The kinetics of KNO_3 sorption by crown-containing polymer

G. N. Al'tshuler and G. Yu. Shkurenko*

Institute of Carbon Materials Chemistry, Siberian Branch of the Russian Academy of Sciences,
18 Sovetsky prosp., 650099 Kemerovo, Russian Federation.
Fax: 007 (384 2) 36 4966. E-mail: sorbent@sorben.kemerovo.su

The kinetics of sorption of KNO_3 from aqueous solutions by a granulated polymer containing fragments of dibenzo-18-crown-6 was studied. Internal diffusion of the electrolyte in the polymer was shown to be a rate-limiting step of sorption of KNO_3. The effective coefficient of diffusion of the electrolyte in the polymer was calculated.

Key words: kinetics, polymer, dibenzo-18-crown-6, KNO_3, diffusion coefficient.

The ionic conductivity of the crown-containing gel polymers has been detected previously.[1] The thermodynamics of KNO_3 sorption from aqueous solutions by a granulated sorbent based on dibenzo-18-crown-6 (CE) has also been studied.[2] The electrolyte transfer from a solution to the polymeric phase was shown[2] to be described by the reaction

$$K^+ + NO_3^- + \overline{CE} \longrightarrow \overline{[KCE]^+} + \overline{NO_3^-} \qquad (1)$$

(the bar denotes that the component belongs to the sorbent phase). In this case the adsorption centers are energetically equivalent.[2]

In this work, the kinetics and mechanism of the process (1) have been considered. If the interaction with the solvent is not taken into account, then KNO_3 sorption from aqueous solution (1) can be represented as two independent processes: diffusion of the ions into the sorbent phase

$$K^+ + NO_3^- \longrightarrow \overline{K^+} + \overline{NO_3^-} \qquad (2)$$

and formation of the complex in the polymeric phase

$$\overline{K^+} + \overline{CE} = \overline{[KCE]^+}. \qquad (3)$$

The system studied in this work is anisotropic; for this system the diffusion flows and the rates of the direct and reverse chemical reactions of complex formation can have the same tensor dimensionality. In this connection one can suggest that the rate of chemical reaction and the rate of diffusion transfer mutually affect each other.

In the case of spherical symmetry, the slow diffusion accompanied by the chemical reaction is described[3] by a system of differential equations

$$\begin{cases} \dfrac{\partial C}{\partial t} = D\left(\dfrac{\partial^2 C}{\partial r^2} + \dfrac{2}{r}\dfrac{\partial C}{\partial r}\right) - \dfrac{\partial S}{\partial t}, \\ \dfrac{\partial S}{\partial t} = \lambda C - \mu S. \end{cases} \qquad (4)$$

where C is the concentration of the diffusing component inside the grain; S is the concentration of immobilized component; D is the diffusion coefficient; t is time; and λ and μ are the rate constants of the direct and reverse reactions, respectively.

In our case the kinetics of complex formation in the sorbent (3) are described by the equation

$$\frac{\partial \overline{m}_{KCE}}{\partial t} = \lambda' \overline{m}_{K^+} \cdot \overline{m}_{CE} - \mu \overline{m}_{KCE}. \qquad (5)$$

Since the kinetic measurements were carried out at low concentrations of the electrolyte in the sorbent ($\overline{m}_{CE} \approx$ const), the reaction of complex formation (3) can be pseudozero order with respect to the crown ether and first order with respect to free cations. Hence, the equation for the rate of the complex formation can be written as

$$\frac{\partial \overline{m}_{KCE}}{\partial t} = \lambda \overline{m}_{K^+} - \mu \overline{m}_{KCE}, \qquad (6)$$

where $\lambda = \lambda' \cdot$ const.

Equation (6) corresponds exactly to the second equation of system (4).

Experimental

The granulated cross-linked polymer synthesized according to the procedure described previously[4] by the polycondensation of the macrocyclic polyester of the dibenzo-18-crown-6 with formaldehyde in an emulsion medium in the presence of a strong electrolyte was used as sorbent. The sorbent containing carbon

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1549—1551, August, 1997.

