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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Adsorption of Phenol and Toluene from the Gas Phase and Aqueous Solutions on Cellulose

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Abstract—Adsorption of toluene and phenol from the gas phase and aqueous solutions on various celluloses was studied.

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Sorption from solutions on polymeric materials forms the basis of many physicochemical processes. In particular, these are processes associated with the vital activity of a living body, which depends on the capability to sorb through respiratory and digestive organs and through skin various substances that stimulate or prevent normal functioning of the body. Industrial processes also involve accumulation of certain compounds and utilization of by-products.

Polymeric sorbents exhibit certain specific features governed by their properties and structure. On the molecular level, these materials are mixtures of macromolecules of different lengths and irregular structure. The supramolecular structure of the polymers is characterized by the existence of areas significantly differing in the extent of macromolecular ordering. To a first approximation, sorbing amorphous regions and sorption-inactive crystallites can be distinguished [1].

Despite a large number of papers dealing with sorption properties of polymers, the mechanism of the interaction of polymers with mixtures of low-molecular-weight liquids (solutions or emulsions) is still poorly understood.

In this paper we consider sorption of two aromatic compounds differing in the nature of substituents (hydrophilic in phenol, hydrophobic in toluene) from the gas phase and aqueous solutions on various celluloses differing in the ratio of amorphous and crystalline phases.

EXPERIMENTAL

To obtain adsorption isotherms, we used the isothermal saturation method. The concentration of organic substances in water before (c_0) and after (c_e) sorption was determined by UV spectrophotometry. The adsorption value c_p was calculated by the equation

$$c_e = \frac{(c_0 - c_e)V}{m}, \quad (1)$$

where c_0 and c_e are the initial and equilibrium sorbate concentrations, respectively (M); V, solution volume (l); and m, adsorbent weight (g).

To determine the water retention, a wet cellulose sample was centrifuged at 8000 rpm for 15 min [2]. Such treatment yields a cellulose sample with the water content virtually equal to that obtained by sorption of water from the gas phase. The water-retaining power (%) was determined by the formula

$$W_{sp} = (m_2/m_1)\times 100\%, \quad (2)$$

where m_1 is the dry cellulose weight (g) and m_2, cellulose weight after centrifugation (g).

Adsorption of toluene and phenol from the gas phase was monitored gravimetrically. A cellulose sample was placed in a desiccator with the atmosphere saturated with toluene or phenol vapor. The equilibrium was attained within 17–35 days.

The physicochemical properties of the celluloses used as adsorbents and the maximal values of phenol

Table 1. Physicochemical properties of cellulose samples studied

Sample no.	Sample	Water retention, %	Moisture content of air-dry sample, %	Degree of crystallinity, %	Lignin content, %	Degree of polymerization	Adsorption from gas phase, mM	
							toluene	phenol
1	Flax cellulose, fiber	149.5	5.79	62	4.5	3000	0.414	1.548
2	Sulfite cellulose, fiber	145.4	5.88	67	0.1	800	0.389	1.186
3	Sulfite cellulose, powder, chemical disintegration	140.3	4.50	-	0.1	500	0.392	1.148
4	Sulfite cellulose, powder, mechanical disintegration	130.5	4.28	-	0.1	700	0.415	1.076
5	Microcrystalline cellulose (MCC)	129.6	4.59	73	0.0	250	0.403	1.100

and toluene adsorption form the gas phase are given in Table 1.

The cellulose samples in hand differ in the raw material, preparation procedure, and chemical composition. Flax cellulose was prepared from intermediate flax by the alkali–peroxide procedure. Sulfite wood pulp [GOST (State Standard) 3914–89] was the starting material for preparing sample nos. 3 and 4 by chemical and mechanical processing. Cotton microcrystalline cellulose met TU (Technical Specification) 64-11-129–92.

As seen from Table 1, adsorption of toluene from the gas phase is virtually independent of the kind of cellulose. Adsorption of phenol is 3–4 times higher than that of toluene and only slightly increases with an increase in the relative amount of the amorphous phase in cellulose.

The pattern of the sorption of organic compounds from water on cellulose is complex. This is due to the fact that both components of the binary solution water–organic component interact with cellulose. Sorption occurs by the displacement mechanism on the surface of pores of cellulose swollen in water.

