# DIFFUSION OF ORGANIC CATIONS IN SULFOCATION EXCHANGERS

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## Abstract

## Full Text

## PHYSICAL CHEMISTRY

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# DIFFUSION OF ORGANIC CATIONS IN SULFOCATION EXCHANGERS

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Boyd and Soldano $^{(1,2)}$ investigated the rate of diffusion of inorganic ions in ion exchangers based on a copolymer of styrene and divinylbenzene (DVB). They established that the rate of diffusion of the ions studied in resins decreases, while the activation energy of diffusion increases as the DVB content in the ion exchangers increases. Similar investigations involving sorption of organic ions by ion exchangers have not been carried out.

In the present article we give the results of determinations of the diffusion rate of ions of organic amines (the dyes methylene blue and basic dark blue 2K*, codeine, tetramethylammonium, tetraethylammonium, and tetrabutylammonium) at various temperatures in KU-2 sulfocation exchangers with different DVB contents from 2 to 20%. The cation exchangers were taken in the H-form. The rate of sorption was determined in the initial periods of exchange (the sorbed amounts of organic ions did not exceed 10% of the equilibrium values) under static conditions. The exchange rate was monitored from the change in the concentration of the organic amine in the external solution in the system: H-form of the cation exchanger—solution of the salt of the organic amine. The kinetics of the sorption process in all experiments was intradiffusional. The diffusion coefficients of ions in the resin phase were calculated by a known method $^{(4)}$.

**Fig. 1.** Dependence between the activation energy of diffusion of organic ions in KU-2 sulfocation exchangers and the degree of crosslinking of the ion exchangers.
1 —methylene blue, 2 —basic dark blue 2K, 3 —codeine, 4 —tetramethylammonium, 5 —tetraethylammonium, 6 —tetrabutylammonium

**Table 1**

Diffusion coefficients (cm$^2$/sec) of methylene-blue ions in H-forms of KU-2 cation exchangers with different DVB contents, at different temperatures

| Temp., °C | 2% | 3% | 6% | 8% | 10% | 12% | 16% |
|---|---|---|---|---|---|---|---|
| 25 | $2.78 \cdot 10^{-10}$* | $2.78 \cdot 10^{-10}$ | $6.34 \cdot 10^{-11}$ | $7.37 \cdot 10^{-11}$ | $1.62 \cdot 10^{-11}$ | $5.03 \cdot 10^{-12}$ | $4.27 \cdot 10^{-12}$ |
| 40 | $1.44 \cdot 10^{-9}$ | $1.18 \cdot 10^{-9}$ | $1.66 \cdot 10^{-10}$ | $2.75 \cdot 10^{-10}$ | $5.60 \cdot 10^{-11}$ | $1.87 \cdot 10^{-11}$ | $1.32 \cdot 10^{-11}$ |
| 60 | $8.25 \cdot 10^{-9}$ | $5.00 \cdot 10^{-9}$ | $8.23 \cdot 10^{-10}$ | $4.92 \cdot 10^{-10}$ | $1.47 \cdot 10^{-10}$ | $3.94 \cdot 10^{-11}$ | $2.62 \cdot 10^{-11}$ |
| 75 | $7.35 \cdot 10^{-8}$ | $2.37 \cdot 10^{-8}$ | $2.68 \cdot 10^{-9}$ | | | | |

* At 23°.

Tables 1–3 present the results of calculations of the diffusion coefficients of the ions studied in the phase of sulfocation exchangers with different contents

* For the structural formulas of the dyes, see (3).

DVB at different temperatures. The diffusion coefficients of the most mobile tetramethylammonium ion are approximately two orders of magnitude smaller than the values found for diffusion in analogous ion exchangers of monovalent metal cations (1). The rate of diffusion in the exchangers of tetraalkylammonium ions decreases as the ion size increases. Noteworthy is the fact that diffusion in sulfocationites of dye ions and codeine proceeds at a very low rate, which is connected with the strong retarding action of the ion-exchanger matrix on the ions diffusing in it.

**Table 2**

Diffusion coefficients (cm$^2$/sec) of ions in the H-forms of KU-2 cation exchangers with different DVB contents at different temperatures

| DVB, % | Basic dark blue 2K | Basic dark blue 2K | Basic dark blue 2K |
|---|---|---|---|
| DVB, % | 16° | 33° | 50° |
| 2 | $8.18 \cdot 10^{-10}$ | $2.80 \cdot 10^{-9}$ | $2.31 \cdot 10^{-8}$ |
| 6 | $7.84 \cdot 10^{-11}$ | $2.94 \cdot 10^{-10}$ | $1.31 \cdot 10^{-9}$ |
| 10 | $3.44 \cdot 10^{-11}$ | $8.93 \cdot 10^{-11}$ | $3.56 \cdot 10^{-10}$ |
| 16 | $7.36 \cdot 10^{-12}$ | $1.84 \cdot 10^{-11}$ | $4.34 \cdot 10^{-11}$ |
| DVB, % | Codeine | Codeine | Codeine |
| DVB, % | 18° | 30° | 47° |
| 6 | $3.04 \cdot 10^{-9}$ | $7.53 \cdot 10^{-9}$ | $1.99 \cdot 10^{-8}$ |

