Moscow University
Chemistry Bulletin
Vol. 61, No. 3, pp. 46–49, 2006

Vestnik Moskovskogo
Universiteta. Khimiya
UDC 541.183.678.664

SORPTION OF ZWITTERIONIC DYES ON HYPERCROSSLINKED POLYSTYRENE FROM WATER SOLUTIONS

P. A. Kebets, Yu. V. Leonenko, M. V. Malozemov, and P. N. Nesterenko

The sorption of methyl orange and patented blue zwitterionic dyes from water solutions on hypercrosslinked polystyrene (HCPS) was investigated. It was shown that additives of strong electrolytes increased the dye sorption.

Hypercrosslinked polystyrene (HCPS) is an efficient sorbent for sorption of various polar organic substances from water solution, such as phenols [1, 2], aliphatic amines [3], dioxyphenols [4], and organic dyes [5]. Owing to the high affinity of HCPS for aromatic compounds [6], it can be used as matrix to prepare dynamically modified sorbents used in ion chromatography. Previously, dynamic modification by zwitterionic dye methyl orange (MO) was employed to prepare a highly selective ion exchanger for separation of the cations of alkali and alkaline-earth metals as well as for simultaneous separation of inorganic cations and anions [7].

Thus, development of sorbents by modifying the HCPS surface with zwitterionic molecules is a simple and convenient technique for preparing zwitterionic sorbents. Tentative conclusions about the stability and quantitative characteristics of the adsorbed layer and about the processes that occur on the sorbent surface can be drawn through studying adsorption isotherms [8]. In this work, we investigated the sorption of two zwitterionic dyes, methyl orange (MO) and patented blue (PB) on HCPS from water solutions with an additive of potassium chloride and without it.

EXPERIMENTAL

The initial solutions of dye with a concentration of 10 mmol/l were prepared by dissolving precisely weighed samples in distilled water. The solution ionic strength was changed using a solution of potassium chloride with a concentration of 1 mol/l, analytical grade (Reakhim, Moscow). The sorbent was hypercrosslinked polystyrene MN-200 (Purolote Int. Ltd, Great Britain), particle size 0.3–1.2 mm, specific surface 800–1000 m^2/g.

Procedure of Sorption under Static Conditions

Place accurately weighed samples (20 mg) of the sorbent in 10 ml test tubes, add the required amount of potassium chloride solution, an aqueous solution of the dye, and distilled water. Seal hermetically the test tubes and shake them until equilibrium sets in. After that, separate the solution from the sorbent by decanting and determine the dye concentration in the water phase on a UV-2201 spectrophotometer (Shimadzu, Japan). Calculate specific adsorption by the equation

$$a = (c_0 - c)\frac{V}{m_c},$$

where a is the dye specific adsorption, mmol/g; c_0 and c are the initial and equilibrium concentrations of the dye in solution, mmol/l; V is the volume of the aqueous solution, l; and m_s is the weight of the sorbent sample, g.

RESULTS AND DISCUSSION

MO and PB dyes are zwitterionic aromatic molecules containing sulfo- and amino groups (Fig. 1). Spectrophotometry is a convenient method for determining the dye concentration in solution here because of the intense absorption in the visible light region of the spectrum. The dye concentrations in solution were determined using absorption maxima in the spectral regions at 467 and 630.5 nm for MO and PB, respectively.

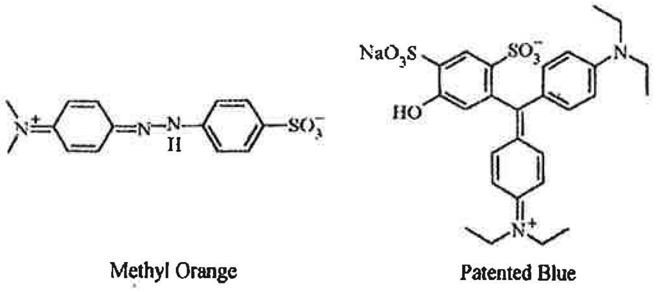

Fig. 1

Structural formulas of the dyes.

