPPyrN (CF$_3$SO$_2$)$_2$) were prepared from 1-butyl-1-methyl-pyrrolidinium iodide (BMPyrI) and 1-methyl-1-propyl-pyrrolidinium iodide (MPPyrI), respectively, and lithium bis(trifluoromethane sulfonyl) imide [28]. Ionic liquid : 1-ethyl-3-methylimidazolium triflate (EMIm CF$_3$SO$_3$) was obtained by reacting EMImBr with silver triflate (Merck) [29].

Measurements

Cryptate stability constants were measured potentiometrically using silver wire as the indicating electrode and Ag/Ag$^+$ in DMSO as the reference electrode:

$$\text{Ag} \mid \text{Ag}^+, 222 \text{ in IL} \parallel \text{Ag}^+ 0.01 \text{ mol/dm}^3 \quad (1)$$
$$\text{in DMSO} \mid \text{Ag}$$
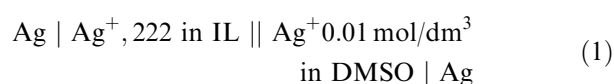
Typically, 0.5 ml of Ag$^+$ 0.01 mol/dm^3 solution in ionic liquid was titrated with 0.02 mol/dm^3 solution of 222 in ionic liquid or 0.5 ml 0.02 mol/dm^3 solution of 222 was titrated with 0.01 mol/dm^3 solution of Ag$^+$. The reagents were stirred continuously. The vessel with a water jacket was thermostated at 25.0 °C by means of a water-circulating thermostat. The system was protected

from the light with an aluminum foil. The potential was measured with the 5170 Elwro pH-meter.

Results and discussion

Silver(I) forms 1:1 inclusion complexes with cryptand 222 in all ionic liquids studied. Figure 1 shows a typical titration curve. The equilibrium potential was established over a long period (of ca. 5–10 h). Stable concentration stability constants, defined as $K = [\text{Ag}^+ 222]/[\text{Ag}^+][222]$, were obtained for the [222]/[Ag$^+$] ratio higher than 1.5. The stability constant values, obtained from at least three separate titrations and at least 30 experimental points at [222]/[Ag$^+$] > 1.5 are collected in Table 1, together with the corresponding free enthalpy change during the complexation reaction. ($\Delta_c G = -RT \ln K$). As can be seen from the table, the stability constants, expressed in log K scale, are within the broad range of 8.4–17.2. The complexation of the silver cation takes place in competition with its solvation by ionic liquids. In the case of classical solutions in molecular liquids, such as water, acetonitrile, DMSO etc., the cation forms solvato-complexes with electrically neutral solvent molecules. Ionic liquids consist entirely of ions and their charged and neutral combinations, and hence, the solvation of the cation is mainly due to ion-ion interactions, in contrast to typical solutions in molecular solvents. The stability constant, K, free enthalpy, or corresponding complexation free enthalpy, $\Delta_c G$, depends on the solvation free enthalpy of all species involved in the process. The properties of any solute in any solution are described by its free enthalpy of solvation, $\Delta_s G$, defined as the energy necessary to transfer it from a vacuum to an infinitely diluted solution. Both the final and the initial states are hypothetical, and hence, of practical value could be such a function that makes it possible to compare different solvents or solutions. Therefore, instead of the free enthalpy of solvation, the free enthalpy of the solute transfer, $\Delta_t G$, from a medium A to another medium B is

usually used. The transfer of the Ag^+-222 system from a molecular liquid (ML) to an ionic liquid (IL) brings about changes in the solvation of the cation, cryptand and the cryptate, expressed by the proper transfer enthalpies, and by the resulting change of the equilibrium constant K, according to the following scheme and Equation (2)
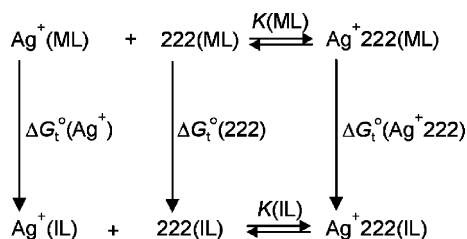
$$RT \ln[K(IL)/K(ML)] = \Delta_t G(Ag^+) + \Delta_t G(222) - \Delta_t G(Ag^+222) \quad (2)$$
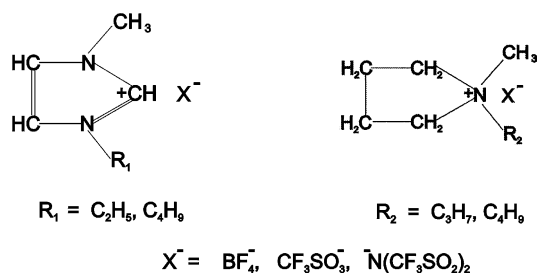

