ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 9, pp. 1524–1526. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © V.N. Pak, A.A. Kurova, S.M. Shilov, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 9, pp. 1487–1489.

Benzene Adsorption and Protonation in Perfluorosulfonic Membrane

V. N. Pak, A. A. Kurova, and S. M. Shilov

Herzen Russian State Pedagogical University, nab. r. Moiki 48; St. Petersburg, 191186 Russia
e-mail: pakviacheslav@mail.ru

Received April 4, 2012

Abstract—Benzene adsorption in a perfluorosulfonic membrane was performed through deep dehydration of the latter over the phosphoric anhydride. The subsequent UV irradiation is accompanied by a gradual transition of the benzene π-complexes in the protonated form $C_6H_7^+$ that allows us to consider the perfluorosulfonic membrane as a solid superacids. The photoexcitation on the absorption band of adsorbed carbonium ion causes its fluorescence in the region of 450–600 nm.

DOI: 10.1134/S1070363212090113

Protonation of benzene as a result of adsorption evidences the presence on the surface of the adsorbent of strong proton-donor sites [1,2]. The formation of the carbonium ion $C_6H_7^+$ on the surface was first discovered at the hard UV irradiation of benzene adsorbed on strong acidic surface of the silica–alumina catalyst purified in a high vacuum [1]; the formation of the cation was evidenced by the appearance of the absorption band with the maximum at 460 nm. A similar result was obtained after the adsorption of benzene on the surface of the titanium-containing silica gel, which has powerful proton-donor cites [2, 3]. In that case the absorption band maximum of the $C_6H_7^+$ cation was observed at 435 nm [2]. There is a reason to expect a possibility of protonation of benzene in perfluorosulfonic Nafion membranes, whose strong acidity is determined by the sulfonic groups fixed on the walls of the narrow channels and cavities of the fluorocarbon framework [4–6]. According to [5, 6], the membrane cavities have an effective diameter of about 4 nm and are connected by narrow channels of ~1 nm diameter. Additional protonation by the $-SO_3H$ group hydrogen is due to the polarizing effect of the framework and the high electric field gradients in the nanostructured space of the membrane. The possibility of optical detection of the benzene adsorption is provided by the high transparency of membrane over a wide wavelength range 200–800 nm.

In this paper we used perfluorosulfonic membrane MF-4SK of Russian production. The first experiments showed that a low threshold temperature stability of its porous structure, $T \leq 100°C$, prevented the adsorption of benzene [4] because of incomplete removal of water. A long dehydration of membrane with subsequent keeping in either the saturated vapor, or in liquid benzene, does not lead to its steady fixation. Exposing of the membrane to air leads to a complete benzene evaporation, as shown by the absence of its absorption in the UV spectral region. The cause preventing adsorption is the screening of sulfonic acid groups of the membrane by the tightly bound water molecules not removable within the permissible conditions of heat treatment.

To perform the adsorption in the environment free of residual water, the membrane, pre-dried at 100ºC, was placed in a hermetically stoppered flask over phosphorus pentoxide where also a beaker with benzene was placed. After keeping under these conditions for 24 h in the UV spectrum of the membrane exposed to air the characteristic absorption band of benzene was reliably detected which persisted over time (Fig. 1), indicating the formation of its adsorption π-complex with the hydrogen atom (proton) of sulfonic groups. It is interesting to estimate the degree of filling the inner surface of the membrane with benzene achieved in this way. Since the spectrum of adsorbed molecules is almost identical with the spectrum of liquid benzene, we adopt the extinction coefficient at the maximum of 255 nm of the most intense band of π–π * transition to be equal $\varepsilon_{255} = 230$ [8]. When the plate thickness is 0.25 mm and the optical density $D_{255} = 0.82$ (Fig. 1), the benzene

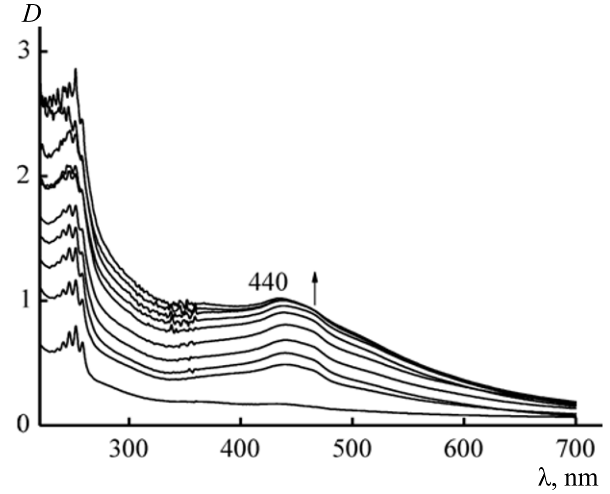

Fig. 1. The spectrum of benzene π-complex in the membrane (lower curve) and its successive changes at the UV-irradiation.

