

## SATURATION OF ACTIVATED CARBON WITH HEXACHLOROPLATINIC ACID

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Received December 19th, 1979

The course of saturation of activated carbon with hexachloroplatinic acid was studied in dependence on the solvent of the active component; the solvent was found to have a marked effect on the rate of saturation as well as on the attained concentration of chloroplatinic acid on the support. The effects of the saturation temperature and of the solvent type on the shape of the adsorption isotherm of chloroplatinic acid on the support were also investigated.

Catalysts of the type of platinum on activated carbon are frequently employed in hydrogenations of double bonds, aromatic nitro groups, in hydrogenolytic reactions, *etc.*<sup>1-3</sup>. The knowledge of the optimal preparation conditions allows us to prepare catalysts with low contents of platinum (2.5–10%), still exhibiting high activity. Most frequently are supported platinum catalysts prepared by saturation of the support with the active component followed by its subsequent reduction with hydrogen. The various operations involved in the preparation of this catalyst type have been described in detail, *e.g.*, in refs<sup>1-4</sup>.

Obviously, the first step, *viz.* coating of the support with the active component, plays an exceedingly important role in the subsequent formation of the catalyst properties<sup>1,5,6</sup>. For this reason, we have concerned ourselves with this problem in detail.

### EXPERIMENTAL

**Chemicals.** Hexachloroplatinic acid hexahydrate *p.a.* (Safina, Vestec). Ethanol denatured with 2% petrol (Spojené lihovary, Prague) was rectified prior to use; b.p. 78°C/98.06 kPa. Methanol *p.a.*, acetone *p.a.* (both Lachema, Brno). Methyl ethyl ketone *p.a.*, methyl isobutyl ketone pure (both Int. Enc. Ltd., Windsor, England). 2-Methoxyethanol pure (Downs Develop. Chem. Ltd., Milton, England). Activated carbon Supersorbon H8-3 (Degussa, GFR) extrudates, length 6 mm, diameter 4 mm, surface area (BET) 1513 m<sup>2</sup>/g, pore volume 0.98 cm<sup>3</sup>/g, porosity 65.6%. Activated carbon Norit RBI (Norit, The Netherlands) extrudates, length 4 mm, diameter 1 mm, surface area (BET) 1177 m<sup>2</sup>/g, pore volume 0.82 cm<sup>3</sup>/g, porosity 61.7%. The supports were dried prior to use 6 h at the temperature 90°C and pressure 2 kPa; after then, they were boiled in the corresponding solvent for 1 h.

**Course of saturation.** The usual saturation procedure, *viz.* mixing of the support with the active component solution with stirring was replaced by a new one, allowing the active component

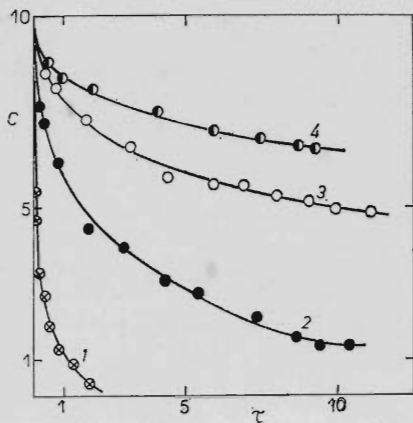


FIG. 1

Effect of solvent of chloroplatinic acid on the course of saturation of Supersorbon H8 3 support at 20°C. 1 Water, 2 methanol, 3 ethanol, 4 methoxyethanol

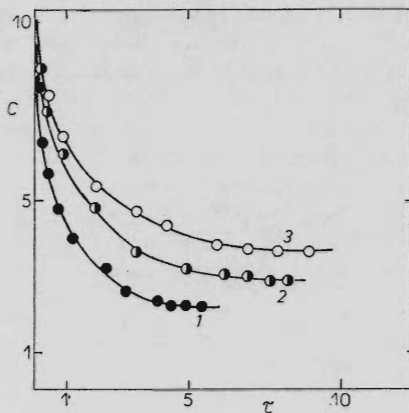


FIG. 2

Effect of solvent of chloroplatinic acid on the course of saturation of Supersorbon H8 3 support at 20°C. 1 Acetone, 2 methyl isobutyl ketone, 3 methyl ethyl ketone

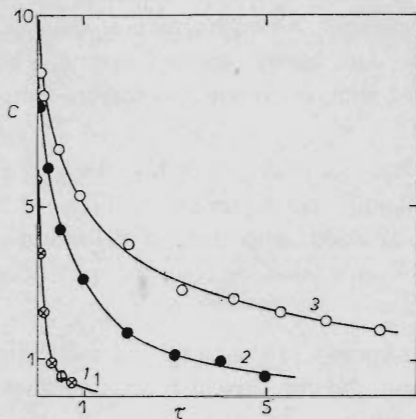


FIG. 3

Effect of solvent of chloroplatinic acid on the course of saturation of Norit RB1 support at 20°C. 1 Water, 2 methanol, 3 ethanol

