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EFFECT OF CHEMICAL GRAFTING ON THE SURFACE STRUCTURE OF POROUS BENTONITE AS A SUPPORT IN GAS CHROMATOGRAPHY.

By

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تأثير التطعيم الكيميائي في البنية السطحية للبنتونيت المسامي كعامل في الكروماتوغرافيا

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في هذا البحث تم دراسة تأثير تكرار المعالجة الكيميائية والحرارية على تغير المساحة السطحية النوعية للبنتونيت حيث وجد أن مساحة سطح البنتونيت المعالج عند ٩٥٠° ثم بحمض ECL تبلغ ٣,٠١ م٢/جرام .

كما تم دراسة تأثير التطعيم الكيميائي للبنتونيت (المعالج حرارياً وكيميائياً ، وفقاً لما ذكر أعلاه) بالبولي اثيلين جليكول M 20 (PEG - 20 M) على بنيته السطحية ، حيث أصبحت البنية السطحية له هي بنية البولي ايثيلين جليكول M 20 . وقد ساهم هذا مساهمة فعالة في التمكن من فصل مزائج الفحوم الهيدروجينية اللاقطبية من C_5 إلى C_{12} بشكل أكثر دقة وحساسية من استخدام البنتونيت العاري أو المشروب بالبولي ايثيلين جليكول M20.

Key Words: Chemical grafting, Surface structure, Porous bentonite, Gas chromatography

ABSTRACT

The effect of thermal and chemical treatments on the variation of specific surface area of porous bentonite as a support was studied. The surface area of bare bentonite thermally treated at 950°C and then washed with 6N HCl was measured to be 3.01 m^2/g. Chemical grafting for the same treated bentonite by the condensation of PEG-20 M at 280° C formed a non-extractable monomolecular layer of PEG-20M. This grafting process changed the surface structure of bare bentonite and contributed to the good separation of hydrocarbon mixture C_5-C_{12} with a very good precision and sensitivity.

INTRODUCTION

Aleppo bentonite is considered as a porous cheap material naturally occurring in Syria. Aleppo bentonite contains several metallic oxides where silica and alumina represent the major constituents[1]. Bentonite was used as a support in classical liquid chromatography for separating some mixtures of different metallic ions[2]. It was also used as a support in gas chromatography after loading it with several stationary phases to separate mixtures of polar and non-polar solvents[3].

The grafting process was carried out on siliceous supports using different polymers, as linear polyethylene of average molecular weight = 5 x 10^4, carbowax 20 M and OV-101[4-7] Chromosorb W was also modified by grafting with layer of polyethylene oxide[6].

Washing of chromosorbs P and W with 6 N HCl leads to the removal of some metallic oxides, removal of 95% of iron oxide from P and W chromosorbs was possible[8].

EXPERIMENTAL

Apparatus: The chromatograms were obtained by using chromatograph GC-9A with chromatopac C-R3A printer (Shimadzu Co.), spectrophotometer UV-240 (Shimadzu Co.), copper chromatographic columns and

special reactor for grafting. The surface area was obtained from the adsorption of methylene blue and octadecanol.

METHODS

Thermal and Acid Washed Treatments

Aleppo bentonite was calcined in the temperature range (800-1100)°C for 2 hours to obtain a firm solid granules (100-315) micron. The specific surface areas obtained for every last treatment temperatures were found to range between 0.83 and 35 m^2/g. Bentonite was then washed with 6 N HCl in a Soxhlet[4-7] and then with distilled water in a buchner funnel to neutrality before drying at 150°C, and the bentonite was treated once again in the same range of temperatures.