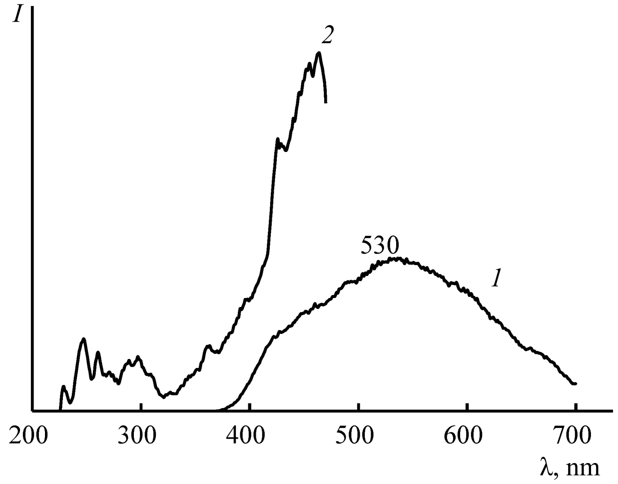

Fig. 2. The spectra of fluorescence (*1*) and its excitation (*2*) of the $C_6H_7^+$ ion in the membrane.

concentration is ~ 0.14 M, and its recalculation with accounting for the membrane weight (its density in the dry state is ~2 g cm^{-3} [4]) leads to ~0.07 mmol g^{-1}. The comparison of the measured value with the full content of sulfonic acid groups in the membrane [SO_3H] = 0.84 mmol g^{-1} [9, 10] indicates that benzene consumption in the process of adsorption is performed by only ~8% of the active sites. Such a low degree of surface coverage suggests that the benzene π-complexes are formed mainly on the walls of the narrow channels of the membrane with a high adsorption capacity. It is possible, therefore, that the value of ~8% reflects in the first approximation the ratio of surfaces of the cannels and cavities of nano-structured space of the Nafion membranes, unknown from the literature.

Irradiation of the membrane containing the adsorbed benzene with a full spectrum of mercury lamp SVD-120A is accompanied by the emergence and rapid increase in the intensity of the broad absorption band with a maximum at 440 nm (Fig. 1), corresponding to the formation of the protonated form $C_6H_7^+$ [1, 2]. The kinetics of the increase in the optical density at $\lambda = 440$ nm corresponds to the second order equation with a constant $k = 0.078$ s^{-1}. A large band width may be due to structural and energy inhomogeneity of the surface of membrane channels, which determines the difference in the degree of perturbation of the electronic structure of adsorbed ions. In contrast to the π-complex, the carbonium ion $C_6H_7^+$ (also called σ-complex) is a true chemical compound, in which the proton and hydrogen atom are arranged symmetrically on either side of the plane of the benzene ring [11,12]. Thus, the structure of the ion refers to the point group symmetry C_{2v}, and the observed band with $\lambda_{max} = 440$ nm in accordance with the well-known interpretation [11], corresponds to the $1a_2 \rightarrow 3b_1$ transition. Note that with increasing intensity of the characteristic band at $\lambda_{max} = 440$ nm the absorption in the UV spectral region becomes more complicated and significantly increases. These observations are apparently due to the short-wavelength transitions of carbonium ion ($1a_2 \rightarrow 2a_2$, $2b_1 \rightarrow 2a_2$ and others [11]) that define the band in the range 200–250 nm.

A characteristic feature of the $C_6H_7^+$ ion state in the membrane is its intrinsic fluorescence recorded as a broad, slightly structured band covering almost the entire visible region (Fig. 2). The luminescence excitation is mainly due to the quants of visible light in the main absorption band of $C_6H_7^+$ (Fig. 2). As in the case of the absorption spectra, a significant broadening of the luminescence band, apparently, is caused by a different degree of polarization of the ions adsorbed on the inhomogeneous surface of the membrane channels.

Thus, the benzene molecule acts as a luminescent-spectral tag, characterizing the surface of the so-called solid superacids [1, 2, 13], among which the perfluorosulfonic membrane may be ranked.

The UV spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The fluorescence spectra were obtained on a Fluorate-02-Panorma spectrophotometer.

REFERENCES

1. Terenin, A.N., *Kompleksoobrazovanie v katalize* (Complex Formation at the Catalysis), Moscow: Nauka, 1968, p. 27.
2. Pak, V.N., Kol'tsov, S.I., and Aleskovskii, V.B., *Zh. Obshch. Khim.*, 1975, vol. 45, no. 1, p. 234.
3. Pak, V.N., Tikhomirova, I.Yu., Burkat, T.M., and Lobov, B.I., *Zh. Fiz. Khim.*, 1999, vol. 73, no. 11, p. 2024.
4. Maurit, A.K. and Moore, R.B., *Chem. Rev.*, 2004, vol. 104, no. 10, p. 4535.
5. Gierke, T.D., Munn, G.E., and Wilson, F.C., *J. Polym. Sci.*, 1981, vol. 19, no. 11, p. 1687.
6. Heiter-Wirguin, C., *J. Membr. Sci.*, 1996, vol. 120, no. 1, p. 1.
7. Lage, L.G., Delgado, P.G., and Kawano, Y., *Eur. Polymer J.*, 2004, vol. 40, no. 7, p. 1309.
8. Pretsch, E., Buhlmann, P., and Affolter, C, *Structure Determination of Organic Compounds*, Moscow: Mir, 2006, p. 396.
9. Petushkov, A.A., Shilov, S.M., and Pak, V.N., *J. Lumin.*, 2006, vol. 116, nos. 1–2, p. 127.
10. Shilov, S.M., Gavronskaya, K.A., Borisov, A.N., and Pak, V.N., *Zh. Obshch. Khim.*, 2008, vol. 78, no. 9, p. 1544.
11. Muller, N., Pickett, L.W., and Mulliken, R.S., *J. Am. Chem. Soc.*, 1954, vol. 76, no. 10, p. 4770.
12. Garkusha, I., Fulara, J., Nagy, A., and Maier, J.P., *J. Am. Chem. Soc.*, 2010, vol. 132, no. 42, p. 14979.
13. Tanabe, K., *Solid Acids and Bases*, Moscow: Mir, 1973.