STABILITY CONSTANT OF $Cr(DMSO)_6^{3+}$ AND $Fe(NCS)_6^{3-}$ OUTER-SPHERE COMPLEX

By

L. Ilcheva* and Zs. Szabó-Ákos

Department of General and Analytical Chemistry, Technical University, Budapest
Presented by Prof. Dr. E. Pungor

In the literature is no data available on $Cr(DMSO)_6^{3+}$ and $Fe(NCS)_6^{3-}$ outer-sphere stability constant. This paper deals with its determination by applying conductivity measurements.

Experimental

$Cr(DMSO)_6(NO_3)_3$ was obtained and purified according to the procedure given in (1, 2). The solution of $Fe(NCS)_6^{3-}$ was received by mixing the solutions of $Fe(NO_3)_3$ and KSCN in ratio Fe : SCN = 1 : 6 (3). The purple precipitate of $Cr(DMSO)_6Fe(NCS)_6$ was received, separated from the solution and carefully washed as described in (4). 6.10^{-4}M solubility of the outer-sphere complex $Cr(DMSO)_6Fe(NCS)_6$ determined by atomic absorption was found. The solutions of different concentrations of $Cr(DMSO)_6Fe(NCS)_6$ were carefully prepared by using conductivity water of low specific conductance ($1.93 \cdot 10^{-6}$ohm^{-1}cm^{-1}). The cell constant was 0.6185 as determined with standard potassium chloride solution. The measurements were carried out at 25 °C using water thermostate.

Results and discussion

The conductivity of $Cr(DMSO)_6Fe(NCS)_6$ solutions measured at different equivalent concentrations are shown in columns 1 and 2 of Table 1. We tried to work at equivalent concentration smaller than 3.10^{-4}, but probably due to the instability of $Fe(NCS)_6^{3+}$ the conductivity of the solution increased very much.

The mobility of the ions was determined by Onsager's equation:

$$\lambda = \lambda_0 - (a'\lambda_0 + b')C^{1/2} = \lambda_0 - sC^{1/2} \tag{1}$$

* Department of Analytical Chemistry, Chemico-Technological Institute, Sofia, Bulgaria

Table 1

$\sqrt{C} \cdot 10^3$	λ	α	$I \cdot 10^4$	$\lg \cdot K'$
1.73	484.0	0.8309	7.476	3.3891
1.64	489.9	0.8384	6.789	3.4076
1.55	497.1	0.8478	6.102	3.4229
1.50	500.0	0.8512	5.745	3.4376
1.40	510.0	0.8652	5.085	3.4407
1.34	512.0	0.8665	4.677	3.4701
1.28	518.0	0.8748	4.302	3.4762
1.20	526.0	0.8857	3.825	3.4825
1.09	533.5	0.8948	3.219	3.5170
0.95	548.9	0.9156	2.472	3.5262
0.84	556.0	0.9236	1.965	3.5785
0.77	565.7	0.9374	1.684	3.5519

where λ_0 is the zero concentration mobility; a' and b' at 25 °C for $Z = 3$ are 3.572 and 313.5, respectively; Z is charge carried by cation and anion; C is the concentration in gram equivalent per liter. Figure 1 shows the plot of λ against $C^{1/2}$. The deviation between theoretical Onsager line (line 1) and the experimental one can be entirely attributed to the outer-sphere $Cr(DMSO)_6^{3+}$

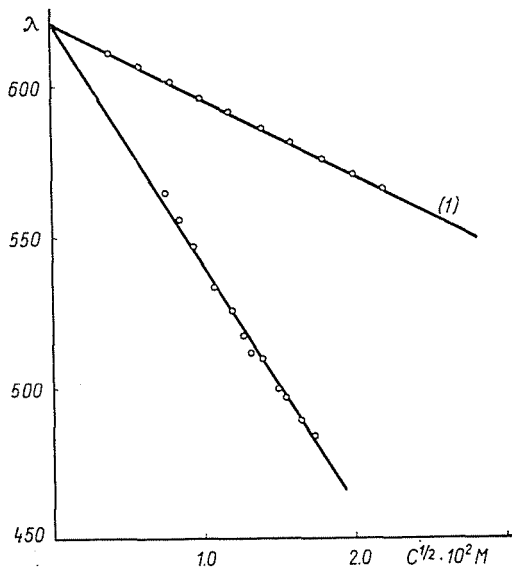*Fig. 1.* Onsager plots of $Cr(DMSO)_6$ $Fe(NCS)_6$ in aqueous solutions at 25 °C; (line 1) is a theoretical Onsager line

and $Fe(NCS)_6^{3-}$ interaction. Its outer-sphere stability constant is expressed by the equation:

$$K = \frac{[Cr\,(DMSO)_6\,Fe\,(NCS)_6]}{[Cr\,(DMSO)_6^{3+}]\,[\,Fe\,(NCS)_6^{3-}]} \qquad (2)$$