| DVB, % | Basic dark blue 2K | Basic dark blue 2K | Basic dark blue 2K |
|---:|---:|---:|---:|
| 10 | $1.03 \cdot 10^{-9}$ | $1.73 \cdot 10^{-9}$ | $3.61 \cdot 10^{-9}$ |
| 16 | $2.59 \cdot 10^{-10}$ | $3.01 \cdot 10^{-10}$ | $3.91 \cdot 10^{-10}$ |
| 20 | $4.00 \cdot 10^{-11}$ | $4.45 \cdot 10^{-11}$ | $4.72 \cdot 10^{-11}$ |

**Table 3**

Diffusion coefficients (cm$^2$/sec) of tetraalkylammonium ions in the H-forms of KU-2 cation exchangers with different DVB contents at different temperatures

| Temp., °C | 6% DVB | 10% DVB | 16% DVB |
|---:|---:|---:|---:|
| Tetramethylammonium | Tetramethylammonium | Tetramethylammonium | Tetramethylammonium |
| 19 | $3.65 \cdot 10^{-8}$ | $2.30 \cdot 10^{-8}$ | $1.23 \cdot 10^{-8}$ |
| 31 | $4.06 \cdot 10^{-8}$ | $2.59 \cdot 10^{-8}$ | $1.68 \cdot 10^{-8}$ |
| 41 | $4.92 \cdot 10^{-8}$ | $2.90 \cdot 10^{-8}$ | $1.98 \cdot 10^{-8}$ |
| Tetraethylammonium | Tetraethylammonium | Tetraethylammonium | Tetraethylammonium |
| 18 | $3.33 \cdot 10^{-8}$ | $1.29 \cdot 10^{-8}$ | $4.43 \cdot 10^{-9}$ |
| 30 | $3.80 \cdot 10^{-8}$ | $1.62 \cdot 10^{-8}$ | $6.92 \cdot 10^{-9}$ |
| 40 | $3.95 \cdot 10^{-8}$ | $2.08 \cdot 10^{-8}$ | $9.40 \cdot 10^{-9}$ |
| Tetrabutylammonium | Tetrabutylammonium | Tetrabutylammonium | Tetrabutylammonium |
| 18 | $6.91 \cdot 10^{-9}$ | $1.34 \cdot 10^{-9}$ | $1.77 \cdot 10^{-10}$ |
| 30 | $1.02 \cdot 10^{-8}$ | $1.98 \cdot 10^{-9}$ | $3.51 \cdot 10^{-10}$ |
| 40 | $1.30 \cdot 10^{-8}$ | $3.07 \cdot 10^{-9}$ | $5.43 \cdot 10^{-10}$ |

From the temperature dependence of the diffusion rate, the activation energies of diffusion of the ions studied in sulfocationites with different DVB contents were calculated. The results of the calculations are shown in Fig. 1. As can be seen from these data, as the cross-linking of the resins increases, the activation energy of diffusion in them for tetraalkylammonium ions increases (as also in the diffusion of inorganic ions), while for dye ions and codeine it decreases. It is possible that such an anomalous dependence in the latter case is explained by a decrease in the distance between fixed groups, which leads to a decrease in the magnitude of the activated jump made by the diffusing ions in passing over the potential barrier. In the diffusion of tetraalkylammonium ions (as also in the diffusion of inorganic ions) in sulfocationites, the magnitude of the activation energy of diffusion is apparently influenced mainly by the decrease in the mobility of water molecules in the resins as the degree of their cross-linking increases, which leads to an increase in the work of hole formation in the diffusion medium. This circumstance, apparently, cannot play a decisive role in the diffusion in sulfocationites of dye ions and codeine, since our determination of the sorption isotherms of water vapor by sulfocationites in which the counterions are methylene blue ions indicates a weak interaction of water molecules with the ions in the resin.

