

COORDINATION COMPOUNDS

Effect of the Composition of an Acetonitrile–Dimethyl Sulfoxide Solvent on Stability of the Silver(I) Complexes with 18-Crown-6 Ether

A. N. Golikov, I. A. Kuz'mina, and V. A. Sharnin

Ivanovo State University of Chemical Technology, Ivanovo, Russia

E-mail: oxt703@isuct.ru

Received June 6, 2006

Abstract—The effect of the composition of an acetonitrile–dimethyl sulfoxide (AN–DMSO) mixed solvent on the stability of silver(I) complexes with 18-crown-6 ether (18C6) is studied by potentiometry. An insignificant increase in the stability of $[\text{Ag}18\text{C}6]^+$ (0.34 log units) is observed on going from acetonitrile to dimethyl sulfoxide. The effect of solvation on the shift of complex formation equilibrium is considered.

DOI: 10.1134/S0036023607110174

Interest in crown ethers as ligands is due to their unique property to bind metal ions with high selectivity, incorporating them into the inner cavity of their ring-shaped molecule. A large amount of study has been carried out to elucidate the effect of aqueous–organic and individual solvents on the stability of complexes of *d*-metal ions with macrocyclic ligands. However, there is no data on the effect of binary mixtures of nonaqueous solvents on the thermodynamics of complex formation reactions. Therefore, in this work we studied potentiometrically the effect of AN–DMSO solvent composition on the stability of 18-crown-6 ether (18C6) complexes with Ag^+ ions.

EXPERIMENTAL

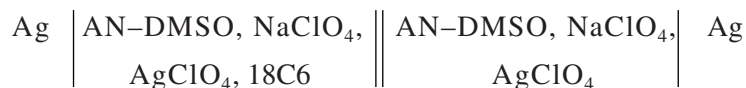
18-Crown-6 ether (reagent grade) was dried at room temperature in vacuo for several days. Sodium perchlorate (pure grade) was purified by triple recrystallization from distilled water and dried in vacuo at 70°C to constant weight. Silver perchlorate was synthesized by

adding dilute perchloric acid to silver carbonate, which was synthesized by mixing aqueous solutions of silver nitrate and sodium carbonate [1]. A solution of $\text{K}[\text{Ag}(\text{CN})_2]$, necessary for electrode coating, was prepared using a method proposed by us [2]. Dimethyl sulfoxide (reagent grade) and acetonitrile (high purity grade) were purified and dehydrated according to procedures described in work [3] and [4], respectively. Water in the solvents was determined according to the Fischer method. In the final products, water was 0.045 wt % for DMSO and 0.023 wt % for AN.

18-Crown-6 ether, NaClO_4 , and AgClO_4 were stored in weighed bottles closed with well-ground plugs and stored in a desiccator over P_2O_5 . The bottle with AgClO_4 was darkened.

Silver electrodes were produced by electrodeposition of silver on a platinum gauze from cyanide solutions according to work [2].

The stability constants of silver(I) complexes with 18C6 were determined potentiometrically using the galvanic cell



Two solutions were brought in contact through an unlubricated ground joint [5].

During an experiment, 20 mL of a solution of AgClO_4 (the initial Ag^+ concentration was $\sim 1 \times 10^{-2}$ mol/L) were titrated with a solution of 18C6 ($c_{18\text{C}6}^\circ \sim 0.25$ mol/L). The Ag^+ concentration in a reser-

voir of the reference electrode was the same as $c_{\text{Ag}^+}^\circ$ in the working cell. The standard solution was identical to the test solution in both the solvent composition and the content of the supporting salt. The solution ionic strength was adjusted by a 0.1 M solution of sodium perchlorate. The temperature in the reaction volume was 298.15 K.

Stability constants of silver(I) with 18C6 in AN–DMSO solvents at 298.15 K and $I = 0.1$ mol/L (NaClO_4)

x_{DMSO} , mole fraction	$\log K^\circ$
0	0.42 ± 0.05
0.1	0.54 ± 0.10
0.2	0.63 ± 0.08
0.4	0.66 ± 0.08
0.6	0.67 ± 0.08
0.8	0.74 ± 0.02
1.0	0.76 ± 0.02

The performance ability of the electrode system was verified by calibrating it in each composition of the AN–DMSO mixed solvent.

RESULTS AND DISCUSSION

In the mixed nonaqueous solvent studied system, the stability of Ag^+ complexes with 18-crown-6 ether increases insignificantly on going from AN to DMSO. The difference between the $\log K^\circ$ values reaches ~ 0.34 while the DMSO mole fraction in the mixture ranges from 0.0 to 1.0 (see table). The errors in $\log K^\circ$ are represented as standard root-mean-square deviations taking into account the Student test [6, 7] with a confidence probability of 0.95 for a set of experiments in each molar fraction of the mixed solvent, which was calculated by the formula

$$\delta = t \sqrt{\frac{\sum (\bar{n} - n_i)^2}{i(i-1)}},$$

where t is the Student coefficient, $\bar{n}$ is the mean value, n_i is the current value, and i is the number of experiments in the set.

Presumably, a decrease in the stability of the complex in AN is predominantly due to the formation of

stable solvates between the solvent and ligand molecules, which is favored by the linear conformation of strongly polar AN molecules and the optimal distances between the donor atoms of the crown ether [8–10]. Addition of dimethyl sulfoxide destabilizes the solvation shell of the ligand, favoring an increase in the stability of $[\text{Ag}18\text{C}6]^+$. However, the Ag^+ ion is stabilized with increasing DMSO content in the binary solvent, which is due to the formation of rather stable solvates of silver(I) with DMSO [11, 12]. Therefore, the overall increase in the stability of the complex ions is not so significant as expected from the change in the solvate state of the ligand.

REFERENCES

1. M. Ignaczak and A. Grzejdzia, *Monatsh. Chem.* **115**, 943 (1984).
2. A. M. Yampol'skii and V. A. Il'in (Mashinostroenie, Leningrad, 1981) [in Russian].
3. A. Cassol, P. Pi Bernardo, and P. Zanonato, *J. Chem. Soc., Dalton Trans.* **657** (1987).
4. J. F. Coetzee, *Anal. Chem.* **34**, 1139 (1962).
5. *Handbook of Electrode Technology* (Orion Research, Cambridge (USA), 1982; Mir, Moscow, 1986).
6. D. Skoog and D. West, *Fundamentals of Analytical Chemistry* (Holt, Rinehart, Winston, New York, 1976; Mir, Moscow, 1979), Vol. 1.
7. K. Doerffel, *Statistik in der analytischen Chemie* (Deutscher Verlag fuer Grundstoffindustrie, Leipzig, 1990; Mir, Moscow, 1994).
8. R. L. Garrel, J. C. Smyth, F. R. Fronczek, et al., *J. Inclusion Phen.* **6**, 73 (1988).
9. P. D. J. Grootenhuys and P. A. Koolman, *J. Am. Chem. Soc.* **111** (24), 4046 (1989).
10. R. Fush, G.E. McGary, and J. L. Blumfield, *J. Am. Chem. Soc.* **83**, 4281 (1961).
11. I. A. Kuz'mina and V. A. Shormanov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **43** (4), 71 (2000).
12. I. A. Kuz'mina and V. A. Shormanov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **43** (5), 138 (2000).