Scheme 1. Molecular structures of ionic liquids.

The equilibrium constants can be determined experimentally in both media, and hence $K(ML)$ as well as $K(IL)$ have a strict thermodynamic meaning. However, the transfer energies of single ions, such as Ag^+ or Ag^+222, are not accessible on the basis of strict thermodynamics; they can be only estimated applying extra-thermodynamic assumptions. There are several methods of an arbitrary nature of the 'experimental' determination of single-ion transfer properties. The assumptions and their justification have been extensively reviewed and discussed [30–33]. Consequently, $\Delta_t G$ values for individual ions, estimated with the use of any method, can be neither proved nor disproved. One of these methods, often called the 'cryptate assumption', is based on the approximation that the inclusion complex of a cation with a cryptand, should interact similarly with the environment in comparison to uncomplexed cryptand, and hence, the free enthalpy of cryptate and cryptand transfer should be comparable: $\Delta_t G(222) \cong \Delta_t G(Ag^+222)$ [34]. Consequently, under such an assumption the equation (2) is reduced to the following equation:

$$2.3RT[\log K(IL) - \log K(ML)] \cong \Delta_t G(Ag^+, ML \rightarrow IL) \quad (3)$$

Table 1. Stability constants, expressed as $\log K$, for Ag^+ complexation by cryptand 222, together with the corresponding free enthalpy change, $\Delta_c G$, as well as free enthalpy of Ag^+ transfer, $\Delta_t G$, from DMSO to ionic liquids

Medium	$\log K$	$\Delta_c G$ kJ/mol	$\Delta_t G$ kJ/mol
DMSO	7.3	−41.7	0.0
EMIm BF_4	8.4	−47.9	6.3
EMIm CF_3SO_3	11.6	−66.2	24.5
EMIm $N(CF_3SO_2)_2$	13.6	−77.6	35.9
BMIm BF_4	10.3	−58.8	17.1
BMIm $N(CF_3SO_2)_2$	10.0	−50.7	15.4
MPPyr $N(CF_3SO_2)_2$	15.8	−90.1	48.5
BMPyr $N(CF_3SO_2)_2$	17.2	−98.1	56.5

Table 1 contains silver(I) cation transfer energies from DMSO as a reference molecular liquid to ionic liquids, as estimated from the approximation (3). Inspection of the transfer free enthalpies collected in the table indicates the broad solvation energy range difference by ca. 50 kJ/mol. The solvation of silver(I) is the weakest in EMImBF$_4$, and comparable to that characteristic for DMSO. However, DMSO is a molecular solvent showing a strong solvation ability towards the Ag^+ cation [33,35]. The first three ionic liquids listed in Table 1 consist of the same EMIm$^+$ cation, and therefore, the difference in silver(I) solvation in these media is due to the different anion. It can be seen that the silver(I) solvation in ILs containing different anions decreases in the order $BF_4^- > CF_3SO_3^- > N(CF_3SO_2)_2^-$. In general, both ions forming the ionic liquid (its cation Z^+ and anion X^-) may react with the silver(I) cation, forming neutral and charged species. However, the Ag^+ cation complexes formed with the ionic liquid anion X^- should be predominating: $AgX_n^{-(n-1)}$. Hence, the transfer of the silver(I) from a molecular liquid S to the ionic liquid Z^+X^- is described by the following equilibrium:

$$Ag^+S_m + nX^- \rightarrow AgX_n^{-(n-1)} + mS \quad (4)$$
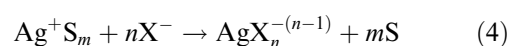
The complexation of the silver(I) in ionic liquids can be approximated as follows:

$$AgX_n^{-(n-1)} + 222 \rightarrow Ag^+222 + nX^- \quad (5)$$
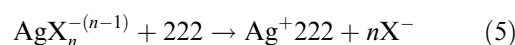
Here, the free enthalpy of silver(I) in ionic liquids having the imide anion $(N(CF_3SO_2)_2^-.)$ is higher than that in ionic liquids based on EMIm$^+$ and consisting of triflate or tetrafluoroborate anions. The complexing ability of the anions X^- which form the $AgX_n^-(n-1)$ complex decreases in the series $BF_4^- > CF_3SO_3^- > N(CF_3SO_2)_2^-$. However, comparison of stability constants and free enthalpies of transfer for BMIm BF_4 and BMIm $N(CF_3SO_2)_2$ does not indicate any significant difference between BF_4^- and $N(CF_3SO_2)_2^-$ anions. On the other hand, a strong influence of the ionic liquid cation, Z^+, on both $\log K$ and $\Delta_t G$ values, can be seen. For ionic liquids based on the imide anion $(Z^+N(CF_3SO_2)_2^-)$, the stability constant and the corresponding transfer energy increases

in the order: $BMIm^+ < EMIm^+ < MPPyr^+ < BM\text{-}Pyr^+$. This is probably due to the possibility of the $AgX_n^{-(n-1)}$ complex interaction with the Z^+ cation, with formation of the $AgZ_mX_n^{-(n-1+m)}$ complex. Therefore, the simple reaction of the cryptate formation (5) should rather be rewritten in the following form:

$$AgZ_mX_n^{-(n-1+m)} + 222 \rightarrow Ag^+222 + mZ^+ + nX^-$$

$$(6)$$
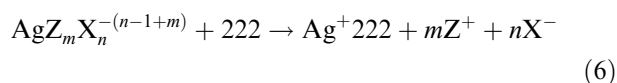
The transfer free enthalpies obtained here with the 'cryptate assumption' may be compared to those determined previously from the 'negligible liquid junction potential assumption' applied to the potentiometric measurements in a cell: Ag | Ag^+, 0.01 mol/dm^3 in DMSO || Ag^+, 0.01 mol/dm^3 in IL | Ag [36]. The ionic liquids consisted of $EMIm^+$, $BMIm^+$, $MPPyr^+$ and $BMPyr^+$ cations as well as Cl^-, Br^-, BF_4^-, PF_6^- or $N(CF_3SO_2)_2^-$ anions. The transfer of Ag^+ from DMSO to ionic liquids brought about positive or negative changes of the silver(I) solvation free enthalpy. Ionic liquids based on halide ions ($X^- = Cl^-$ or Br^-) were the solvents showing the strongest solvation ability towards the tested cations, including silver(I). In Table 1 there are no stability constants for ionic liquids consisting of halide ions, as a number of experimental observations showed such strong silver(I) solvation in such media that no formation of the Ag^+222 cryptate was observed.

Conclusions

1. The silver(I) ion forms with cryptand 222 1:1 inclusion complexes in a number of ionic liquids.
2. The stability of the Ag^+222 complexes, expressed as log$K$, depends strongly on the ionic liquid. The log$K$ value increases in the order: $EMImBF_4EMImBF_4 > EMI\ mCF_3SO_3 > EMImN(CF_3SO_2)_2 > BMImBF_4 \approx BMImN(CF_3SO_2)_2 > MPPyrN(CF_3SO_3)_2 > BMPyrN(CF_3SO_2)_2$.
3. The complexation thermodynamics is influenced by both cation and anion forming the ionic liquid.
4. Ionic liquids based on halide anions solvate silver(I) so strongly that the formation of the Ag^+222 complexes was not observed.