As has been shown previously [2], HCPS is characterized by the high rate of the setting in of sorption equilibrium. For example, for the sorption of zwitterionic dyes from an aqueous solution, equilibrium sets in after a few minutes. Chromatographic separation of ions on zwitterionic exchangers is usually performed using dilute solutions of strong electrolytes. For this reason, we studied the effect of the presence of a strong electrolyte in the dye solution on the dye adsorption. An increase in potassium chloride concentration in solution up to 0.1 mol/l results in a significant increase in the zwitterionic dyes adsorption on HCPS (Fig. 2). Note also that at higher dye concentrations in solution, an increase in the solution ionic strength may decrease their solubility due to the salting out effect.

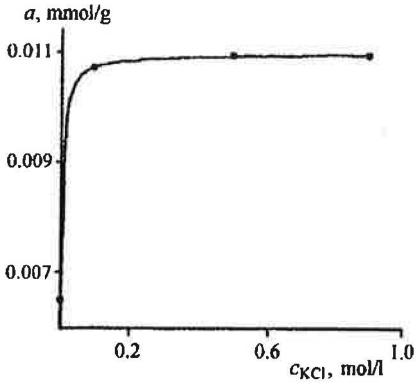

Fig. 2

Dependence of PB specific adsorption on HCPS from water solutions on potassium chloride concentration ($c_{PB} = 0.5$ mmol/l; $m_s = 0.020$ g, $V = 5$ ml).

It is well known that HCPS in water solutions exhibits anion exchange properties [9, 10]. For this reason, its surface is charged negatively. On the one hand, as ionic strength increases, the charges on the surface are screened and their contribution to the interaction with charged molecules decreases. On the other hand, an increase in ionic strength causes screening of the charged groups of the dye and the dye adsorption on the hydrophobic surface increases. It follows that an increase in the strong electrolyte concentration enhances the adsorption of zwitterionic dyes on HCPS. For this reason, the stability of the adsorbed layer under the conditions of ion chromatography will be higher when electrolyte solutions are used as eluants.

The dye adsorption isotherms were obtained both in the presence of potassium chloride in solution and without it (Fig. 3). Figures 1-3 show that the isotherms for PB and MO have a similar pattern. The isotherms are linear in the region of equilibrium concentrations of the dyes in an aqueous solution. The basic physicochemical parameters of adsorption (Table 1) were calculated by the least squares method using the linear form of the Langmuir equation:

$$\frac{1}{a} = \frac{1}{a_m} + \frac{1}{Dc},$$

where a is the dye specific adsorption, mmol/g; c is the dye equilibrium concentration in an aqueous solution, mmol/l; a_m is the sorbent sorption capacity, mmol/g; and D is the distribution coefficient, l/g.

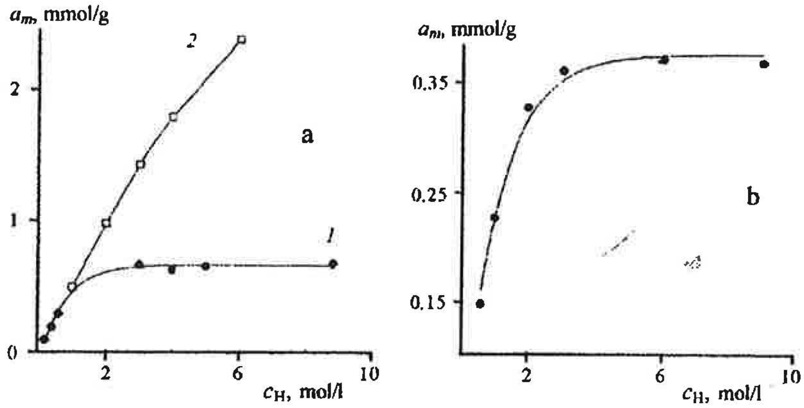

Fig. 3

Isotherms of the adsorption of MO (a) and PB (b) on HCPS from water solutions at c_{KCl}, M: *1*, 0 and *2*, 0.1 ($m_s = 0.020$ g, $V = 5$ ml).