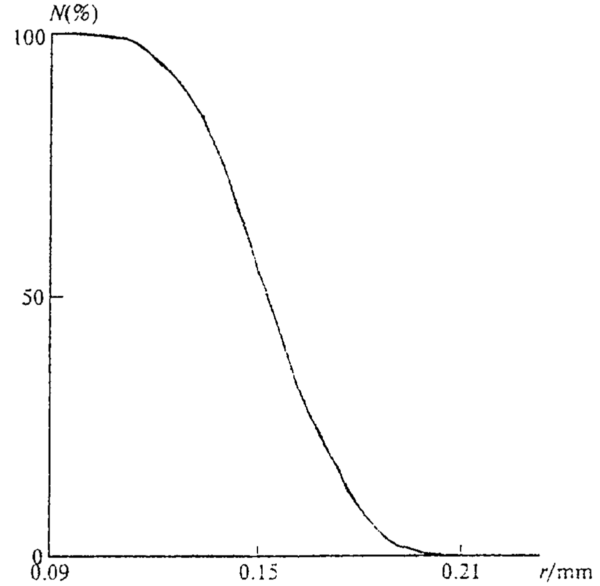

Fig. 1. The integral curve of the size distribution of spherical sorbent granules; N is the number of spherical particles of the sorbent with radius larger than r.

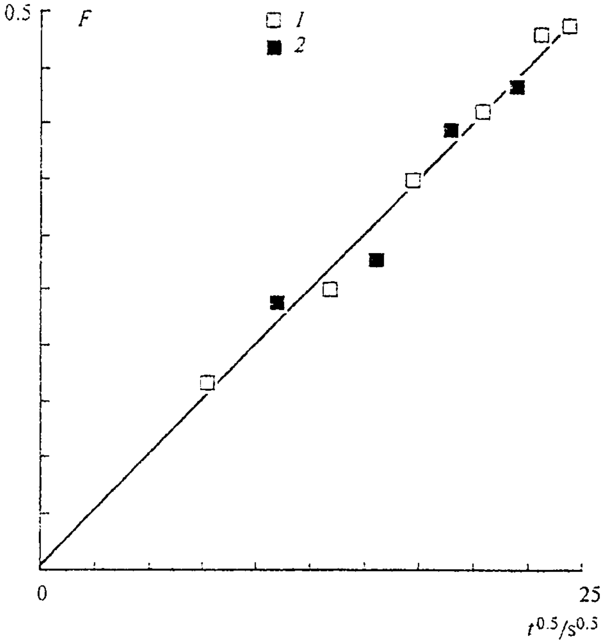

Fig. 2. The dependence of the degree of conversion (F) on time (t) for the sorption of the electrolyte by the granulated crown-containing sorbent from aqueous KNO_3 solutions with concentrations of 0.1 (*1*) and 0.05 mol L^{-1} (*2*).

(69.2%), hydrogen (6.8%), and crown ether (2.4 mol kg^{-1}) was obtained as spherical granules with controlled size. The integral curve of the size distribution of spherical sorbent granules in the polymeric sample prepared for investigation is shown in Fig. 1. The average diameter of the particles of the sorbent sample studied was calculated as the arithmetic mean of the sizes of 1000 spheres and was equal to 0.142 mm.

The kinetics of KNO_3 sorption were studied by the thin layer method[5] for the sorption from infinite volumes of KNO_3 solutions with concentrations of 0.1 mol L^{-1} and 0.05 mol L^{-1} at 298.15 K. The degree of conversion (F) was calculated by the formula

$$F = g_t/g, \tag{7}$$

where g_t is the amount of KNO_3 sorbed by the time t; g is the equilibrium capacity of the sorbent layer for the sorption of KNO_3 from solution.

The kinetic dependences of the overall process (1) of KNO_3 sorption from aqueous solutions by the sorbent based on the dibenzo-18-crown-6 at various concentrations of the solutions are shown in Fig. 2.