Grafting with polyethylene glycol 20 M (PEG-20M)

The acid washed and thermally treated bentonite was deactivated by grafting it with PEG-20M. This was made by the slow addition of a 5% polymer solution to a suspension of bentonite in chloroform, during gentle stirring. After standing for 1 hour, the mixture was freed of solvent in vacuum and the resulted impregnated granules with PEG-20 M were treated at 280°C under a very slow flow of pure nitrogen for 24 hours. The bentonite was allowed to cool in a stream of pure nitrogen. The product was extracted with chloroform for 48 hours and later with dichloromethane for 24 hours to remove the remaining chloroform. After extraction, the product was dried at 105°C, packed into copper column (4 m x 4 mm I. D) and tested in Shimadzu GC-9A with FID. A relationship log Vs = F(1/T) for several test solutes was plotted to ensure that there is no transition at melting point of PEG-20 M, indicating the formation of monolayer.

RESULTS AND DISCUSSION

The surface area of bentonite decreases with the rise of the thermal treatment temperature. The surface area of 800° C calcined bentonite was measured to be 35.0 m^2/g and decreased to 0.83 m^2/g with the rise of the calcination temperature to 1100° C. Calcination between 950 and 1000° C was selected to obtain solids with surface areas suitable for gas chromatographic analysis. The effect of number of calcination cycles on the surface area was also studied. Constant surface area was obtained upon calcination at certain temperature for 2 hours (Table 1).

Table 1
Effect of duration of thermal treatment on bentonite specific surface area (treatment period 2 hours)

Temperature treatment t, °C	Surface area, m^2/g	
	One time	twice
950	7.98	8.30
975	5.50	4.35
1000	2.44	2.20
1025	1.70	1.58
1050	1.40	1.05

Table 2
Calculation of the specific surface area using methylene blue and octadecanol as adsorbates

Temperature treatment t, °C	Surface area, m^2/g	
	One time	Octadecanol
950	3.01	3.08
975	2.79	2.89
1000	1.90	2.16

Washing with 6 N HCl in a Soxhlet removed the soluble salts and meanwhile decreased the surface area. The surface area of bentonite calciined at 950, 975 and 1000°C, followed by treatment with 6N HCl are given in (Table 2).

The surface areas were determined from adsorption of methylene blue using a spectrophotometric technique[9]. The adsorption of octadecanol was also measured to determine the surface area, using the chromatographic technique[10]. This method was made by impregnation of bentonite by octadecanol with a load larger than the critical load to form a monomolecular layer of octadecanol. Then the impregnated support was packed in a copper columns (1 m x 4 mm I. D) and the columns were chromatographically tested within the range (25-100°C). log Vs (Vs = retention volume) for normal octane versus reciprocal of the absolute temperature was plotted (Fig. 1).

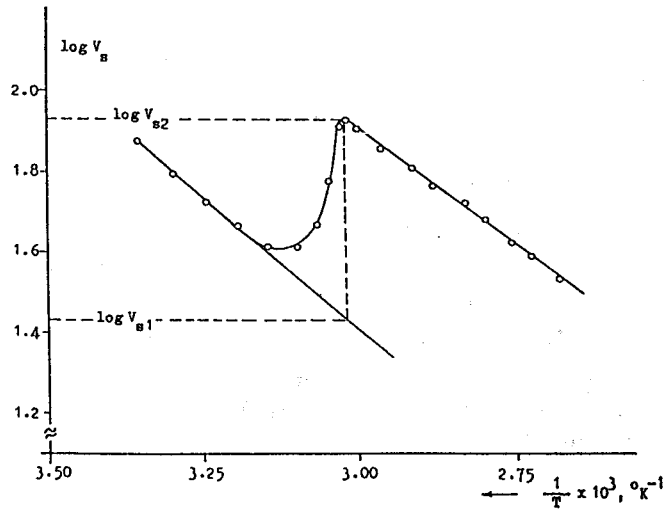

Fig. 1 Variation of log. Vs with 1/T (increasing in the direction of the arrow) for n-octane as a solute on column of bentonite which was treated thermally at 950°C, then with HCl(6 N) and impregnated by octadecanol, (flow of carrier gas (N_2), 80 ml/min.).

