Evaluation of the hydrophobicity of polyurethane foams

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A method for estimating the hydrophobicity of polyurethane foams in comparison with other sorbents is proposed using the distribution coefficient of pyrene between the sorbent and aqueous, acetonitrile–water and ethanol–water solutions as a measure of hydrophobicity.

The application of polyurethane foams (PUFs) for concentrating inorganic and organic compounds is relatively recent. Great achievements in this area are presented in a monograph[1] and reviews.[2–4] To describe the sorption of metal acidocomplexes, some mechanisms (a cation-chelated mechanism, ligand connection or exchange and extraction[1,5]) are proposed.

Our previous studies[5–11] allowed us to conclude that the mechanism of extraction by PUFs depends on both the nature of the sorbed compound (this is rather obvious) and the chemical structure of the monomer unit of the polymers: based on ethers (R^1–NH–CO–O–[R^2–O]$_n$–), esters (R^1–NH–CO–O–[CO–R^2–O]$_n$–) and their copolymers (R^1–NH–CO–O–[R^2O–CO–R^3–CO]$_n$–).

To evaluate the PUF hydrophobicity (and virtually the contribution of the extraction mechanism to sorption processes), we used pyrene as a model nonpolar compound. Previously, pyrene was used for determining the hydrophobicity of the internal region of n-β-octylglucoside micelles.[12] The distribution coefficients (D) of pyrene between the micelles and aqueous solutions in comparison with the D values for aqueous–organic systems served as a measure of hydrophobicity. This seems to be reasonable because the distribution coefficient is directly related to the free energy for the transfer of pyrene molecules between the phases.

Pyrene was adopted for solving the problem because, as we found previously, its distribution coefficient is independent of the aqueous phase acidity within the range from pH 14 to 6 M HCl and of the concentration of alkali metal cations regardless of the chemical nature of PUFs. Moreover, pyrene solutions exhibit intense luminescence. This fact can be used for determining the high distribution coefficients of pyrene because the limit of detection is rather low (1×10^{-4} μg ml^{-1} in aqueous solution).

There are several ways for estimating the hydrophobicity of substances, *i.e.* a versatile hydrophobicity scale is absent. A generally accepted way is to use the Hansh parameter, which is the logarithm of the distribution constants of substances in aqueous–organic systems.[13] n-Octanol is the most frequently used organic phase.

The aim of this work is to compare the hydrophobicity of polyurethane foams with that of other sorbents, which are applied for concentrating polycyclic aromatic hydrocarbons (silica modified with alkyl groups and active carbons) using the distribution coefficient of pyrene between the sorbent and aqueous, acetonitrile–water and ethanol–water solutions as a measure of hydrophobicity.

The following sorbents were used (the trade names are given in parentheses): polyurethane foams based on ethers (M-40, 5-30, 140), esters (2200, 35-08) and their copolymers (VP). The foams were obtained from NPO Polimersintez (Vladimir, Russia) and GPO Radical (Kiev, Ukraine). Diasorbs C_4, C_8, C_{16}, phenyl and carboxyl (particle sizes of 6, 10, 10, 10 and 6 μm, respectively, the amount of carbon at the surface was 6.0, 10.2, 14.6, 10 and 0.5%, respectively) from BioKhimMak (Russia), Amberlite XAD-8 from Serva (USA), microcrystalline cellulose for column chromatography from Reanal (Hungary), cellulose triacetate synthesised at the Department of Analytical Chemistry, M. V. Lomonosov Moscow State University and AX-21 active carbon were also used. The polyurethane foams were used as tablets (10 mm in height and 16 mm in diameter; the sample weight varied from 0.04 to 0.09 g depending on the PUF type) cut from commercial polymer sheets. The sorption was carried out in the batch mode. A tablet was immersed in the test solution and pressed out with a glass stick to remove air bubbles. In other cases, a sorbent sample (~0.06 g) was placed in a vessel with the test solution. The vessels were shaken using a shaker until the sorption equilibrium was attained (no longer than for 60 min for all of the sorbents). The equilibrium concentrations of pyrene were determined on a MPF-2A Hitachi spectrofluorimeter. The distribution coefficients were calculated from the following equation:

$$D = \frac{RV}{(100 - R)m},$$

where R is the degree of pyrene extraction (%), V is the volume of the pyrene solution (ml) and m is the weight of the sorbent (g).