The toluene and phenol adsorption isotherms that we obtained (Fig. 1) were described by the equation of the theory of volume filling of micropores [3–5]. Table 2 presents the parameters of the Dubinin–Radushkevich equation for sorption from solutions:

$$\ln c_p = \ln c_{sol} - (RT/E)^n [\ln (c_\infty/c_p)]^n , \quad (3)$$

where c_p and c_{sol} are the sorbate concentrations in the polymer (mol g^{-1}) and solution (M), respectively; c_∞, limiting adsorption (mol g^{-1}); c_s, limiting solubility of the sorbate in the given solvent (M); E, characteristic energy of adsorption; and n, coefficient showing by what factor the adsorption potential corresponding to the mean volume of sorbent pores is higher than the adsorption potential on the sorbent surface.

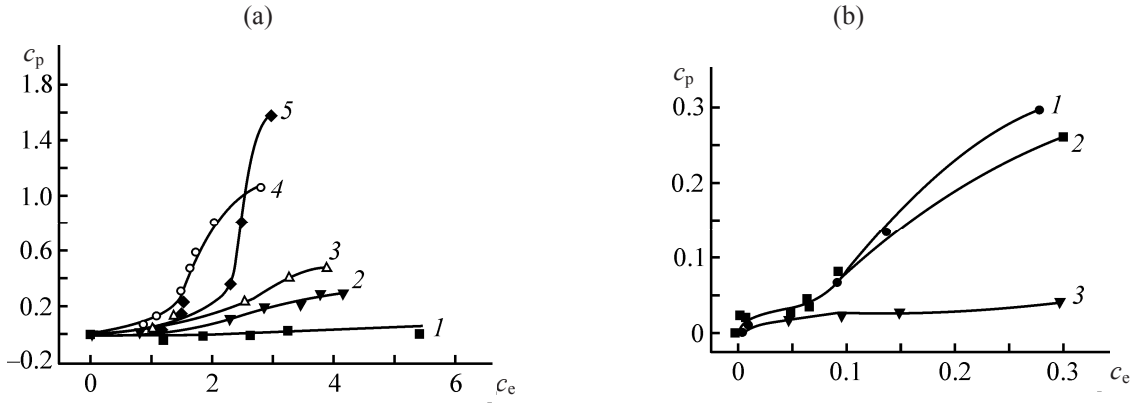

Fig. 1. Isotherms of adsorption (c_p, mmol g^{-1}) of (a) toluene and (b) phenol from water on celluloses. (c_e, mmol g^{-1}) Equilibrium concentration. Figures at curves are sample nos. in Table 1.

Table 2. Parameters of the equation of the theory of volume filling of micropores for adsorption of organic compounds from aqueous solution at 298 K

Sample no.	c_{sol}, mM	c_∞, mmol g^{-1}	n	E, kJ mol^{-1}	k
			Adsorption of toluene		
1	5.42	0.0098	2	1.216	0.999
2	5.42	0.300	2	2.399	0.994
3	5.42	0.600	2	1.924	0.999
4	5.42	1.959	2	2.443	0.993
5	5.42	2.534	2	1.983	0.984
			Adsorption of phenol		
1	924.45	3.251	2	12.257	0.972
2	924.45	1.301	2	13.368	0.995
3	924.45	0.200	2	15.799	0.993
4	924.45	0	–	–	–
5	924.45	0	–	–	–

The correlation coefficient k of the dependence $\ln c_p$–$[\ln (c_s/c_{sol})]^n$ shows that Eq. (3) reasonably well approximates the experimental data.

As can be seen (Figs. 1, 2), phenol and toluene show essentially different dependences of the adsorption on the kind of cellulose. Celluloses that well adsorb toluene poorly adsorb phenol, and vice versa. Therefore, it can be assumed that phenol and toluene are adsorbed on different sites of cellulose. Since the degrees of crystallinity were determined not for all the celluloses studied, the fraction of the amorphous phase was characterized by the water retention [2]. This integral quantity characterizing the water content of cellulose depends on the content of noncellulose components, degree of degradation of polymer macromolecules, and kind of supramolecular structure. To a greater extent, the water retention is proportional to the relative amount of the amorphous part, because the sorption of water and its interaction with hydroxy groups of cellulose occur specifically in the amorphous part.

