

# Adsorption of metal ions on dehydrochlorinated poly(vinyl chloride)

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*Dedicated to Professor Ing. A. Hrivík, CSc., in honour of his 60th birthday*

The adsorption of metal ions from their aqueous solutions on dehydrochlorinated poly(vinyl chloride) has been experimentally studied and tested by Langmuir's isotherm. It has been found that the amount of Hg(II) adsorbed increases with increasing temperature and the adsorption enthalpy of the process is  $-17 \text{ kJ mol}^{-1}$ . Adsorption on dehydrochlorinated PVC has been observed also in the case of Ag(I), Pb(II), and Fe(II). Ni(II), Zn(II), Pd(II), Ca(II), and Cu(II) exhibit no adsorption.

Проведено экспериментальное изучение и проверка с помощью изотермы Ленгмюра процесса адсорбции металлических ионов из водных растворов на дегидрохлорированном полихлорвиниле. Обнаружено, что количество адсорбированной ртути(II) возрастает при повышении температуры, и энтальпия адсорбции равна  $-17 \text{ кДж моль}^{-1}$ . Адсорбция на дегидрохлорированном ПВХ наблюдалась также в случае ионов Ag(I), Pb(II) и Fe(II). Не адсорбировались ионы Ni(II), Zn(II), Pd(II), Ca(II) и Cu(II).

Dehydrochlorinated poly(vinyl chloride) (DPVC) represents a polymer with a system of conjugated double bonds. It is a relatively less known substance because there are only a few papers devoted to the study of its chemical and physicochemical properties [1—7]. It has been found that the DPVC adsorbs oxygen [1], halogens [2], hydrogen chloride [1, 3, 4], exhibits stabilization effect on PVC [5] and has many other interesting properties [1, 2].

On the other hand, it is well known that ions of some metals, *e.g.* Ag, Cu, Hg, Pd, *etc.* are characterized by the ability of solutions of their simple salts (usually halides, nitrates or perchlorates) to react with olefins forming a metal—olefin complex [8—10]. Surprisingly, no experimental data are available in literature on interaction of metal ions with DPVC or with other solid polymers containing

double bonds. The aim of the present work is to follow the adsorption of some ions from their aqueous solutions on DPVC.

## Experimental

### *Materials*

DPVC was prepared from suspension poly(vinyl chloride) Neralit 702 (Czechoslovakia) which was used without any purification, according to the procedure described in [4]. The degree of dehydrochlorination determined from the mass loss was 96.0 %. Finally, DPVC was milled so that the maximal diameter of particles was 40  $\mu\text{m}$ . It was stored under air atmosphere.

The percentage of elements in DPVC is the following: C — 84.2 %, H — 5.0 %, Cl and N have not been found. In ESR it exhibits a singlet with  $g$  value of 2.0028.

### *Employed technique*

Adsorption equilibria are established by contacting aqueous solution of a metal ion with DPVC in a special shaken glass vessel which is thermostatted with accuracy of  $\pm 0.1$  °C. Adsorption equilibrium is reached in 20 min. The mass of used DPVC is 0.5 g and the volume of ion solution is 50  $\text{cm}^3$ . The adsorbed amount of ion,  $a$ , is calculated from the concentration difference of the solution before and after adsorption

$$a = (c_0 - c)V/m \quad (1)$$

where  $c_0$  and  $c$  are the concentrations of a metal ion in solution before and after adsorption, respectively,  $V$  is the volume of solution and  $m$  stands for the mass of DPVC.

Each experimental point is obtained from three parallel measurements. The limit error of  $a$  determination is 7 %.

### *Analytical procedures*

Hg(II), Cu(II), Ni(II), Ca(II), Zn(II), and Pb(II) are determined chelatometrically, Ag(I) by precipitation with NaCl and Fe(II) and Pd(II) photometrically according to the standard analytical procedures.

## Results and discussion

The following metal ions have been subjected to the adsorption on DPVC: Hg(II), Pd(II), Ni(II), Zn(II), Ca(II), Fe(II) in the form of chlorides and Ag(I) and Pb(II) in the form of nitrates. The adsorption of Hg(II) has been studied most in detail, at five temperatures in the range of 10—50 °C. The adsorption isotherms are shown in Fig. 1. Langmuir's isotherm fits better the experimental curves than

Freundlich's one. The former isotherm is given by

$$a = a_m \cdot \frac{K c}{1 + K c} \quad (2)$$

where  $a_m$  is the maximal amount of a metal ion adsorbed on DPVC and  $K$  is the equilibrium adsorption—desorption constant.

