

Adsorption of hydrogen chloride on dehydrochlorinated poly(vinyl chloride)

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In this study the adsorption of hydrogen chloride on dehydrochlorinated poly(vinyl chloride) in the temperature range 10—50 °C and atmospheric pressure of hydrogen chloride has been investigated by volumetric method, the degree of dehydrochlorination of poly(vinyl chloride) being 96 %. The adsorption enthalpy found is equal to (-36.4 ± 4.3) kJ mol⁻¹. It has been ascertained that one adsorbed molecule of hydrogen chloride falls on eight and more —CH=CH— groups.

В работе объеметрическим методом изучается адсорбция хлористого водорода на дегидрохлорированном поливинилхлориде со степенью дегидрохлорирования 96 %, в диапазоне температур 10—50 °C при атмосферном давлении хлористого водорода. Найденная энтальпия адсорбции равна $(-36,4 \pm 4,3)$ кДж моль⁻¹. Было обнаружено, что одна адсорбированная молекула хлористого водорода приходится на 8 и более групп —CH=CH—.

The dehydrochlorination of poly(vinyl chloride) (PVC) is paid considerable attention, but there are only few papers dealing with the physicochemical properties of dehydrochlorinated poly(vinyl chloride) [1—6]. The dehydrochlorinated poly(vinyl chloride) (DPVC) adsorbs oxygen [1], halogens [4], exhibits stabilization effect on PVC [2] and has a lot of other interesting properties [1, 4]. In papers [1, 3], the adsorption of hydrogen chloride on DPVC was studied on qualitative level. In this study, we attempted to complete some hitherto published data concerning this process.

Experimental

Measuring procedure

For measuring the adsorption of HCl on DPVC, the volumetric method was used. A weighed amount of pulverized DPVC (30—50 mg) was poured into an ampoule which

was thermostatted accurate to ± 0.3 °C. Then this ampoule was joined to horizontal burette in which the volume of adsorbed HCl was measured. A movable mercury closure serving as indicator of adsorbed volume separated hydrogen chloride in the burette from environs. During measurements, the pressure of HCl was constant (atmospheric). The volume of adsorbed hydrogen chloride was measured after reaching the equilibrium state of adsorption at 17 °C.

Chemicals

DPVC was prepared from suspension PVC Slovinyl S-621 which was used without further purification. The dehydrochlorination was performed thermally at 230 °C in HCl atmosphere in a nonsealed glass ampoule of spherical shape of 5 cm diameter up to constant mass of the degraded polymer. As the ampoule was not closed, HCl split off from PVC could freely escape and thus formed a dehydrochlorination atmosphere. A constant mass of PVC was reached approximately after 2 h and the degree of dehydrochlorination determined from the mass loss of PVC was 96 %. The prepared DPVC was mat black. It was stored in air.

Results and discussion

The adsorption of HCl on DPVC was measured at five temperatures in the temperature range 10–50 °C. The volumes of HCl adsorbed on 1 g of DPVC at different temperatures are given in Table 1. These data have been evaluated as follows.

Table 1

Volume of hydrogen chloride adsorbed on 1 g of dehydrochlorinated PVC as a function of temperature

$\theta/^\circ\text{C}$	11.0	23.0	30.0	39.5	50.0
$v/(\text{cm}^3 \text{ g}^{-1})$	81.0	74.2	63.5	47.6	33.2

The adsorption of HCl on DPVC may be described by the following kinetic equation

$$\frac{da}{dt} = k_a p (a_m - a) - k_d a \quad (1)$$

where a is the instantaneous and a_m is the maximum possible degree of coverage and t , p , k_a , and k_d stand for time, HCl pressure, rate constant of adsorption, and rate constant of desorption, respectively.

If we consider that it holds $da/dt = 0$ for the investigated equilibrium states and include the constant pressure of HCl into the equilibrium constant of adsorption K , we can obtain from eqn (1)

$$K = \frac{v}{v_m - v}$$

because the degree of coverage of the surface of DPVC by hydrogen chloride at a certain temperature is proportional to the volume v of the adsorbed HCl and the maximum possible degree of coverage of the surface is proportional to the maximum possible volume of HCl v_m which can be adsorbed.

The adsorption enthalpy of HCl on DPVC and the value of v_m were determined from the integrated equation of reaction isobar

$$\ln K = \ln \frac{v}{v_m - v} = A - \frac{\Delta H}{RT} \quad (2)$$

where A , ΔH , R , and T are constant, adsorption enthalpy, gas constant, and temperature, respectively. The data given in Table 1 were treated by means of eqn (2) using the nonlinear least-squares method. The following values were obtained: $\Delta H = (-36.4 \pm 4.3) \text{ kJ mol}^{-1}$, $v_m = 113.1 \text{ cm}^3 \text{ g}^{-1}$. The dependence of $\ln K$ on $1/T$ is plotted in Fig. 1.

Up to the present, the mechanism of HCl adsorption on DPVC is not fully clear. In attempt to explain the autocatalytic effect of HCl on dehydrochlorination of PVC, several mechanisms were proposed for the interaction of HCl with the dehydrochlorinated sequences of PVC chain [4, 7, 8]. All these mechanisms call for addition or association of HCl with the unsaturated $-\text{CH}=\text{CH}-$ groups. The

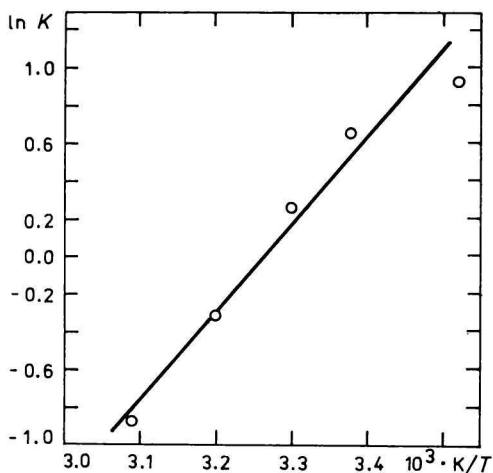


Fig. 1. Logarithm of equilibrium adsorption constant as a function of T^{-1} for $v_m = 113.1 \text{ cm}^3 \text{ g}^{-1}$.

chemical character of adsorption is also foreshadowed by the results presented in [1] according to which the bands of the conjugated C=C bonds in infrared spectra vanish owing to adsorption of HCl on DPVC. Our results, too, support the idea of chemical character of this process. It may be shown by the *Benson* method of group additivity [9] that the measured value of adsorption enthalpy is to be found in the interval of reaction enthalpies corresponding to addition of HCl to 1—3 conjugated C=C bonds. However, we cannot unambiguously create a conception of the character of active centre of chemisorption on the basis of the facts hitherto known.

Assuming the whole sample of PVC consists of the —CH=CH— groups, it results from the value of ν_m that eight double bonds at least fall on one adsorbed molecule of HCl. Therefore long polyene sequences are still present in DPVC even after establishment of adsorption equilibrium, which is also indicated by the fact that the colour of samples did not change during adsorption.

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