PHYSICAL CHEMISTRY

G. V. SAMSONOV and A. A. SELEZNEVA

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

G. V. SAMSONOV and A. A. SELEZNEVA

THERMODYNAMIC THEORY OF THE SORPTION OF IONS OF ORGANIC SUBSTANCES

(Presented by Academician A. N. Frumkin on 30 XI 1961)

In studying the sorption of organic substances by ion-exchange resins, it was established (1) that the constants of ionic exchange in the system quaternary ammonium bases—ammonium ion on sulfocation exchangers reach ten for bases with aliphatic radicals, and several tens when an aromatic radical is present in the sorbed ion. Further complication of the structure of ions of organic substances leads to greater selectivity in comparison with the sorption of sodium or hydrogen ions in the case, for example, of a tetracyclic structure of the radicals of ions absorbed by the sorbent (2). Obviously, this phenomenon is not only incompatible with, but even directly contradicts, the selective sorption of ions of small radii observed in the exchange of univalent metal ions (3). Indeed, an increase in the selectivity of sorption in organic substances is, as a rule, observed with an increase, and not with a decrease, in ion radii.

The study of the quantitative laws of sorption, as well as of the nature of the sorbate-sorbent bond, led to the development of ideas about the formation of additional bonds, in addition to Coulombic ones, between ions of organic substances and ion-exchange resins (4–6). Such additional interaction may have the character of the formation of both van der Waals and hydrogen (or other type) bonds.

From the thermodynamic point of view, the magnitude of the ionic-exchange constant of univalent ions may be determined by the enthalpy or entropy factor, or by both factors jointly:

$$\Delta\Phi^0 = -RT\ln K, \qquad K = \frac{\bar{a}_1 a_2}{a_2 \bar{a}_1}, \qquad \Delta\Phi^0 = \Delta H^0 - T\Delta S^0, \tag{1}$$

where a_1, a_2 are the activities of the ions in solution; $\bar{a}_1, \bar{a}_2$ are the activities of the ions in the ion-exchanger phase; K is the ionic-exchange constant; $\Delta\Phi^0$ is the standard free energy; ΔH^0 is the standard thermodynamic enthalpy; ΔS^0 is the entropy of ionic exchange.

Since the ionic-exchange constant in the system organic ion—sodium, organic ion—hydrogen (or in other analogous systems) varies within the interval 1-1000, the standard thermodynamic potential of ionic exchange is 0-4000 cal/g-equiv. Thus, systems can be divided into slightly selective ones with a value of $\Delta\Phi^0$ not exceeding 1000-1400 cal/g-equiv ($K = 1$–10), systems with increased selectivity, for which these values lie in the interval 1400-2800 cal/g-equiv ($K = 10$–100), and systems with high sorption selectivity ($\Delta\Phi^0 = 2800$–4000 cal/g-equiv, K 100–1000).

Let us consider possible variants of sorption selectivity determined by a change in enthalpy (energy effect). In accordance with the above, the enthalpy factor (or energy factor, since the system is at constant p and V) of the selective absorption of ions of organic substances must be determined by an additional, but not Coulombic,

interaction of the ion with the ion exchanger. In this connection it should be borne in mind that the energy of the additional bond must exceed the values of $\Delta\Phi^0$ given above, since the main Coulomb interaction decreases when metal ions are replaced by ions of organic substances. Thus, the energy of the additional bond in the selective absorption of ions of organic substances must exceed 1000-2000 cal/g-equiv, and sometimes also 4000 cal/g-equiv. It is clear that low selectivity of sorption may be associated with van der Waals interaction or with an interaction having a large bond energy. If, however, increased or high selectivity of sorption is considered, then the additional bond must be characterized only by a large magnitude of energy. For example, here one may expect the formation of an additional hydrogen bond ion—ion exchanger. Taking into account the absence of a universal possibility, for many ions of organic substances, of forming intermolecular additional bonds with large energy values, one should seek other possible causes determining the high selectivity of sorption of ions of organic substances in ion exchange.

A second factor of this kind is the entropic selectivity of sorption. It is known that the presence of a second electrovalent bond in the exchange of metal ions is manifested precisely in the entropic cause of selective absorption of divalent ions by ion exchangers as compared with monovalent ions ([7], [8]). It may be assumed that the occurrence of a second non-Coulomb bond in the sorption of ions of organic substances is also a cause of an increase in entropy in the system. A model of such a phenomenon should be the presence of a series of states for the sorbed ion with a lower energy level, corresponding to the absence of an additional bond, and with a series of levels caused by various types of additional interactions of the ion with the functional groups of ion exchangers. In this case, the standard entropy of ion exchange must be calculated as the result of permutations in coexisting states

$$\Delta S^0 = k \ln \frac{N!}{\prod N_i!}. \tag{2}$$

If in the system there is one state with the additional energy of sorption interaction E, then equation (2) takes the form

$$T\Delta S^0 = R\left[\ln\left(1+e^{-E/kT}\right)+\frac{\dfrac{E}{kT}e^{-E/kT}}{1+e^{-E/kT}}\right]. \tag{3}$$

For an interval of energies of additional interaction between 0 and several values of kT (which occurs in real systems), the value $T\Delta S^0$ does not differ very greatly from 400 cal/mole for room temperature.