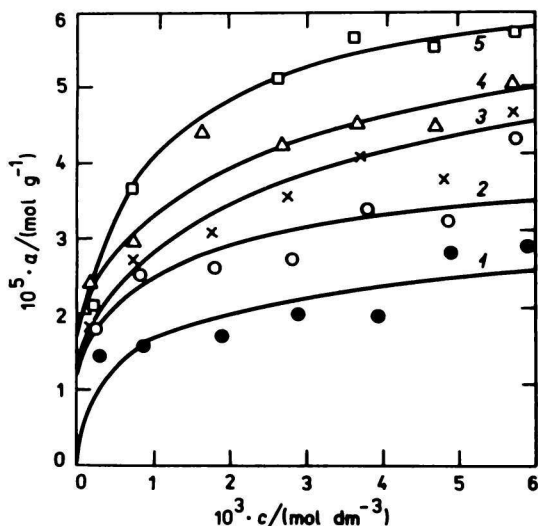


Fig. 1. Adsorption isotherms of Hg(II) on DPVC at various temperatures  $\theta/^\circ\text{C}$ : 1. 10; 2. 20; 3. 30; 4. 40; 5. 50.

The parameters  $a_m$  and  $K$  for different temperatures were calculated after linearization of eqn (2) by the least-squares method; they are listed in Table 1. As can be seen from Table 1 and also from Fig. 1, the amount of adsorbed Hg(II) increases with increasing temperature. The enthalpy of adsorption obtained from  $K$  values has been found to be  $-17 \text{ kJ mol}^{-1}$ . This value is within the range of adsorption enthalpies of olefins on metal salts [10].

Table 1

Parameters of Langmuir's isotherm for adsorption of Hg(II) on DPVC at various temperatures

$\theta/^\circ\text{C}$	10	20	30	40	50
$10^5 \cdot a_m/\text{mol g}^{-1}$	3.1	4.2	4.8	5.2	6.2
$K/(\text{dm}^3 \text{g}^{-1})$	4.8	6.1	7.2	12.3	10.0
Correlation coefficient	0.944	0.954	0.981	0.994	0.999

Comparison of adsorbed amounts of Hg(II) and Ag(I) at 30 °C is shown in Fig. 2. The adsorbed amount of Hg(II) on 1 g of DPVC is greater than that of Ag(I). The same relation between these ions occurs in adsorption of olefins on metal salts [10]. It has been also found that Fe(II) and Pb(II) adsorb on DPVC (Fig. 2). In the case of Fe(II), the adsorption is probably supported by the presence of carbonyl groups in DPVC, as it is known that Fe(II) forms carbonyl—olefin complex compounds [8]. There is no analogy in olefin—metal complexes for adsorption of Pb(II) on DPVC.

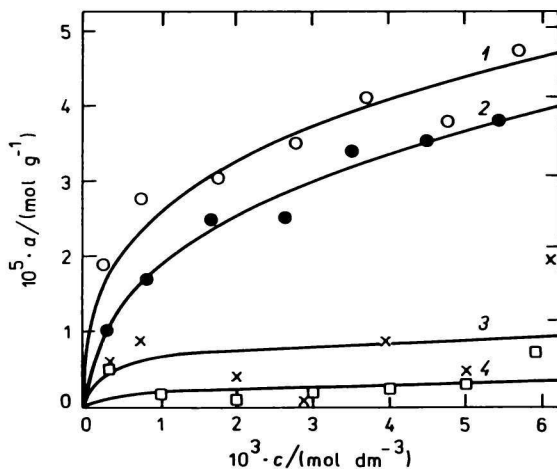


Fig. 2. Adsorption isotherms of some metal ions on DPVC at 30 °C: 1. Hg(II); 2. Ag(I); 3. Fe(II); 4. Pb(II).

No adsorption is exhibited by Ni(II), Zn(II), Ca(II), Cu(II), and Pd(II). The case of Pd(II) is rather surprising because from the analogy with olefin—metal complexes [8—10], the adsorption of Pd(II) could be expected almost with certainty. Absence of the adsorption can be explained by the fact that DPVC is a polymer with a conjugated *trans*-polyene system [11]. It has been proved that in general, *trans*-olefins form less stable metal—olefin complexes than *cis*-olefins and, in addition, it has been ascertained for silver that dienes give a lower stability constant than the corresponding monoene [10]. Transferring these findings to the adsorption of Pd(II), it can be supposed that both effects — *trans* configuration of double bonds in DPVC and their conjugation — prevent the adsorption of Pd(II) on DPVC.

From the above-said results it is obvious that DPVC specifically adsorbs heavy metal ions, mainly Hg(II) and Ag(I). From the analogy with metal—olefin complexes it can be supposed that the ions are bound on C=C bonds, but, the case of Fe(II) adsorption indicates that the presence of other groups can play a certain

role in the process. As the composition of DPVC reveals, mainly oxygen-containing groups can be present that are formed *via* adsorption of oxygen during DPVC storing.

As can be seen from Figs. 1 and 2, the efficiency of the adsorption is high in the range of small concentrations of ion solutions (less than  $5 \times 10^{-4}$  mol dm<sup>-3</sup>). But, a technological employment of this feature of DPVC, for example, in purification of waste water, is not realistic because of its small adsorption capacity (mole ratio of metal to  $\sim\text{CH}=\text{CH}\sim$  groups is about 1:1000).

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