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Investigation of solid surfaces by high-performance liquid chromatography

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ABSTRACT

Strong and weak points of chromatography as a method for physico-chemical research of properties of solid surfaces are discussed. The method was applied for studying the surface properties of γ-iron oxide and their changes during the various treatments.

INTRODUCTION

Chromatography, owing to its high separation efficiency, is firmly established as an important group of techniques for determining and separating substances in complex mixtures. Less attention has been paid to applying chromatography in physico-chemical investigations, however, although there has been research to obtain data on adsorption equilibria in binary [1] and multi-component [2] systems, and to investigate porous structures [3], intermolecular interactions [4] and the comparison and characterization of reversed phases [5] and surfaces [6].

In considering chromatography as a method for physico-chemical studies, we should point out its strong and weak points. The former include the following.

(1) The possibility of identifying and studying very small differences in intermolecular interactions. Unlike stationary research methods employed in studying a one-time distribution or redistribution of substances, chromatographic processes feature multiple redistributions of a substance between the mobile and stationary phases. Each distribution is determined by the difference between the substance interaction energies and that between the mobile and the stationary phases. Therefore, in a study of the distribution under stationary conditions in order to determine differences large enough to be measured, the distribution coefficients ought to be sufficiently high, *i.e.*, the differences in intermolecular interactions ought to be significant. Owing to multiple repetition of the distribution in a chromatographic process, multiplication of intermolecular interactions occurs in proportion to the number of redistribution acts, *i.e.*, to the number of theoretical plates in a chromatographic column.

The application of a chromatographic method makes it possible to determine extremely small differences in intermolecular interactions, which is accounted for by the high efficiency of the method (which, of course, depends on the efficiency of the chromatographic column used). The adsorption isotherm of a binary solution has the form [1]

$$\frac{x_1^s \gamma_1^s}{x_1 \gamma_1}\left(\frac{x_2 \gamma_2}{x^s \gamma^s}\right)^{m_2/m_1} = \exp\left(\frac{\Phi_2^0 - \Phi_1^0}{m_1 RT}\right) \quad (1)$$

where x_i, x_i^s are mole fractions of component i in the bulk phase and in the surface phase at equilibrium, respectively; γ_i, γ_i^s are activity coefficients of component i in the balk phase and in the surface phase, respectively; m_i is limiting adsorption of pure component i (mmol/g), and in the case of monolayer adsorption $m_i = S/\omega_0 N$, where S is the specific surface area, N is Avogadro's number and ω_0 is the cross-sectional area of the molecule; Φ_i^0 is the change in free energy of wetting of the adsorbent with pure component i; R is the gas constant; and T is absolute temperature.

At low concentrations, when $x_i \to 0$, $x_i^s = n_i^e/m_s$ and eqn. 1 takes the form

$$\frac{n_i^e \gamma_i^s}{x_i \gamma_i m_s} = \exp\left(\frac{\Phi_s^0 - \Phi_i^0}{m_i RT}\right) = K \tag{2}$$

where n_i^e is the excess adsorption of component i, m_s is the limiting adsorption of the solvent and K is the equilibrium constant.

The point with concentration x moves through the column at a rate [7]

$$U_{x_i} = U/V_c + \frac{dn_i^e}{dx_i} \tag{3}$$

where V_c is the free volume of the column, including the volume of the adsorbent pores, and U is the flow-rate of the eluent. From eqn. 3, it follows that

$$\frac{dn_i^e}{dx_i} = \frac{U}{U_{x_i}} - V_c = V_{Ri} - V_c \tag{4}$$

and from eqn. 2 we have

$$\frac{dn_i^e}{dx_i} = K \cdot \frac{m_s \gamma_i}{\gamma_i^s} \tag{5}$$

In the region of symmetrical peaks, dn_i^e/dx_i = constant = K_H, where K_H is Henry's constant. From eqns. 5 and 4, it follows that

$$K_H = K \cdot \frac{m_s \gamma_i}{\gamma_i^s} = V_{Ri} - V_c = V'_{Ri} \tag{6}$$