The dependences of the limiting sorption of phenol and toluene from water on the water retention of celluloses (Fig. 2) show that the adsorption of phenol increases, and that of toluene decreases, with an increase in the relative amount of the amorphous part. In adsorption of toluene from water (Fig. 2a), the adsorption value can be both higher (cellulose nos. 4,

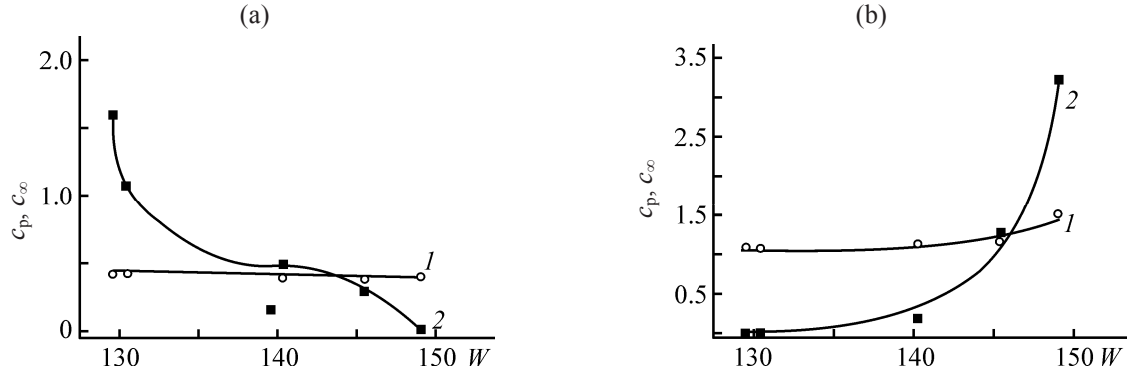

Fig. 2. (*1*) Adsorption c_p (mmol g^{-1}) of (a) toluene and (b) phenols from the gas phase and (*2*) c_∞ (mmol g^{-1}) limiting adsorption from water as functions of the water retention W of cellulose nos. 1–5 (Table 1).

5) and lower (cellulose no. 1), compared to the adsorption from the gas phase. Hence, the presence of water can both promote adsorption of toluene on cellulose (owing to diffusion) and prevent it.

An increase in toluene adsorption in the presence of water is observed on cellulose samples (nos. 4, 5) with the maximally destroyed initial supramolecular structure of the fiber, high degree of crystallinity, and well pronounced surface of the crystallites. Presumably, displacement of water molecules with toluene molecules from the crystallite surface is more favorable energetically.

A decrease in toluene adsorption in the presence of water is observed on the cellulose sample (no. 1) with the preserved fiber structure, in which the relative amount of the amorphous phase is larger than in microcrystalline cellulose. There is no interface between the amorphous and crystalline regions. Therefore, even in the presence of water the accessibility of the crystalline regions to toluene does not increase, and in the case of sample no. 1 it even decreases.

Phenol is not noticeably adsorbed from aqueous solutions on cellulose samples with a high degree of crystallinity (sample nos. 4, 5). For sample nos. 1–3, with an increase in the relative amount of the amorphous phase, the phenol adsorption increases. Hence, it can be assumed that the phenol adsorption occurs in the amorphous part of cellulose.

The characteristic energy of adsorption, calculated by Eq. (3), is different for adsorption of toluene and phenol. For the sorption of phenol, E = 12–16 kJ mol^{-1}, which corresponds to the adsorption in micropores. For the sorption of toluene, E is lower by an order of magnitude, 1–2 kJ mol^{-1}, which is more typical of surface sorption.

CONCLUSION

Phenol is sorbed in the amorphous part of cellulose, whereas the sorption of toluene involves interaction on the surface of crystallite regions of cellulose and depends on the accessibility of these regions to toluene.

REFERENCES

1. Tager, A.A., *Fizikokhimiya polimerov* (Physical Chemistry of Polymers), Moscow: Khimiya, 1978.
2. Jayme, G. and Roffael, E., *Papier*, 1970, vol. 24, no. 4, p. 181.
3. Dubinin, M.M. and Astakhov, V.A., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1971, no. 1, p. 11.
4. Grebennikov, S.F., Grebennikova, O.D., and Serpinskii, V.V., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1980, no. 2, p. 453.
5. Koganovskii, A.M., Klimenko, N.A., Levchenko, T.M., and Roda, I.G., *Adsorbtsiya organicheskikh veshchestv iz vody* (Adsorption of Organic Substances from Water), Leningrad: Khimiya, 1990.