Outer-sphere electron transfer in aqueous solutions of lithium hexacyanoferrates

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Electron transfer between the hexacyanoferrate anions in the presence of the Li^+ cations in aqueous solutions was studied by spectrophotometry. The results obtained were compared with the data for the K^+- and Me_4N^+-containing systems. The proposed explanation of the observed cationic catalysis effect of the thermal electron transfer in homogeneous and heterogeneous systems is based on the analysis of electron-transfer distances (*viz.*, contact distances between the anions) in the activated complexes.

Key words: hexacyanoferrates, cationic catalysis, electron transfer.

Processes involving electron transfer between reactants have a special place among numerous chemical reactions. These reactions can occur between cations and anions and also between likely charged ions. The specific feature of the processes in solutions involving two anions is the dependence of the reaction rate on the nature of counterions that do not directly participate in the reaction. This phenomenon was named "cationic catalysis." [1—9] Presently, the nature of cationic catalysis of the anion interaction is disputable. Similar effects were also observed in heterogeneous electron-transfer reactions only in the case of reduction of anions in solutions on negatively charged electrode surfaces.[10—12]

Electron transfer between the hexacyanoferrate(II) and hexacyanoferrate(III) anions catalyzed by the singly charged cations (Eq. (1)) is one of the most studied symmetrical activation-controlled processes.[3—5,8,9,13] It has been shown for the $K_3[Fe(CN)_6]$—$K_4[Fe(CN)_6]$ system that the activation energies of thermal and optical electron transfers coincide.[9] The experimental[9] and calculated[14] electron-transfer rate constants are also quantitatively consistent. The latter were calculated using the characteristics of the bands related to charge transfer between the hexacyanoferrate anions[9] and the contact distance between the anions in concentrated solutions. This value numerically coincides with the contact distance between the anions in solid hexacyanoferrates.[15]

$$[Fe(CN)_6]^{3-} + n\,M^+ + [Fe(CN)_6]^{4-} = \\ = [Fe(CN)_6]^{4-} + n\,M^+ + [Fe(CN)_6]^{3-} \qquad (1)$$

This correspondence suggests a relation between the "cationic catalysis" effect and a change in the contact distances between anions in solutions of supporting electrolytes when countercations are replaced. In this work, we studied by spectrophotometry the Li^+ system containing the hexacyanoferrate anions. The results obtained were compared with analogous data for the K^+- and Me_4N^+-containing systems,[13] and the relations of the spectroscopic and kinetic characteristics of the electron-transfer processes between the hexacyanoferrate anions were simulated in the framework of the Marcus—Hush theory.

Experimental

Solutions of lithium hexacyanoferrates with an overall lithium concentration of 2.2—5 mol L^{-1} were prepared from solutions containing $K_3[Fe(CN)_6]$ (0.3 mol L^{-1}), $K_4[Fe(CN)_6]$ (0.3 mol L^{-1}), and KOH (0.1 mol L^{-1}) by addition of excess solid $LiClO_4$. After the system was stirred for 30 min, the $KClO_4$ precipitate was filtered off. Solutions of lithium hexacyanoferrates with the overall lithium concentration above 5 mol L^{-1} were prepared by the addition of dried solid LiCl to the resulting solutions. The electronic absorption spectra of lithium- and potassium-containing solutions were recorded on a Cary 100 spectrophotometer (Varian) at 25 °C in quartz cells with an optical length of 1 cm.

Results and Discussion

Maxima of the charge-transfer bands between the hexacyanoferrate anions in the transient absorption spectra

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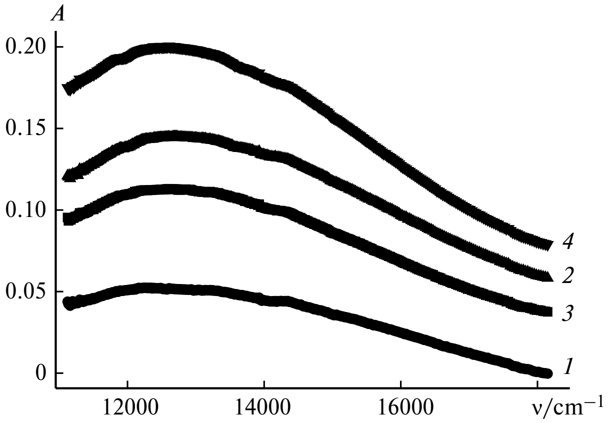