The selectivity coefficient of a column for components 1 and 2 is

$$\alpha = x_1^s x_2 / x_1 x_2^s \tag{7}$$

From eqn. 2, it follows that

$$\alpha = \frac{n_1^e x_2}{n_2^e \cdot x_1} = \frac{\gamma_1 \gamma_2^s}{\gamma_1^s \gamma_2} \cdot \exp\left(\frac{\Phi_s^0 - \Phi_1^0}{m_1 RT} - \frac{\Phi_s^0 - \Phi_2^0}{m_2 RT}\right) \tag{8}$$

If we assume that $\gamma_1 \gamma_2^s / \gamma_1^s \gamma_2 \approx 1$ and $m_1 = m_2$ (this means that the components do not differ much from each other in their physico-chemical properties), then

$$\alpha = K_{H1}/K_{H2} = V'_{R1}/V'_{R2} = k'_1/k'_2 \approx K_1/K_2$$

From eqn. 3, it follows for components i and j that

$$\ln \alpha = (\Phi_j^0 - \Phi_i^0)/mRT \tag{9}$$

Now we can estimate the sensitivity of the method.

Assuming $T = 300$ K and $m = 1$ mmol/g for $\alpha =$ e we obtain (from ref. 9) $\Delta\Phi = \Phi_2^0 - \Phi_1^0 = mRT = 8.314 \times 300 \times 1.10^{-3} = 2.4$ J/g. In other words, even with a high degree of selectivity, the value of $\Delta\Phi$ can be measured, which is normally unattainable through static measurement methods.

(2) The method is not material-intensive and allows small surface areas to be measured.

(3) Measurements can be carried out at various temperatures in the presence of foreign substances.

(4) Studies can be carried out in multi-component solvent systems and for several components simultaneously.

(5) The method can be considered to be rapid and can easily be automated.

The disadvantages of the method refer to the question of mass transfer and achieving an equilibrium. In cases when the equilibrium is achieved slowly, it is doubtful whether the data obtained actually correspond to equilibrium. These difficulties can be overcome by decreasing the flow rate, facilitating the mass transfer by employing small-sized particles for filling the column and increasing the temperature, where possible, for the system under investigation.

One of the limitations of the method in terms of the equipment employed may manifest itself as a difficulty in selecting a suitable detector, especially if the solvent and the substance under investigation have similar physico-chemical properties. On the other hand, the fact that we can not always prepare a column of high efficiency may depend, of course, on the material under investigation.

As new types of materials emerge, they necessitate the development of rapid methods for studying their surface characteristics. In our opinion, chromatography is one of the major methods for this purpose. This paper reports a liquid chromatographic method for studying the properties of γ-iron oxide (γ-Fe_2O_3) and of changes in the surface properties during the course of various treatments.

EXPERIMENTAL

A Milichrom chromatograph (Nauchpribor, USSR) with a UV detector was used. When working with substances that do not absorb in the UV region, an RIDK-101 (Czechoslovakia) refractometer was used as the detector.

Stainless-steel columns (60–120 mm × 2 mm I.D.) diameter were filled with powdered γ-Fe_2O_3 by the dry method. The size of the powder particles was < 0.5 μm. The agglomerated fraction of the γ-Fe_2O_3 particles of 0.08–0.25 mm was used. Filling the columns presented certain difficulties as the high density of the column packing causes an increase in its resistance, and when the column packing was highly porous the efficiency of the column was very low and the peaks were very diffuse.

The experiment was designed to measure the retention times of different substances featuring various types of intermolecular interactions, and benzene, toluene, nitrobenzene, benzaldehyde, benzyl alcohol, phenol and aniline were chosen as test substances. In preliminary tests, the retention of a test substance was measured on a new column each time.

n-Heptane and toluene were used as eluents. A certain amount of the test substance was introduced into the column and its retention volume was determined at a flow-rate of 100 μl/min. V_c was measured as V_R of an unretained component (*n*-octane). When modified samples of γ-Fe_2O_3 were tested, the original sample was first treated with the respective modifier until it was saturated, then the adsorbent obtained was used to measure the retention time of the test substance.