Thus, the value $\Delta\Phi^0$, completely determined by the entropic term $T\Delta S^0$, for such systems is 300-400 cal/mole, which corresponds to low selectivity of sorption.

The presence of a series of states with energy levels differing by the value kT leads to an entropy of sorption calculated by the equation

$$T\Delta S^0 = R\left[\ln\sum_{i=0}^{n} e^{-i}+\sum_{i=0}^{n}\frac{i+1}{e^{i}\sum_{i=0}^{n} e^{-i}}-1\right], \tag{4}$$

where n is the number of additional bonds, i is the ordinal number of the additional bond.

This expression gives a value for $\Delta\Phi^0$ (determined only through $T\Delta S$) of the order of 300-1400 cal/mole for $n \sim 0$-10.

Thus, the presence of a series of discrete states for the sorbate may lead to increased selectivity in ion sorption. To interpret more significant entropic quantities of sorption, it is necessary to introduce other considerations, such as allowance for changes in the degree of swelling and also, possibly, cooperative changes in the polymeric sorbent during ion exchange.

Examples of two types of processes of selective absorption by ion-exchange resins of monovalent cations of organic substances, according to energy and entropy mechanisms, are the sorption of the antibiotics oxytetracycline ($C_{22}H_{24}O_9N_2$) by the sulfonic cation exchanger SBS-2 and erythromycin ($C_{37}H_{67}O_{13}N$) by the carboxyl cation exchanger KFUKh. In both cases the competing ions were sodium ions.

The calculation of $\Delta\Phi^0$ was carried out from equation (1), where the quantity K was understood, in accordance with previously developed methods for calculating activity coefficients in the resin phase (^{9}), as the expression

$$K = \int_0^1 K'\,dx,$$

where x is the mole fraction of one of the ions in the ion exchanger; $K' = m_1C_2/m_2C_1$; m_1, m_2 are the amounts of ions absorbed by the sorbent; C_1, C_2 are the concentrations of ions in solution.

Table 1

Thermodynamic functions of ion exchange

System	Sorbent	t, °C	$\Delta\Phi^0$, cal/g-eq	ΔH^0, cal/g-eq	$T\Delta S^0$, cal/g-eq
Terramycin—sodium	SBS-2	25.4	−2820	−3570	−750
Terramycin—sodium	SBS-2	35.4	−2830	−3570	−740
Terramycin—sodium	SBS-2	45.4	−2800	−3570	−770
Terramycin—sodium	SBS-2	55.4	−2830	−3570	−740
Erythromycin—sodium	KFUKh	10	−1710	2790	4500
Erythromycin—sodium	KFUKh	20	−2150	2790	4890
Erythromycin—sodium	KFUKh	35	−2260	2790	5050

Both oxytetracycline and erythromycin are absorbed by the corresponding sorbents with exceptional selectivity. At the same time, as is evident from Table 1, the selective absorption of oxytetracycline is a phenomenon primarily of an energetic order, where the additional interaction must have the character of hydrogen-bond formation between sorbate and sorbent, whereas the sorption of erythromycin is an entropic phenomenon.

Institute of Macromolecular Compounds
Academy of Sciences of the USSR

Received
9 XI 1961

CITED LITERATURE

1. T. R. E. Kressman, J. A. Kitchener, J. Chem. Soc., 1949, 1208.
2. G. V. Samsonov, L. V. Shuvalova et al., Kolloid. zhurn., 18, 474 (1956).
3. R. F. Nachod, W. J. Wood, J. Am. Chem. Soc., 67, 629 (1945).

4. N. A. Izmailov, S. Kh. Mushinskaya, DAN, 100, 101 (1955).

5. G. V. Samsonov, V. V. Vedeneeva, A. A. Selezneva, DAN, 125, 594 (1959).

6. G. V. Samsonov, N. P. Kuznetsova, DAN, 115, 351 (1957).

7. E. N. Cruickshark, P. Meares, Trans. Farad. Soc., 53, 1289 (1957).

8. O. D. Bonner, R. R. Pruett, J. Phys. Chem., 63, N 9, 1420 (1959).

9. W. J. Argersinger, A. W. Davidson, O. D. Bonner, Trans. Kansas Acad. Sci., 53, 404 (1950).

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