Fig. 1. Transient absorption spectra in the region of charge-transfer bands between the hexacyanoferrate anions at $C_{\rm Li}$ = 2.5 (*1*), 7.5 (*2*), 10 mol L^{-1} (*3*), and $C_{\rm K}$ = 2.2 mol L^{-1} (*4*).

for the Li^+ system appear at 12300 cm^{-1}, coinciding with the maxima for the K^+ system (λ = 12200 cm^{-1}) within the experimental error (±100 cm^{-1}). Some of the curves are presented in Fig. 1. The replacement of the K^+ cations by Li^+ is accompanied by an approximately twofold decrease in the absorbance of solutions. An increase in the concentration of Li^+ ions (*C*) in the system increases the absorbance (*A*) of the maximum of the band, and this relation is virtually linear (Fig. 2, points *2—7*) in the interval of the Li^+ ion concentrations from 2.2 to 5 mol L^{-1}.

We considered the crystal structures of hexacyanoferrates to interpret the results obtained. According to the previously published data,[16] in the $Li_3[Fe(CN)_6] \cdot 7H_2O$ structure (Fig. 3) the contact distances between the hexacyanoferrate anions (Fe—Fe distances) are 7.584 and 7.591 Å. In further calculations, the value of 7.6 Å was used, which is certainly longer than the distance between the anions in the $K_3[Fe(CN)_6]$ complex (~6.7 Å)[17] and shorter than the distance between the anions in the $(Me_4N)_2Cs[Fe(CN)_6]$ complex (~8.9 Å).[18] Therefore, the Fe—Fe distance in crystals correlates with the absorbance of solutions in absorption maxima. The latter, according to the previously published[13] and our data, decreases in the series K^+—Li^+—Me_4N^+.

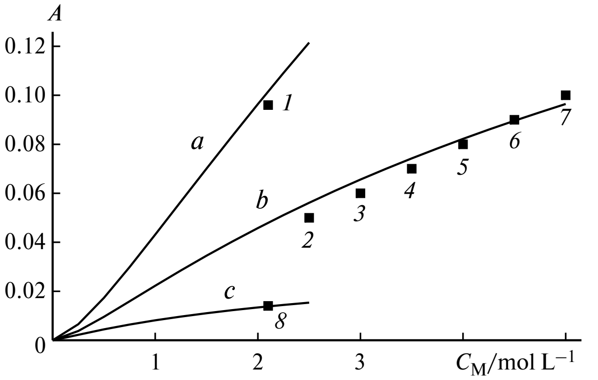

Fig. 2. Plots of the optical density *vs.* cation concentrations calculated by a known procedure[20] for the K^+- (*a*), Li^+- (*b*), and Me_4N^+-containing systems (*c*) at 60 (*a*, *c*) and 25 °C (*b*). The experimental values for the K^+- (*1*, see Ref. 13), Li^+- (*2—7*, obtained in this work), and Me_4N^+-containing systems (*8*, extrapolated by the previously published data[13]) are marked by figures.

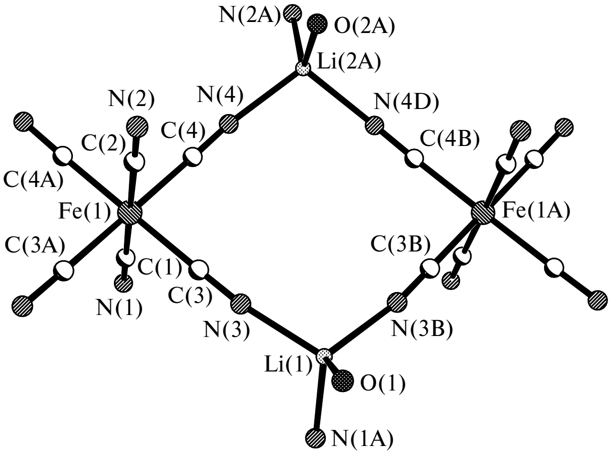

Fig. 3. Fragment of the $Li_3[Fe(CN)_6] \cdot 7H_2O$ structure.