DISCUSSION AND RESULTS

Table I gives the results for the retention of test substances using the initial sample of γ-Fe_2O_3. Phenol and aniline, featuring acidic and basic properties, respectively, show the strongest retention. Phenol is not eluted even at $k' = 105$, and aniline behaves similarly. It could be suggested that they are adsorbed by the γ-Fe_2O_3 at basic and acidic centres, respectively. In order to measure the number of such centres, a method arbitrarily referred to as "chromatographic titration" was used. Its essence is as follows: a certain amount of a substance is introduced into the column and is eluted until it reaches a volume equivalent to about $k' = 50$; if the substance is still retained in the column, an additional amount of the substance is introduced and the procedure is repeated. After the substance has been detected at the outlet, the total amount of it introduced into the column is calculated. When a further amount of the substance is subsequently introduced, one can observe the process of the column modification.

TABLE I

RETENTIONS OF TEST SUBSTANCES ON ORIGINAL γ-Fe_2O_3

Substance	V_g (μl/g)	$k' = V_g'/V_c$
Benzene	81	0.055
Toluene	90	0.061
Nitrobenzene	694	0.47
Benzaldehyde	1314	0.89
Benzyl alcohol	1889	1.28
Phenol	154 000	>105
Aniline	70 000	>85

TABLE II

"CHROMATOGRAPHIC TITRATION" OF γ-Fe_2O_3 WITH PHENOL

Volume of phenol (1% solution in n-heptane) introduced (μl)	V_g (μl/g)	k'	Peak present
10	>125 000	–	No
17	158 000	–	No
27	110 000	72.3	Yes
37	25 000	15.7	Yes
57	7200	3.8	Yes
77	6750	3.5	Yes
97	6660	3.4	Yes

Table II gives the results of studies on the phenol modification of γ-Fe_2O_3. After introducing 27 μl of 1% phenol solution, a phenol peak was obtained. When additional phenol was introduced, the peak increased in height and shifted towards smaller k' and lower retention volume (V_g). After 77 μl of the solution had been introduced, the surface modification of the γ-Fe_2O_3 was practically completed.

Table III gives corresponding results for aniline modification. When 20 μl of 1% aniline solution had been introduced, an aniline peak was detected. As more aniline solution was introduced, the peak increased in height and shifted to smaller k' and lower retention volume. After introducing 40 μl of 1% aniline solution, the surface modification of the γ-Fe_2O_3 was practically completed.

TABLE III

"CHROMATOGRAPHIC TITRATION" OF γ-Fe_2O_3 WITH ANILINE

Volume of aniline (1% solution in n-heptane) introduced (μl)	V_g' (μl/g)	k'	Peak present
10	>125 000	–	No
20	35 830	22.9	Yes
30	9170	5.11	Yes
40	8417	4.61	Yes
50	8520	4.67	Yes

In order to establish the mode of filling of the active centres with phenol and aniline, samples of 1% aniline solution were introduced into a phenol-modified column. As with the initial γ-Fe_2O_3, the initial amounts of the aniline introduced were irreversibly adsorbed on the phenol-modified γ-Fe_2O_3, with no phenol desorption occurring. In order to investigate the modified surface properties, test substances were used. Results for the retention of the test substances on the initial, phenol-modified and phenol- and aniline-modified surfaces are given in Table IV.