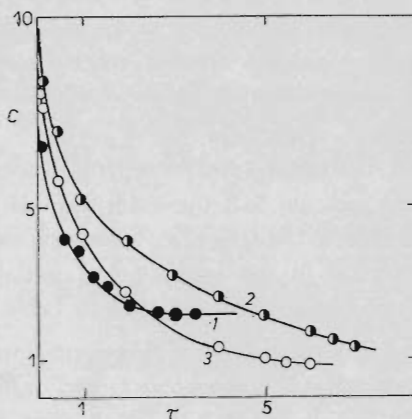


FIG. 4

Effect of solvent of chloroplatinic acid on the course of saturation of Norit RB1 support at 20°C. 1 Acetone, 2 methyl isobutyl ketone, 3 methyl ethyl ketone

to be applied in a defined manner. The support is placed in a Teflon basket with perforated bottom. The basket is accommodated in a thermostated glass vessel, volume 600 ml. The outer wall of the basket is separated from the glass cylinder by four baffles, preventing the basket from revolution and at the same time facilitating circulation of the liquid through the support bed. In the centre of the basket is the shaft of a pump stirrer. Owing to the rotation of the stirrer the solution passes vigorously through the layer of the support, whereby a defined application of the active component is provided. The course of the saturation was expressed as the dependence of the chloroplatinic acid concentration in the solution on the saturation period. The amount of chloroplatinic acid was chosen such that the platinum content in the solution corresponded to 5% wt. of the support. The initial concentration of chloroplatinic acid was 10 g/l in all cases. The acid concentration was determined colorimetrically at 400 nm by using a Spekol colorimeter (Zeiss, Jena, GDR).

*Adsorption isotherm.* Support particles (1.8 g) were poured into a thermostated glass vessel, volume 100 ml. The vessel was placed on a shaking machine, thermostated to the desired temperature (20, 40°C) and filled with the saturating solution of the appropriate concentration (2–80 g of chloroplatinic acid in 1 l solution). After 12 h, when the equilibrium had established, the equilibrium concentration of the acid in the solution was determined colorimetrically. The adsorption isotherm was expressed as the dependence of the adsorbed quantity of chloroplatinic acid per unit weight amount of the support on the equilibrium concentration in the solution.

*The heats of wetting* were measured in the usual manner in an adiabatic calorimeter<sup>7</sup>.

## RESULTS AND DISCUSSION

### *Course of Saturation*

The effect of solvent of chloroplatinic acid on the course of adsorption on activated carbon was studied by using the following solvents: water, methanol, ethanol, 2-methoxyethanol, acetone, methyl ethyl ketone, and methyl isobutyl ketone. The measurements included two types of support with different origin and texture parameters.

The course of adsorption from alcohols and ketones is shown in Figs 1–4. The results indicate that the adsorption of chloroplatinic acid varies considerably with solvent as to the rate of saturation as well as the attained concentration of the active component in the support. The initial rates of saturation and sorbed quantities of chloroplatinic acid are given in Table I.

The solvent probably affects the saturation basically in two ways, as underlain by the following concepts: 1) Chloroplatinic acid and the solvent form associates, which may be the bulkier, the bulkier is the solvent molecule; this hinders the penetration of the active component into the support. 2) The various solvents may display different adsorption affinity towards the support, and by their competitive sorption may hinder adsorption of chloroplatinic acid on the support. The resultant effect is likely to comprise both phenomena. A pronounced solvent effect on the saturation of carbon of both types appears notably in the case of water and the alcohol series.

The initial rate of saturation as well as the adsorbed quantity of chloroplatinic acid on the two supports increases markedly in the order 2-methoxyethanol < ethanol < methanol < water (Table I).

In the ketone series the differences are not so high and the solvent order for the two supports is not the same. In order to facilitate the interpretation of the solvent effect, the heats of wetting for the solvents on the support were measured calorimetrically in the alcohol series, since in fact, the heat evolved on the interaction of the support with the solvent may to an extent serve as a measure of adsorption affinity and thus of adsorption force on the support. The measured heats of wetting are given in Table I. Qualitatively, the order of the heat values corresponds to that of the solvent effect in that a solvent with a higher heat of wetting effects a slower saturation of the support by chloroplatinic acid. This supports the concept 2 concerning the competitive sorption of solvent during the saturation.