Table 4 compares the values of the diffusion coefficients, activation energies, and entropy factors in the diffusion of the ions studied in sulfocationites with different DVB contents. The calculations were carried out by a known method (5). From the presented calculation results it is seen that, in the diffusion of tetraalkylammonium ions in resins, the decrease in the diffusion coefficients of the ions as the cross-linking of the resins increases is determined by an increase in the activation energy of diffusion and, accordingly, the entropy

Table 4

Entropy factor $d(e^{\Delta S^*/R})^{1/2}$, activation energy $\overline{E}$, and diffusion coefficients $\overline{D}$ of ions in sulfonic cation exchangers with different DVB contents

| DVB, % | $\overline{D}$, cm$^2$/s | $\overline{E}$, cal/mol | $d(e^{\Delta S^*/R})^{1/2}$, cm |
|---:|---:|---:|---:|
| Tetramethylammonium, | Tetramethylammonium, | Tetramethylammonium, | Tetramethylammonium, |
| $T = 292°$ K | $T = 292°$ K | $T = 292°$ K | $T = 292°$ K |
| 6 | $3.65 \cdot 10^{-8}$ | 1800 | $2.23 \cdot 10^{-10}$ |
| 10 | $2.30 \cdot 10^{-8}$ | 2500 | $3.22 \cdot 10^{-10}$ |
| 16 | $1.28 \cdot 10^{-8}$ | 3800 | $7.40 \cdot 10^{-10}$ |
| Tetraethylammonium, | Tetraethylammonium, | Tetraethylammonium, | Tetraethylammonium, |
| $T = 291°$ K | $T = 291°$ K | $T = 291°$ K | $T = 291°$ K |
| 6 | $3.33 \cdot 10^{-8}$ | 1800 | $2.12 \cdot 10^{-10}$ |
| 10 | $1.29 \cdot 10^{-8}$ | 3660 | $6.55 \cdot 10^{-10}$ |
| 16 | $4.43 \cdot 10^{-9}$ | 6040 | $2.95 \cdot 10^{-10}$ |
| Tetrabutylammonium, | Tetrabutylammonium, | Tetrabutylammonium, | Tetrabutylammonium, |
| $T = 291°$ K | $T = 291°$ K | $T = 291°$ K | $T = 291°$ K |
| 6 | $6.91 \cdot 10^{-9}$ | 4950 | $2.45 \cdot 10^{-9}$ |
| 10 | $1.34 \cdot 10^{-9}$ | 5850 | $1.38 \cdot 10^{-9}$ |
| 16 | $1.77 \cdot 10^{-10}$ | 9200 | $2.78 \cdot 10^{-9}$ |
| Methylene blue, | Methylene blue, | Methylene blue, | Methylene blue, |
| $T = 298°$ K | $T = 298°$ K | $T = 298°$ K | $T = 298°$ K |
| 2 | $2.78 \cdot 10^{-10}$ | 15000 | $1.21 \cdot 10^{-6}$ |
| 16 | $6.34 \cdot 10^{-11}$ | 13700 | $1.96 \cdot 10^{-7}$ |
| 10 | $1.62 \cdot 10^{-11}$ | 13400 | $7.70 \cdot 10^{-8}$ |
| 16 | $4.27 \cdot 10^{-12}$ | 11700 | $9.60 \cdot 10^{-9}$ |
| Basic dark blue | Basic dark blue | Basic dark blue | Basic dark blue |
| 2K, $T = 289°$ K | 2K, $T = 289°$ K | 2K, $T = 289°$ K | 2K, $T = 289°$ K |
| 2 | $8.18 \cdot 10^{-10}$ | 18300 | $5.09 \cdot 10^{-5}$ |
| 6 | $7.84 \cdot 10^{-11}$ | 14900 | $8.66 \cdot 10^{-7}$ |
| 10 | $3.44 \cdot 10^{-11}$ | 12600 | $7.75 \cdot 10^{-8}$ |
| 16 | $7.36 \cdot 10^{-12}$ | 9800 | $3.12 \cdot 10^{-9}$ |
| Choline, | Choline, | Choline, | Choline, |
| $T = 291°$ K | $T = 291°$ K | $T = 291°$ K | $T = 291°$ K |
| 6 | $3.04 \cdot 10^{-9}$ | 11000 | $1.80 \cdot 10^{-7}$ |
| 10 | $1.03 \cdot 10^{-9}$ | 7300 | $4.30 \cdot 10^{-9}$ |
| 16 | $2.59 \cdot 10^{-10}$ | 2500 | $2.98 \cdot 10^{-11}$ |

| DVB, % | $\overline{D}$, cm$^2$/s | $\overline{E}$, cal/mol | $d(e^{\Delta S^*/R})^{1/2}$, cm |
|---|---|---|---|
| 20 | $4.00 \cdot 10^{-11}$ | 1260 | $4.60 \cdot 10^{-12}$ |

factor changes very little. In the diffusion of dye ions and choline in sulfonic cation exchangers, a compensation effect occurs: the decrease in the activation energy of diffusion of ions in the resins as their degree of crosslinking increases is compensated by a considerable decrease in the entropy factor. Thus, the decrease in the diffusion rate of these ions with increasing DVB content in the ion exchangers is associated with a change in the entropy of activation.

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*Note: Figure translations are in progress. See original paper for figures.*