The starting pyrene concentration (1×10^{-7} M) lies in the linear portion of the sorption isotherm.

Table 1 Distribution coefficients of pyrene (Pyr) on its sorption from aqueous, acetonitrile–water and ethanol–water solutions; $C_{Pyr} = 1\times10^{-7}$ M, $m_{sorbent} \approx 0.06$ g, $V = 25$ ml.

Sorbent	$\lg D \pm \frac{t_p S}{n^{1/2}}$ ($n = 5$, $P = 0.95$)		
	Solvent		
	H_2O	MeCN–H_2O (30:70)	EtOH–H_2O (20:80)
Diasorb carboxyl	2.6±0.1	—	—
Cellulose	2.6±0.1	—	—
Cellulose triacetate	2.9±0.1	—	—
Amberlite XAD-8	4.5±0.2	4.6±0.2	3.1±0.1
Diasorb C_4	4.6±0.2	2.2±0.1	2.8±0.1
Diasorb C_8	4.6±0.2	2.6±0.1	3.0±0.1
PUF M-40	4.6±0.3	5.3±0.2	4.9±0.2
PUF 2200	4.6±0.2	5.2±0.2	4.5±0.2
Diasorb C_{16}	4.8±0.2	4.7±0.2	3.6±0.2
Diasorb phenyl	4.8±0.2	2.5±0.1	3.5±0.1
PUF 5-30	4.8±0.1	5.0±0.2	4.5±0.2
PUF 35-08	4.9±0.2	5.0±0.2	4.6±0.2
Active carbon AX-21	5.0±0.2	5.5±0.2	5.3±0.2
PUF 140	5.2±0.2	—	—
PUF VP	5.2±0.2	5.1±0.2	4.7±0.2

Table 1 shows that the distribution coefficients of pyrene for its sorption from aqueous solutions by different polyurethane foams; Diasorbs C_4, C_8 and C_{16}; Amberlite XAD-8 and AX-21 active carbon are rather high ($\lg D \approx 5$) and do not differ significantly from each other. However, the D values are much greater than the distribution coefficients for less hydrophobic sorbents. To find the differences between the distribution coefficients of pyrene for the most hydrophobic sorbents, we examined the sorption from acetonitrile–water (30:70 v/v) and ethanol–water (20:80 v/v) solutions, in which the solubility of pyrene is higher than in water. Changes in the hydrophobicity series of sorbents (Table 1) for pyrene sorption from aqueous and aqueous–organic solutions are probably connected with the competition between the solvent and pyrene for the potential sorption centres at the surface.

Table 1 shows that all the polyurethane foams are characterised by approximately the same hydrophobicity and lie between Diasorb C_{16} and AX-21 active carbon.

The results obtained allow us to draw two interesting conclusions on the sorption of nonpolar compounds by polyurethane foams.

First, PUFs, regardless of the chemical structure of their monomer units, extract pyrene from aqueous solutions with virtually equal high efficiency ($\lg D \approx 5$; see Table 1). On the contrary, the sorption of polar compounds depends on the structure of monomer units of the polymer. In particular, the extraction of metal acidocomplexes,[5] phenols[10] and naphthols[11] with the use of PUFs based on ethers is more effective than that with PUFs based on esters. Copolymers of ethers and esters occupy an intermediate position.

Second, the distribution coefficients of two other less hydrophobic (in comparison with pyrene) polycyclic aromatic hydrocarbons, naphthalene and phenanthrene, in the sorption by polyurethane foams are virtually equal (the logarithms of their distribution coefficients are equal to 4.7 and 4.9, respectively). Thus, we can assume that the efficiency of the extraction of hydrophobic compounds (at least the polycyclic aromatic hydrocarbons examined) by polyurethane foams is determined by the hydrophobicity of the polymer rather than by their own hydrophobicity. Thus, the hydrophobicity of PUFs is reasonable and insignificantly depends on the chemical structure.

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