Table 1

Physicochemical Parameters of the Sorption of Zwitterionic Dyes from Water Solutions

Sorbate	Phenol [11]	2-Nitrophenol [11]	PB	MO
a_m, mmol/g	—	—	0.29	0.57
D, l/g	1.32	21.7	33.33	45.45
K_i, l/g	4000	43400	66666	90900
$-\Delta G°$, kJ/mol	20.2	26.0	27.5	28.3

We used the procedure described in Ref. [1] to determine equilibrium sorption constants K_i and changes in the standard Gibbs energy (Table 1) using the following equations:

$$K_i = \frac{D}{V_a}, \quad \Delta G° = -RT \ln K_i,$$

where R is the universal gas constant, T is the standard temperature, V_a is the total specific volume of the sorbed substances (for HCPS (MN-200), about 0.5 ml/g [1]).

Our data allow us to conclude that the studied zwitterionic dyes have a stronger affinity for HCPS than the phenol derivatives we studied previously [11]. This can presumably be attributed to the higher hydrophobicity of molecules, because despite the presence of ionic groups, they contain more than one aromatic ring.

Our results indicate a high affinity of HCPS for aromatic zwitterionic dyes. Here, both the calculation sorption capacity and the observed sorption capacity with respect to MO are approximately twofold higher than that with respect to PB (Fig. 3, Table 1), which can be explained by the difference in the molecule size. To summarize, modification of the HCPS surface by the investigated zwitterionic dyes is a simple technique for the preparation of stable stationary phases for ion chromatography.

We are grateful to M. G. Kiseleva, Cand. Sci. (Chem.) (Food Institute, Russian Academy of Sciences) for patented blue dye, which was kindly provided by her.

REFERENCES

1. T.I. Tikhomirova, A.V. Khryashchevskii, V.I. Fadeeva, *et al.*, *Vestn. Mosk. Univ. Khimiya*, vol. 40, p. 365, 1999.
2. G.I. Tsysin, I.A. Kovalev, P.N. Nesterenko, *et al.*, *Sep. Sci. Technol.*, vol. 33, no. 1, p. 11, 2003.
3. T.I. Tikhomirova, P.N. Nesterenko, A.V. Khryashchevskii, and V.I. Fadeeva, *Zh. Fiz. Khim.*, vol. 75, no. 4, p. 617, 2001.
4. N.A. Penner, P.N. Nesterenko, and M.A. Kybalko, *Zh. Anal. Khim.*, vol. 56, no. 10, p. 1067, 2001.
5. V.A. Davankov, A.V. Volynskaya, and M.P. Tsyurupa, *Vysokomol. Soedin., Ser. B*, vol. 22, no. 10, p. 746, 1980.
6. N.A. Penner, P.N. Nesterenko, M.M. Ilyin, *et al.*, *Chromatographia*, vol. 50, p. 611, 1999.
7. M.G. Kiseleva, L.V. Radchenko, P.N. Nesterenko, *J. Chromatogr. A*, vol. 920, p. 79, 2001.
8. A.M. Koganovskii, N.A. Klimenko, and T.M. Levchenko, *Adsorption of Organic Substances from Water* (in Russian), Leningrad, 1990.
9. N.A. Penner and P.N. Nesterenko, *Anal. Commun.*, vol. 36, p. 199, 1999.
10. N.A. Penner and P.N. Nesterenko, *J. Chromatogr. A*, vol. 884, p. 41, 2000.
11. A.V. Khryashchevskii, *Candidate Sci. (Chem.) Dissertation*, Moscow, 1997.

14 April 2005

Department of Analytical Chemistry