The difference ΔVs at the transition concerning the melting point of octadecanol at 58°C was deduced, $\Delta Vs = Vs_2 - Vs_1$, where Vs_1 and Vs_2 are the retention volumes for 1 g of packing before and at melting point of octadecanol, respectively, $\tau_b = \Delta Vs/Vg$ was calculated, Vg = 558 ml, the specific retention volume for n-octane solute, (τ_b = the excess ratio of monomolecular layer) and $\tau_c = \tau - \tau_b$, where

τ_c is the critical load ratio, t the total load ratio. The specific surface area was calculated from the relationship:

$$S = 6.02 \times 10^{23} \times \tau_c \times A/M_f$$

where A = 21 $Å^2$, cross sectional area of octadecanol molecule, M_f the molecular weight of octadecanol. Depending on the results we selected the bentonite treated at 950°C, which showed a suitable GC specific surface ($3.01 m^2/g$). We performed grafting of PEG-20 M and formed a new surface structure of PEG-20 M. Due to chemical bonding between bentonite surface and the non-extractable monomolecular layer, the structure change before and after bentonite grafting by PEG-20 M was determined by plotting the relationship:

$$\log Vs = f(1/T)$$

using n-hexane as a test solute (Fig. 2). The difference between the retention volumes in the two cases indicated

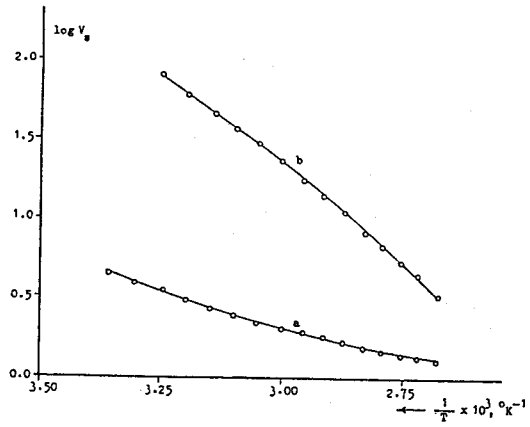

Fig. 2 Variation of log Vs with 1/T (increasing in the direction of the arrow) for n-hexane as a solute:
a- on packed column with bare bentonite.
b- on packed column with grafted bentonite.

the improvement realized by the monomolecular layer of PEG-20 M. We used also two stationary phases namely PEG-1500 and PEG-4000 at different ratios in consequence where a good resolution and separation by packed column with grafted bentonite was found, compared with bare bentonite (Figures 3 and 4).

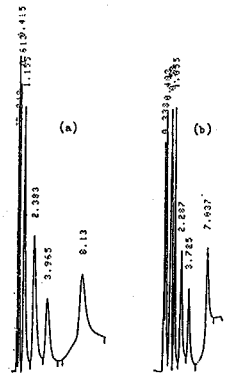

Fig. 3 Separation of C_5-C_{12} mixture on packed column with grafted bentonite impregnated by PEG =1500:
a- temperature program 35° - 85°, 8°/min.
b- temperature program 35° - 100°, 8°/min.

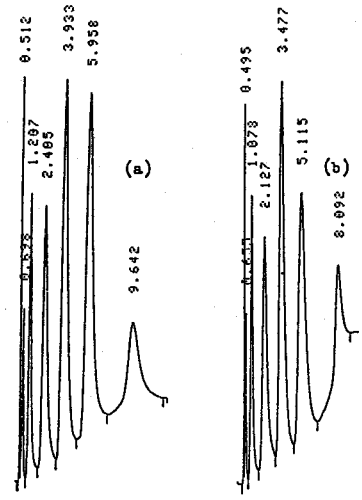

Fig. 4 Separation of C_5-C_{12} mixture on packed column with grafted bentonite impregnated by P.E.G-4000:
a- temperature program 40° - 85°, 8°/min.
b- temperature program 45° - 120°, 10°/min.

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