

Diffusion of cobalt(II) ions in molten sulfates of alkali metals*

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Received 9 March 1976

The diffusion coefficient of cobalt(II) ions and their activation energy were determined using chronopotentiometry in the temperature interval 873—983 K, in molten ternary eutectic mixture $\text{Li}_2\text{SO}_4\text{—Na}_2\text{SO}_4\text{—K}_2\text{SO}_4$ (78.0:8.5:13.5 mole %) as well as in the mixture $\text{Li}_2\text{SO}_4\text{—K}_2\text{SO}_4$ (86.4:13.6 mole %). On the basis of diffusion measurements in these sulfate melts it can be concluded that in the mentioned temperature interval the complex particles Co(II) do not undergo any change either with the concentration or with the kind of alkali cations. This is in a good agreement with literature spectroscopic data on Co(II) in molten alkali sulfates.

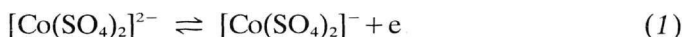
Диффузионный коэффициент ионов кобальта(II) и их энергия активации были определены хронопотенциометрическим методом в интервале температур 873—983 К в расплавленной тройной эвтектической смеси $\text{Li}_2\text{SO}_4\text{—Na}_2\text{SO}_4\text{—K}_2\text{SO}_4$ (78,0:8,5:13,5 мол. %), а также в смеси $\text{Li}_2\text{SO}_4\text{—K}_2\text{SO}_4$ (86,4:13,6 мол. %). На основании диффузионных измерений в выше приведенных сульфатных расплавах можно сделать вывод, что в упомянутом температурном интервале комплексные частицы Co(II) не подвергаются никаким изменениям, ни в зависимости от концентрации, ни от характера щелочного катиона. Это наблюдение находится в хорошем согласии с литературными данными для Co(II) в расплавленных сульфатах щелочных металлов.

At the burning of fuels containing sulfur and alkali elements in the internal combustion turbines the melts are generating containing alkali sulfates as the main components. The corrosion of materials in these sulfates leads to the formation of soluble corrosion products, which occur in the melt as complex ions.

The knowledge of the values of diffusion coefficients and the corresponding activation energies of these complexes can be significant in the study of the metal corrosion mechanism in sulfate melts.

* Based on a paper presented at the 1st Conference of Socialist Countries on Chemistry and Electrochemistry of Molten Salts, Smolenice, November 24—26, 1975.

Umland and *Voigt* [1] have suggested the metal corrosion mechanism under the participation of complex ions in the melt. The authors assume that Co(II) ions in the melts participate in the corrosion process forming the redox system



It is evident that the knowledge of the properties of molten alkali sulfates in the presence of soluble corrosion products, namely of Co(II), is significant for the understanding of the corrosion mechanism of the cobalt-containing alloys. *Matiašovský et al.* [2] dealt with this problem when determining the density, viscosity, and electrolytic conductivity of the ternary eutectic melt $\text{Li}_2\text{SO}_4\text{—Na}_2\text{SO}_4\text{—K}_2\text{SO}_4$ with the addition of LiOH , NiSO_4 , and CoSO_4 . The aim of these measurements was to determine the influence of these additions on the transport properties of the sulfate melts.

There is a lack of data on the diffusion of the soluble corrosion products in sulfate melts. Thus far only the paper by *Inman*, *Jovanovič*, and *White* [3] dealing with diffusion coefficient determination using chronopotentiometric method in the system $\text{Li}_2\text{SO}_4\text{—K}_2\text{SO}_4$ (86.4:13.6 mole %) at 873 K was published. The values of the diffusion coefficients were reported only for the temperature 873 K although the proper measurement was performed in the interval 873—1073 K.

It was found to be of interest to compare the diffusion coefficients of Co(II) ions and the corresponding activation energies in molten sulfate mixtures of various composition. For this purpose the systems $\text{Li}_2\text{SO}_4\text{—K}_2\text{SO}_4$ (86.4:13.6 mole %) and the ternary eutectic mixture $\text{Li}_2\text{SO}_4\text{—Na}_2\text{SO}_4\text{—K}_2\text{SO}_4$ (78.0:8.5:13.5 mole %) were chosen.

Chronopotentiometry and linear voltammetry were used as the methods for the Co(II) diffusion measurement. The voltammetry served above all to obtain a preliminary qualitative information on the purity of the basic electrolyte electrode reaction.