Since the hexacyanoferrate anions demonstrate no tendency to specific hydration, the shortest distances between the anions in both crystals and concentrated solutions of electrolytes are mainly determined by the size of the countercations. This makes it possible to use the above Fe—Fe distances in the corresponding crystalline substances as the shortest distances between the anions in solutions for the simulation of the relation between the absorbance and the ionic strength of solution[19] by a known procedure[20] in a good approximation. According to the Bouguer—Lambert—Beer law,

$$A = \varepsilon C^* l$$

the relation of the optical density of solutions to the distance between the anions is determined by two main factors. On the one hand, the concentration of associates (C^*) containing two hexacyanoferrate anions calculated by the Fuoss equation[20] increases with an elongation of the distance between the anions and an increase in the cation concentration. On the other hand, an elongation of the distance between the anions decreases the molar absorptivity of the associates containing two anions due to a decrease in the overlap of orbitals. Since the experimental molar absorptivities are known only for the K^+ system,[9] we estimated these values for the Li^+ and Me_4N^+ systems. The best agreement between the calculated and experimental data in the framework of the model considered corresponds to a tenfold decrease in the molar absorptivity with the elongation of the distance between the anions by 1.3 Å. This value was used for plotting the calculated relations of the absorbance to the concentration of the cations of the supporting electrolyte (see Fig. 2). For concentrated solutions of the electrolytes, these plots (as well as the plots of the absorbance *vs.* ionic strength of solutions[19]) are close to linear. Therefore, the almost linear plots of the electron-transfer rate constants *vs.* ionic strength of solutions in the polycyanometallate systems[1] are not surprising.

Since the maxima and shapes of the charge-transfer bands for the K^+ and Li^+ systems virtually coincided, we can calculate the plot of the ratio of the electron-transfer rate constants in the K^+ and Li^+ systems *vs.* ionic strength of solutions (Fig. 4) using the data obtained in this work and simplifying the previously derived relationship[14]:

$$k_K/k_{Li} = A_K d_{Li}^2/(A_{Li} d_K^2),$$

where A_K and A_{Li} are the optical densities; d_K and d_{Li} are the Fe—Fe distances for the corresponding systems.

A comparison of this plot with the experimental kinetic data[3,5] obtained by NMR shows that the calculated values are slightly overestimated but the differences are comparable with the error of measurement of the kinetic and optical parameters. According to the calculations, the short-wave shifts of the band maximum for the Li^+ system compared to the K^+ system by 230 cm^{-1} (at low ionic strength see Fig. 4, point *1*) and more than by 80 cm^{-1} (at high ionic strength see Fig. 4, point *2*) are equivalent to the observed ratio of constants.

The published data[21] indicate that an increase in the contact distance between the anions should decrease the reorganization energy of the solvent and, hence, the long-wave shift of maxima of the charge-transfer bands. In fact, the replacement of the K^+ ions by Me_4N^+ results in this shift,[13] which causes, in particular, a higher electron-transfer rate in the Me_4N^+ system than that in the K^+ system.[1] However, the calculated[21] value of the reorganization energy of the solvent in the Li^+ system and the value determined from the spectroscopic data differ by ~0.15 eV. The increase in the reorganization energy of the system over the value predicted by the theory can be explained by a contribution to the total reorganization of the additional component caused by the reorganization of the Li—N bonds (see Fig. 3). Similar bonds are absent from the K^+- and Me_4N^+-containing systems.

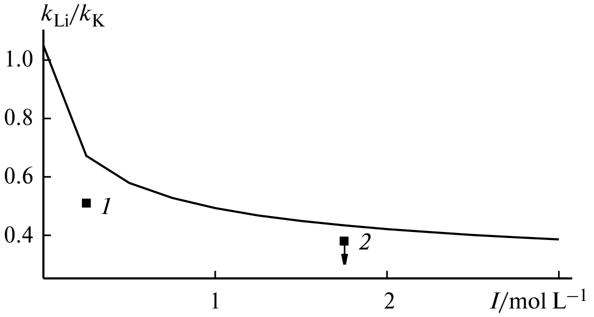

Fig. 4. Calculated relation of the ratio of electron transfer rate constants to the ionic strength of the solution. The experimental values are marked by points *1* (see Ref. 5) and *2* (see Ref. 3).