As can be seen, modification of the surface of γ-Fe_2O_3 resulted in sharp changes in properties. Further studies were made involving substances featuring the same size of molecules but with different functional groups, namely stearic acid (SA)

TABLE IV

RETENTIONS OF TEST-SUBSTANCES ON ORIGINAL AND MODIFIED γ-Fe_2O_3

Substance	k'		
	Original	Phenol-modified	Phenol + aniline-modified
Benzene	0.055	–	0
Toluene	0.061	–	0.029
Nitrobenzene	0.47	–	0.34
Benzaldehyde	0.89	1.42	0.42
Benzyl alcohol	1.28	–	0.35
Phenol	>100	3.5	4.14
Aniline	>100	–	5.29

TABLE V

"CHROMATOGRAPHIC TITRATION" OF γ-Fe_2O_3 WITH STEARIC ACID (SA)

Volume of SA (0.53% solution in toluene) introduced (μl)	V_g' (μl/g)	k'	Peak present
50	>48 500	–	No
100	>46 970	–	No
150	29 122	38.8	Yes
200	7128	9.49	Yes
300	4302	4.73	Yes
350	4300	4.73	Yes

and octadecylamine (ODA). The initial γ-Fe_2O_3 sample was "chromatographically titrated" with SA (0.53% solution in toluene) and ODA (0.32% solution in toluene). Toluene was used as the eluent. The results are given in Tables V and VI.

As can be seen, irreversible adsorption of SA and ODA occurs until the surface active centres are blocked, as with phenol and aniline. Subsequently, symmetrical peaks of both SA and ODA are eluted from the modified γ-Fe_2O_3 surfaces with a constant retention time.

The retention volume of phenol was measured on the ODA-modified γ-Fe_2O_3. Phenol was eluted as a symmetrical peak without displacement of ODA.

In order to demonstrate that the ODA and SA

TABLE VI

"CHROMATOGRAPHIC TITRATION" OF γ-Fe_2O_3 WITH OCTADECYLAMINE (ODA)

Volume of ODA (0.32% solution in toluene) introduced (μl)	V_g' (μl/g)	k'	Peak present
50	>65 800	–	No
100	>43 900	–	No
150	>21 050	–	No
205	100 526	12.48	Yes
255	10 088	11.92	Yes
355	9210	10.80	Yes
405	7456	8.55	Yes
500	7460	8.55	Yes

TABLE VII

"CHROMATOGRAPHIC TITRATION" OF ODA-MODIFIED γ-Fe_2O_3 WITH STEARIC ACID (SA)

Volume of SA (0.53% solution in toluene) introduced (μl)	V_g' (μl/g)	k'
50	6140	3.5
100	5260	3.0
150	4780	2.72
200	3640	2.07
250	2130	1.25
300	2130	1.25

TABLE VIII

NUMBER OF ACTIVE CENTRES ON THE SURFACE OF γ-Fe_2O_3

Substance	Type of centre	No. of centres per m^2 of surface
Phenol	Basic	$1.1 \cdot 10^{17}$
Aniline	Acidic	$3.5 \cdot 10^{17}$
Stearic acid	Basic	$1.3 \cdot 10^{17}$
Octadecylamine	Acidic	$2.2 \cdot 10^{17}$

adsorptions occur at different centres, the retention of SA was measured on the ODA-modified γ-Fe_2O_3 and the results are given in Table VII. These results show that, unlike the initial γ-Fe_2O_3 modification, a peak is observed when 50 μl of SA has been introduced (earlier than on the original γ-Fe_2O_3) and an additional SA modification of the γ-Fe_2O_3 surface occurs. As a result, the retention volume and

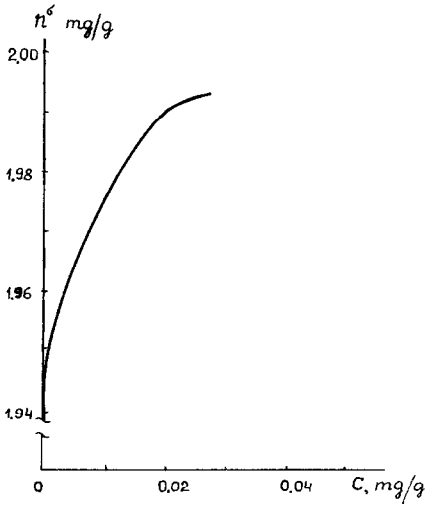

Fig. 1. Isotherm for irreversible and physical adsorption of stearic acid on original γ-Fe_2O_3.

k' values are decreased, and after introduction of 250 μl of the 0.53% of the SA solution the retention volumes become constant.