Acknowledgement

References

1. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, and D. Sen: *Chem. Rev.*, **85**, 271 (1995).
2. R.M. Izatt, K. Pawlak, J.S. Bradshaw, and R.L. Bruening: *Chem. Rev.* **91**, (1991) 1721.
3. R.M. Izatt, K. Pawlak, J.S. Bradshaw, and R.L. Bruening: *Chem. Rev.* **95**, (1995) 2529.
4. J. Bessiere, and M.F. Lejaille: *Anal. Lett.* **12**, 753 (1979).
5. H.J. Buschmann: *Inorg. Chim. Acta* **102**, 95 (1985).
6. A.F. Danil de Namor, and L. Ghousseini: *J. Chem. Soc. Faraday Trans. I* **81**, 781 (1985).
7. A.F. Danil de Namor, L. Ghousseini, and W.H. Lee: *J. Chem. Soc. Faraday Trans. I*, **81**, 2495 (1985).
8. B.G. Cox, J. Garcia-Rosas, H. Schneider, and N.V. Troung: *Inorg. Chem.* **25**, 1165 (1986).
9. H.J. Buschmann: *Inorg. Chim. Acta* **120**, 125 (1986).
10. A.F. Danil de Namor, H. Berroa de Ponce, and E. Contreras Viguria: *J. Chem. Soc. Faraday Trans. I* **82**, 2811 (1986).
11. A.F. Danil de Namor, and H. Berroa de Ponce: *J. Chem. Soc. Faraday Trans. I*, **83**, 1569 (1987).
12. A.F. Danil de Namor, and H. Berroa de Ponce: *J. Chem. Soc. Faraday Trans. I* **84**, 1671 (1988).
13. A. Lewandowski: *J. Chem. Soc. Faraday Trans. I* **85**, 4139 (1989).
14. I. Marolleau, J.P. Gisselbrecht, M. Gross, F. Arnaud-Neu, and M.J. Schwing-Weil: *J. Chem. Soc. Dalton Trans.* 1285 (1990).
15. A. Lewandowski: *Electrochim. Acta* **36**, 1427 (1991).
16. A. Lewandowski: *Electrochim. Acta* **37**, 413 (1992).
17. A. Lewandowski, A. Szukalska, and M. Galiński: *J. Chem. Soc. Faraday Trans. I* **91**, 1097 (1995).
18. C. Kalidas, and R. Raghunath: *J. Electroanal. Chem.* **389**, 79 (1995).
19. A. Lewandowski, A. Szukalska, and M. Galiński: *New. J. Chem.* **19**, 1259 (1995).
20. N. Heidari, A. Thaler, H. Schneider, and B.G. Cox: *Inorg. Chim. Acta* **279**, 186 (1998).
21. A. Thaler, N. Heidari, B.G. Cox, and H. Schneider: *Inorg. Chim. Acta* **286**, 160 (1999).
22. H.-J. Buschmann, and E. Schollmeyr: *Mat. Sci. Eng.* **C23**, 509 (2003).
23. T. Welton: *Chem. Rev.* **99** (1999) 2071.
24. M.J. Earle, and K.R. Seddon: *Pure Appl. Chem.* **72** (2000) 1391.
25. P. Wasserscheid, and W. Keim: *Angew. Chem. Int. Ed.* **39** (2000) 3772.
26. J.D. Holbrey: *J. Chem. Soc. Dalton Trans.* (1999) 2133.
27. P. Bonhote, and A-P. Dias: *Inorg.Chem.* **35** (1996) 1168.
28. D.R. MacFarlane, P. Meakin, J. Sun, N. Amini, and M. Forsyth: *J. Phys. Chem. B* **103** (1999) 4164.
27. R.T. Carlin, H.C. DeLong, J. Fuller, and P.C. Trulove: *J. Electrochem. Soc.* **141**, L73 (1994).
28. A.J. Parker, and R. Alexander: *J. Am. Chem. Soc.* **90**, 3313 (1968).
29. A. J. Parker: *Chem. Rev.* **69**, 1 (1969).
30. Y. Marcus: *Ion Solvation* Wiley, New York (1985).
31. G. Gritzner: *Pure Appl. Chem.* **60**, 1743 (1988).
32. J. Gutknecht, and H. Schneider: *J. Stroka Inorg. Chem.* **17**, 3326 (1978).
33. I. Persson: *Pure Appl. Chem.* **58**, 1153 (1986).
34. A. Lewandowski, and I. Stepniak: *Phys. Chem. Chem. Phys.* **5**, 4215 (2003).