The plot presented in Fig. 4 enables the prediction of weakening of the cationic catalysis effect (at least comparing the Li^+- and K^+-containing systems) with a considerable dilution of solutions. It is difficult to verify this prediction experimentally for the homogeneous electron transfer in the ferro-ferricyanide system. At the same time, the heterogeneous electron transfer at considerable deviations from equilibrium (overvoltages of 1—2 V)[22] can be studied experimentally exactly for solutions with a low (<0.01) ionic strength. Under these conditions, diffusion restrictions are virtually absent, because the process is sharply inhibited because of the repulsion of the reactant by the negatively charged electrode.

The plot of the ratio of the heterogeneous reduction rate of the hexacyanoferrate anion in solutions containing the Li^+ and K^+ cations (1 mmol L^{-1} each) *vs.* electrode potential was calculated by the previously published data[22] and is presented in Fig. 5. When the potential shifts toward more negative values (*i.e.*, with an increase in the negative charge of the electrode), this ratio decreases from 0.6 to 0.3—0.4 and then remains unchanged. At first sight, these results contradict the above conclusions. However, substantial differences in the structures of the reaction layers for the homogeneous and heterogeneous electron transfers should be taken into account. In the latter case, the transfer distance is determined only by a possibility of the approach of the single anion-reactant to the electrode surface and, therefore, the probability of the formation of the reaction center (anolog of the reaction pair in the homogeneous reaction) is independent of the cation nature.

At the same time, the cation size is a factor affecting the configuration of the reaction center. For example, at high negative charges of the electrode, the coverage of the

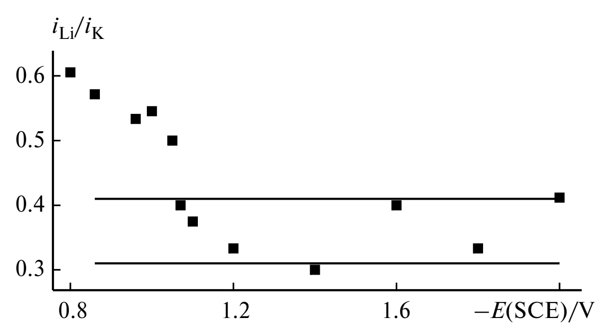

Fig. 5. Ratios of the reduction rates of the hexacyanoferrate anion on a mercury dropping electrode in solutions containing the Li^+ (i_{Li}) and K^+ (i_K) cations (1 mmol L^{-1} each) (see Ref. 22) at different potentials (E). The boundaries of the interval of the expected i_{Li}/i_K ratios are marked by horizontal lines (see text).

closest approach plane with cations is sufficiently high (to 10% of monolayer). Therefore, in the case of reactants with great size, the larger the cation size, the greater the maximum approach of the reactant. Using the hydrodynamic radii[23] for the estimation of the cation radii in dilute solutions, we obtain that this distance for Li^+ is longer by 0.5 Å than that in the case of K^+. The expected inhibition of the process on going from K^+ to Li^+ determined only by weakening of the overlap with an increase in the electron transfer distance corresponds to $i_{Li}/i_K = 0.41$ (to obtain this estimate, the plot of the overlap *vs*. distance was accepted the same as that for the homogeneous reaction). According to the data of quantum-chemical calculations,[24] in the Hg electrode—hexacyanoferrate system the overlap is weakened by an order of magnitude with the distance change by 1.0 Å. In this case, the expected i_{Li}/i_K value is 0.31. As can be seen from the data in Fig. 5, the ratio of the rates, being weakly dependent of the potential in the region of high negative charges, corresponds to this interval of values (horizontal lines in Fig. 5).

In our opinion, weakening of this plot at low negative charges (E is more positive than −1 V) is caused by the fact that the cation concentration in the reaction layer is not too high and many reaction centers are formed without steric hindrances, due to which the dependence on the cation nature is less pronounced.

The proposed interpretation agrees with the earlier qualitative explanations of the cationic catalysts effects based on the concept of formation of ion pairs in the reaction layer.[10]

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