### Adsorption Isotherm

The adsorption isotherms of chloroplatinic acid on carbon were measured at 20 and 40°C with two selected solvents, *viz.* water and acetone. The results are shown in Figs 5 and 6. Obviously, for a given carbon type the shape of the isotherm does not change on replacing one solvent with another or on varying the temperature; these factors, however, affect considerably the adsorbed amount, the latter increasing considerably on raising the temperature and, notably, on using water as the solvent of chloro-

TABLE I

Initial rates of saturation, adsorbed quantities of hexachloroplatinic acid, and wetting heats of support. A Data for the Supersorbon HS 3 carrier, B data for the Norit RBI carrier

Solvent	Initial rate of saturation $r_0$		Adsorbed quantity ( $A$ ) in time $\tau$		Heat of wetting $Q_w$	
	A	B	A <sup>a</sup>	B <sup>b</sup>	A	B
Water	58.8	120.5	0.140	0.140	51	31
Methanol	17.3	27.0	0.116	0.133	135	119
Ethanol	6.4	13.0	0.067	0.113	147	128
2-Methoxyethanol	4.8	—	0.046	—	—	—
Acetone	25.0	50.0	0.110	0.109	—	—
Methyl ethyl ketone	7.8	18.2	0.088	0.127	—	—
Methyl isobutyl ketone	11.5	12.0	0.099	0.116	—	—

<sup>a</sup>  $\tau = 8$  h; <sup>b</sup>  $\tau = 6$  h.

platinic acid. Comparing the two carbon types we find the shapes of the adsorption isotherms somewhat different. The experimental shapes were correlated with the Langmuir and Freundlich isotherm relations; the results obtained with the carrier of Degussa correspond well to the Freundlich relation

$$A = KC_r^n, \quad (1)$$

TABLE II  
Calculated constants of adsorption isotherms

Solvent	Temperature °C	$K^a$	$n^a$	$K_1^b$	$K_2^b$
Water	20	0.25	0.19	0.40	0.75
	40	0.30	0.18	0.45	0.84
Acetone	20	0.07	0.33	0.20	0.79
	40	0.10	0.31	0.30	1.13

<sup>a</sup> Support: Supersorbon H8 3; <sup>b</sup> support: Norit RB1.

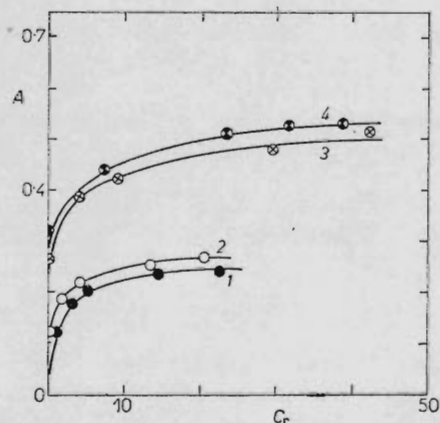


FIG. 5

Adsorption isotherms of chloroplatinic acid on Supersorbon H8 3 support. 1 Acetone, 20°C, 2 acetone, 40°C, 3 water, 20°C, 4 water, 40°C

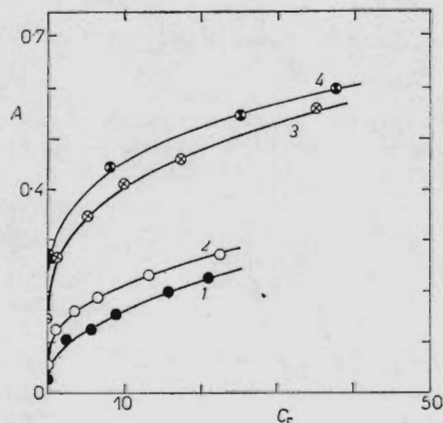


FIG. 6

Adsorption isotherms of chloroplatinic acid on Norit RB1 support. 1 Acetone, 20°C, 2 acetone, 40°C, 3 water, 20°C, 4 water, 40°C

whereas saturation of the Norit support can be described in terms of the Langmuir isotherm

$$A = K_1 C_r / (1 + K_2 C_r). \quad (2)$$

The linearized forms of the adsorption isotherms were processed by the least squares method to obtain the  $K$ ,  $n$ ,  $K_1$ , and  $K_2$  constants given in Table II.

Thus, the results of the present work point definitely to a significant effect of solvent on the course of saturation of activated carbon with chloroplatinic acid.

#### LIST OF SYMBOLS

$A$	adsorbed quantity of chloroplatinic acid (g H <sub>2</sub> Pt/Cl <sub>6</sub> /g support)
$C$	concentration of chloroplatinic acid in solution (g H <sub>2</sub> PtCl <sub>6</sub> /l solution)
$C_r$	equilibrium concentration of chloroplatinic acid in solution (g H <sub>2</sub> PtCl <sub>6</sub> /l solution)
$K$	constant in Eq. (1)
$K_1, K_2$	constants in Eq. (2)
$n$	exponent in Eq. (1)
$Q_w$	heat of wetting of the support with solvent (J/g carrier)
$r_0$	initial rate of saturation (g H <sub>2</sub> PtCl <sub>6</sub> /l h)
$\tau$	saturation period (h)

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Translated by P. Adámek.