The results show that γ-Fe_2O_3 adsorbs phenol and SA irreversibly as acids and aniline and ODA as bases. Knowing the total amount of irreversibly sorbed substance, as the difference between the amounts introduced and eluted, it is possible to calculate the number of active centres. This corresponds to the number of moles of irreversibly adsorbed substances. The results of the calculations are given in Table VIII.

The close correlation of the base centres determined with respect to phenol and SA confirms the validity of the method. The same can be said about

TABLE IX

PROPORTION OF THE SURFACE-MODIFIED γ-Fe_2O_3 SCREENED BY IRREVERSIBLY ADSORBED SUBSTANCES

Substance	$n \cdot 10^{-17}$	ω(v) (nm)	ω(h) (nm)	S_s(v)	S_s(h)
Phenol	1.1	0.24	0.45	0.026	0.049
Aniline	3.56	0.24	0.45	0.085	0.160
Stearic acid	1.3	0.2	–	0.026	–
Octadecylamine	2.2	0.2	–	0.044	–
Phenol + aniline				0.111	0.209

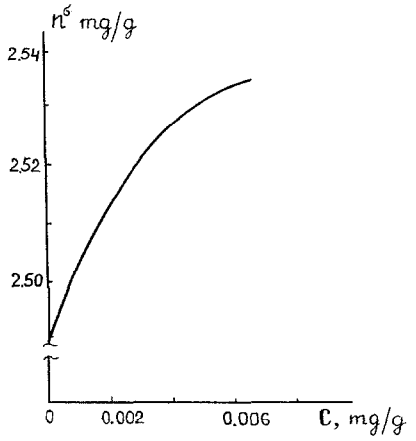

Fig. 2. Isotherm for irreversible and physical adsorption of octadecylamine on original γ-Fe_2O_3.

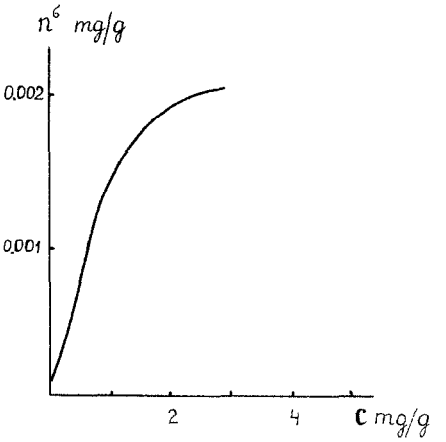

Fig. 3. Isotherm for physical adsorption of aniline on γ-Fe_2O_3 modified by phenol and aniline.

the number of acidic centres, which are about twice as many base centres on the γ-Fe_2O_3 surface. Knowing the number of active centers and the molecular areas of the test substances, the screening of the surface by modifiers can be calculated as

$$S_s = n\omega$$

where S_s is the screened surface area, n is the number of the active centres per 1 m^2 of the surface of γ-Fe_2O_3 and ω is the molecular area of the modifier in horizontal (h) or vertical (v) orientations.

Table IX gives the S_s values calculated on the basis of the data obtained. For aniline and phenol the data were calculated for the vertical and horizontal molecule orientations.

The shape of elution curve [1] made it possible to calculate isotherms for the physical adsorption of SA (Fig. 1) and ODA (Fig. 2) from toluene on γ-Fe_2O_3 modified by these combinations and of aniline on the γ-Fe_2O_3 surface modified by phenol and aniline (Fig. 3). As can be seen, the physical adsorpton (n^e) in the concentration range investigated accounts for only a small part of the total adsorbed substance (n^σ).

In conclusion, this research confirms the possibility of using liquid chromatography as a method for the investigation of the surface properties of solids.

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