Results and Discussion

The dependence shown in Fig. 2 is described by a linear equation

$$F = (0.2\pm1.9)\cdot10^{-2} + [(20.0\pm1.0)\cdot10^{-1}]t^{0.5}. \tag{8}$$

The confidence intervals in Eq. (8) were calculated with a confidence probability of 0.95, and the correlation coefficient is equal to 0.99. The fact that function F linearly depends on $t^{0.5}$ and passes through the origin in accordance with the known criteria[6] indicates that KNO_3 sorption from aqueous solutions by a crown-containing sorbent is controlled by the diffusion of the electrolyte in the polymer ("gel").

The coefficient of KNO_3 diffusion was determined by solving the equation[7] for the intradiffusion ("gel") kinetics by the iteration method using the array of data shown in Fig. 2:

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{Dn^2\pi^2t}{r^2}\right), \tag{9}$$

where D is the diffusion coefficient of the electrolyte, $cm^2\ s^{-1}$; r is the radius of the sorbent grain, cm; and t is time, s.

The diffusion coefficient D calculated using Eq. (9) is equal to $2.25\cdot10^{-9}$ $cm^2\ s^{-1}$.

The solution of Eqs. (4) by the Laplace transform method[3] has been reported previously.[8] For an infinite volume of the system, the dependence of the degree of conversion on time in the course of slow diffusion accompanied by a chemical reaction is described by an equation that formally coincides with Eq. (9). However, the point is that in this case the D value calculated using Eq. (9) is the effective diffusion coefficient related to the true diffusion coefficient by the relationship

$$D_{\text{eff}} = \frac{D_{\text{true}}}{R+1}, \tag{10}$$

where R is the dimensionless value equal to the ratio of the rate constants of the direct and reverse reactions of the complex formation,[8] and $\lambda/\mu >> 1$. In this case, $D_{eff} << D_{true}$. Thus, in accordance with Gupta's theory,[8] the chemical reaction formally results in a decrease in the diffusion rate. Since in our case the λ/μ ratio is equal to the equilibrium constant (3), the $D \cdot \lambda/\mu$ value must correspond to the true diffusion coefficient. Since it is impossible to determine the equilibrium constant in the polymeric phase experimentally, one can use the data on the constants of the formation of the complex of 18-crown-6 with the K^+ cations in water[9] ($\lg K = 2.03$—2.15) for estimating the ratio between D_{eff} and D_{true}. The decrease in the diffusion mobility in the polymeric phase is consistent with decreasing entropy of the system[2] in the case of KNO_3 sorption from aqueous solutions by a granulated crown-containing sorbent.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-33328).

References

1. G. N. Al'tshuler and M. A. Khalyapina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1688 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1534 (Engl. Transl.)].
2. E. V. Ostapova and G. N. Al'tshuler, *Izv. Akad. Nauk, Ser. Khim.*, 1997, in press [*Russ. Chem. Bull.*, 1997, **47**, in press (Engl. Transl.)].
3. J. Crank, *The Mathematics of Diffusion*, Oxford Clarendon Press, London, 1956, 133.
4. G. N. Al'tshuler and E. V. Ostapova, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1025 [*Russ. Chem. Bull.*, 1995, **44**, 989 (Engl. Transl.)].
5. O. P. Fedoseeva, E. P. Cherneva, and N. N. Tunitskii, *Zh. Fiz. Khim.*, 1959, 33, 936 [*Russ. J. Phys. Chem.*, 1959, **33** (Engl. Transl.)].
6. N. R. Mechik and Yu. A. Leikin, *Zh. Fiz. Khim.*, 1983, **57**, 2531 [*Russ. J. Phys. Chem.*, 1983, **57** (Engl. Transl.)].
7. F. Gel'ferikh, in *Ionnyi obmen* [*Ionic Exchange*], Ed. Ya. M. Marinskii, Mir, Moscow, 1968, 281 (Russ. Transl.).
8. A. G. Gupta, *Indian J. Chem.*, 1970, **8**, 1026.
9. R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. J. Lamb, and J. J. Christensen, *Chem. Rev.*, 1985, **85**, 271.

Received April 15, 1997