Experimental

The equipment for linear voltammetry was described in [4]. The fundamental equipment for the chronopotentiometry consisted of a stabilized source TESLA BS 275 and a resistance decade. The current flowing in the circuit was measured by means of DU 20 TESLA. The potential — time curves were recorded using the $x\text{—}y$ recorder BAK-4T. The transition time has been evaluated according to Kuwana [5]. The current impulse was set in such intervals in which the corresponding transition time values were within the range 0.4—2 s. These values enabled us to neglect the influence of the electric double layer charging and cylindrical diffusion on the measured values of the diffusion coefficients. The measurements were performed in the two-electrode arrangement. A Pt wire (\varnothing 0.5 mm,

($l \approx 10$ mm) sealed on one end into Pyrex was used as the cathode while the anode of the measuring cell consisted of the Pt crucible.

The melts were prepared from $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, Na_2SO_4 , K_2SO_4 , and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ of anal. grade purity (Lachema, Brno). After drying at 473 K for 10 h the mixture was placed into Pt crucible in an electric furnace of own construction. After melting at 873 K and mixing with Pt stirrer the melt was bubbled with argon using Pt tube. The temperature was measured by means of PtRh10—Pt thermocouple with the accuracy of ± 5 K. After measurement of the diffusion coefficient the melt was analyzed with respect to the Co(II) content.

Results and discussion

Using the method of cyclic voltammetry it was found that the electrode reaction of Co(II) in both measured systems is irreversible and the product is partly soluble. In this case it was not possible to determine the diffusion coefficient of Co(II) using the mentioned method. On the other hand, it has been found using voltammetry that the electrode reaction in the range 873—983 K is a one-step reaction and the Co(II) content in the electrolyte is not depleted even after 20 measurements.

The values of the Co(II) diffusion coefficients were determined using chronopotentiometry by the Sand equation

$$i\tau^{1/2} = 0.5 \pi^{1/2} nFAcD^{1/2} \quad (2)$$

where i is the current impulse in amps, τ the transition time in s, n is the number of the exchanged electrons, F is the Faraday constant, A is the surface of the measured electrode (m^2), c is the concentration of Co(II) in mol m^{-3} , and D is the diffusion coefficient ($\text{m}^2 \text{s}^{-1}$) of it. Eqn (2) was expressed for each electrode in the form

$$D = Ki^2\tau/c^2 \quad (3)$$

The value of the expression $i^2\tau$ was determined for various currents at each temperature. The measurements were repeated at the given current impulse 3—5 times. The product $i^2\tau$ was found to be independent of the current in both investigated systems, the reproducibility being ± 2 —10%. The density data necessary for determining the concentration (in mol m^{-3}) were taken from [2] in the case of the ternary eutectic mixture and from [6] for the binary system.

The values of the diffusion coefficient of Co(II) ions ($c = 2 \times 10^{-2} \text{ mol kg}^{-1}$) in the ternary sulfate eutectic mixture in the temperature range 893—983 K were found to be within the interval $(3.82$ — $7.74) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, and in the binary system in the temperature range 873—990 K within the interval $(2.80$ — $6.76) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. The dependence $\log D$ vs. $1/T$ is linear (Fig. 1). The activation energy of diffusion was determined by means of the least square method. Its value for Co(II) ions in the ternary eutectic mixture is $(5.5 \pm 0.2) \times 10^4 \text{ J mol}^{-1}$ and in the

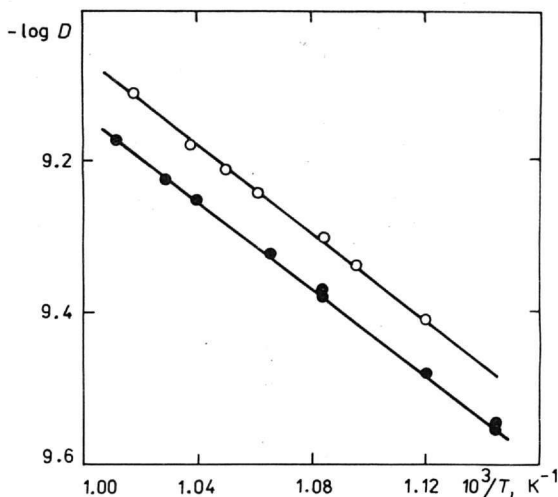


Fig. 1. Temperature dependence of $D_{\text{Co(II)}}$; $c_{\text{Co(II)}} = 2 \times 10^{-2} \text{ mol kg}^{-1}$.