The fraction of free ions at equivalent concentration is obtained from:

$$\lambda = \alpha[\lambda_0 - s(\alpha C)^{1/2}] \qquad (3)$$

$$\alpha = \frac{\lambda}{\lambda_0 - s(\alpha C)^{1/2}} \qquad (4)$$

Substituting the Onsager slope calculated from Eq. (1) into Eq. (4), α can be calculated by successive approximation. The results are given in the third column of the Table. The fourth column shows values of $I = 3\,C\alpha$, whereas the last one gives lg K', which is a value not yet corrected for non-ideal behaviour of the ions. (I is the calculated ionic concentration of the solution). The outer-sphere stability constant referred to pure water as standard state can be determined by a graphic method according to:

$$\text{lg } K' = \text{lg } K - 9.162\,I^{1/2} \qquad (5)$$

If the ions of the solutions of different $Cr(DMSO)_6Fe(NCS)_6$ concentrations obey the Debye—Hückel limiting law the plot lg K' against $I^{1/2}$ will show a straight line with a slope 9.162. This plot is shown in Fig. 2, where the theoretical relationship is observed within an experimental error up to $I = 0.0006$. The outer-sphere stability constant referred to pure water as standard state was found to be lg $K = 3.671 \pm 0.005$. Almost the same value (lg $K = 3.66$) was obtained by extrapolating the plot of lg $K' + \dfrac{8\,A\,I^{1/2}}{1 + B\,a\,I^{1/2}}$
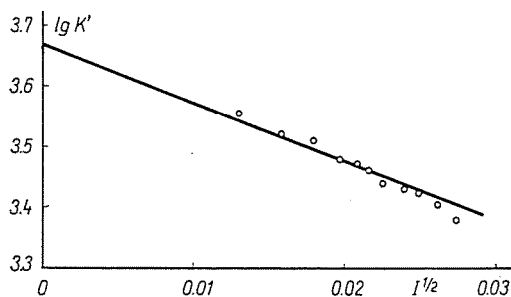

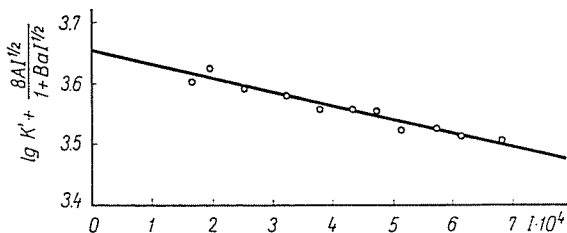*Fig. 2.* Extrapolation of lg K' data according to Eq. (5)

Fig. 3. Extrapolation of lg K' data according to equation:

$$\lg K' + \frac{8\,A\,I^{1/2}}{1 + B\,a\,I^{1/2}} = \lg K^\circ + 2\,C\,I$$

K° is the outer-sphere stability constant referring to pure water as standard state

against I at 7.5 Å. A and B are constants of the Debye—Hückel theory whereas a is the mean effective diameter of the ions of the solutions. K' is the calculated stability constant not corrected for non-ideal behaviour.

The theoretical stability constant of the outer-sphere complex $Cr(DMSO)_6Fe(NCS)_6$ in water can be calculated according to Bjerrum—Fuoss theory (5) with the following considerations: $Cr(DMSO)_6^{3+}$ is not spherical and its effective ionic radius must be less than 7 Å (6). The ionic radius of $Fe(NCS)_6^{3-}$ may be accepted as about 2.5 Å (6). If 7.5 Å is chosen as a contact distance of the outer-sphere complex $Cr(DMSO)_5Fe(NCS)_6$ its calculated theoretical stability constant was lg $K = 3.7$.

In final conclusion, the main reason for the outer-sphere interaction between $Cr(DMSO)_6^{3+}$ and $Fe(NCS)_6^{3-}$ on the analogy of $Co(en)_3^{3+}$ and $Fe(CN)_6^{3-}$ (7) as well as $Co(NH_3)_6^{3+}$ and Cl^- (8) appears to be the electrostatic attraction between the ions.

Summary

The stability constant of the outer-sphere complex $Cr(DMSO)_6Fe(NCS)_6$ has been determined in aqueous solution at 25 °C by conductometry. According to the results lg K = 3.671 ± 0.005.

References

1. COTTON, I. A.—FRANCIS, R.: J. Amer. Chem. Soc. **82**, 2986 (1960)
2. SZABÓ-ÁKOS, ZS.—ORSZÁGH, I.—BAZSA, GY.: Magyar Kémiai Folyóirat **81**, 53 (1975)
3. SZABÓ-ÁKOS, ZS.—SIMON, J.—BECK, M. T.: J. Thermal Anal. **8**, 155 (1975)
4. SZABÓ-ÁKOS, ZS.—SIMON, J.—BECK, M. T.: Hung. Sci. Instr. 1975/33, 25
5. BJERRUM, J.: Proc. 3. Symp. Coord. Chem., Akad. Kiadó Bp. 1975
6. CONWAY, B. E.: Elektrochemische Tabellen, GOVI Verl. GmbH., Pharm. Verl. Frankfurt-a. M., 1957
7. ILCHEVA, L.—BECK, M. T.: Magyar Kémiai Folyóirat **83**, 524 (1977)
8. ILCHEVA, L.—BECK, M. T.: Acta Chim. Acad. Sci. Hung. **97**, 45 (1978)

Dr. Liliana ILCHEVA }
Dr. Zsuzsanna SZABÓ-ÁKOS } H-1521 Hungary