○ $\text{Li}_2\text{SO}_4\text{—Na}_2\text{SO}_4\text{—K}_2\text{SO}_4$ (78.0: 8.5: 13.5 mole %);

● $\text{Li}_2\text{SO}_4\text{—K}_2\text{SO}_4$ (86.4: 13.6 mole %).

$\text{Li}_2\text{SO}_4\text{—K}_2\text{SO}_4$ melt $(5.6 \pm 0.2) \times 10^4 \text{ J mol}^{-1}$. A comparison of the determined values of $D_{\text{Co(II)}}$ with the literature data is possible only in the case of $\text{Li}_2\text{SO}_4\text{—K}_2\text{SO}_4$ mixture. The value of $D_{\text{Co(II)}}$ at 873 K reported in [3] is $2.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, this being in a good agreement with the value determined in this work. The activation energy of diffusion of Co(II) in the mixture $\text{Li}_2\text{SO}_4\text{—K}_2\text{SO}_4$ determined approximately from unpublished values [3, 11] in temperature range 900—970 K was found to be about $5.4 \times 10^4 \text{ J mol}^{-1}$.

It is well known that the activation energies for diffusion and viscosity should be coincident. In [2] the value for the activation energy of viscosity in the ternary eutectic mixture was found to be $(5.1 \pm 0.2) \times 10^4 \text{ J mol}^{-1}$. Our results for the activation energy of diffusion are somewhat higher, $(5.5 \pm 0.2) \times 10^4 \text{ J mol}^{-1}$. Similar values are reported by Mazochin and Schiavon [7] for the activation energy of diffusion and viscosity of Ag(I) in molten nitrates.

According to Angell and Moynihan [8] the scarcity of relevant data thus far makes impossible a theoretical interpretation of the diffusion of a complex particle in diluted solution, where the transport properties are determined by the properties of solvent. The formation of a stable complex should be expressed in the preexponential term of the transport equation. When determining the value of $D_{\text{Ta(V)}}$ in molten fluorides Senderoff and Mellors [9] assumed the existence of the highly coordinated particle $[\text{TaF}_7]^{2-}$ on the basis of the low values of diffusion coefficients and high values of the activation energy of diffusion found for the mentioned complex ion.

Considering the results of diffusion measurements of Co(II) in sulfate melts we can assume that in the investigated systems do not occur any changes of the complex particles. This conclusion is consistent with the results of the spectroscopic study of Co(II) ions in sulfate melts performed by Dickinson and Stone [10].

The authors stated that in the temperature range 823—1173 K the Co(II) ions are present in the form of $[\text{Co}(\text{O}_2\text{SO}_2)_4]^{6-}$ dodecaeders independently of the kind and concentration of alkali ions. This particle will evidently be formed also in the corrosion of cobalt-based alloys in molten alkali sulfates.

References

1. Umland, F. and Voigt, H. P., *Werkst. Korros.* **21**, 254 (1970).
2. Matiašovský, K., Daněk, V., Votava, I., and Balajka, J., *Chem. Prům.* **23**, 349 (1973).
3. Inman, D., Jovanović, D., and White, S. H., *J. Electroanal. Chem.* **43**, 37 (1973).
4. Leško, J., *Chem. Zvesti* **29**, 489 (1975).
5. Adams, R. N., *Electrochemistry at Solid Electrodes*. Dekker, New York, 1969.
6. Štěrba, M., *Thesis*. Institute of Mining and Metallurgy, Ostrava, 1975.
7. Mazochin, G. A. and Schiavon, G., *J. Electroanal. Chem.* **38**, 229 (1972).
8. Angell, C. A. and Moynihan, C. T., in *Molten Salts*. (Mamantov, G., Editor.) Dekker, New York, 1969.
9. Senderoff, S. and Mellors, G. W., *J. Electrochem. Soc.* **112**, 84 (1965).
10. Dickinson, J. R. and Stone, M. E., *Can. J. Chem.* **50**, 2946 (1972).
11. White, S. H., private communication.

Translated by M. Uhrová