Asian Journal of Chemistry Vol. 16, No. 1 (2004), 89–95

Modification of Algerian Bentonite and Using It as Support in Gas Chromatography

M. LAHMEK†, A. ALHAJ SAKUR‡ and A.A. RAMADAN*
Department of Chemistry, Faculty of Science, Aleppo University, Aleppo, Syria
Fax: 00963 21 2670600, E-mail: DRAMADAN@SCS-net.org

Two chromatographic supports were prepared from Algerian bentonite by thermal and chemical treatments. The first support was prepared by thermal treatment of bentonite at 650°C to obtain firm granules, then washed with 6 N HCl to remove the soluble metallic oxides, especially iron oxide, till obtained white granules, with diameter range 125–150 μm. The second one was prepared by thermal treatment of the granules of the first support at 1100°C, and chemically by 6 N HCl. The specific surface areas of support were measured and found 112 and 12 m^2/g respectively. The two yield support granules were silanized with dimethylchlorosilan at 120°C in the vapour phase, under slow flow of dry pure nitrogen, to obtain a new surface structure that possesses chromatographic properties. A suitable amount of bentonite granules ($S = 12\ m^2/g$) were coated with 3% of silicone SE-52 and heated under slow flow of dry pure nitrogen at 280°C for 24 h, and then extracted with chloroform in soxhlet apparatus for 48 h. The grafting process changed the surface structure of bare treated bentonite. The packing obtained participated effectively in separating different mixtures of aromatic compounds and mixtures of normal hydrocarbon compounds with a good sharp chromatographic peak on columns (50 cm × 4 mm), packed with modified bentonite, with good precision and reproducibility.

Key Words: Bentonite, Grafting, Support, Gas chromatography.

INTRODUCTION

Chromatographic supports are prepared from siliceous or natural origin materials such as diatomaceous earth or bentonite, which are treated in different ways to deactivate and modify their surface properties. Acid wash treatment by HCl removes all soluble oxides from the surface of the support[1]. Modification of the support surface by silanization with silane compounds[2] or by condensation of a suitable polymer[3, 4] is well reported. Modification of the support surface by

---

†Department de chimie, Ecole Normale Supérieure, Vieux-Kouba, B.P.: 92, Alger, 16308, Algérie.

‡Department of Analytical and Food Chemistry, Faculty of Pharmacy, Aleppo University, Aleppo, Syria.

reaction with silanol groups was carried out by means of chlorosilane compounds as reactants[5, 6], or by condensation of suitable polymer as PEG-20M, SE-30 and OV-101[7–11].

Many researches were carried out on bentonite; it was deactivated by condensation of polyethylene glycol 20 M (PEG-20M) and used in separation and determination of different mixtures of polar and non-polar compounds[8]. Syrian bentonite deactivated by silanization with dimethylchlorosilane DMCS was also used to separate mixtures of normal hydrocarbons $C_5 - C_{12}$[12]. It was found that the thermal treatment causes a decrease of bentonite-specific surface area with increasing the temperature of thermal treatment[8, 13].

A prolonged washing of bentonite by 6N HCl removes all soluble oxides and about 67% of total iron oxide from the adsorbent, causing decrease of specific surface area and hydrolysis of siloxane groups on the surface of the support to yield more silanol groups[1, 10, 14, 15].

Bentonite is considered as a porous cheap material, naturally occurring in Algeria and many parts of the world. It is used in different fields such as refining mineral oils and edible oils and in the petroleum industry. Algerian bentonite is a gray coloured material. It is not used in gas chromatography until now[16]. This work is the first attempt to use Algerian bentonite in the field of chromatography.

EXPERIMENTAL

The chromatograms were obtained by using a GC-9A gas chromatograph equipped with a flame ionization detector (FID) and chromatopac C-R3A printer (Shimadzu Co.), Gemini Micrometitics III 2375 surface area analyzer (USA), 50 cm × 4 mm copper columns, 1 μL syringe (Hamilton Co.) and special reactor for grafting. All solvents and used chemicals were of extra pure grade. The studied sample came from Roussel quarry, near Maghnia town (northwest Algeria).

Supports preparation

Two supports were prepared from Algerian bentonite, by thermal and acidic treatments. The first one was prepared by thermal treatment of bentonite granules at 650°C for 3 h, then washed with 6 N HCl for 48 h, finally washed by distilled water until the excess Cl^- ions were no longer detectable by the $AgNO_3$ test. We obtained white bentonite granules in the diameter range 125–150 μm. The BET specific surface area was measured by N_2 adsorption at 77 K using Gemini Micromeritics III 2375 Surface Area Analyzer (USA), and was found to be 112 m^2/g. The second support was prepared by thermal tratment of bentonite granules at 650°C for 3 h, followed by washing with 6 N HCl for 48 h, then thermally treated at 1100°C for 3 h to decrease the specific surface area, then washed with 6 N HCl for 10 h; after that the bentonite granules were washed by distilled water to neutrality. Finally we obtained white bentonite granules in the diameter range 125–150 μm, posse a BET specific surface area of 12 m^2/g.

Supports Silanization

The granules of two supports ($S = 112$ and 12 m^2/g) in the diameter range 125–150 μm were deactivated by silanization with dimethylchlorosilan in the vapour phase at 120°C in presence of a stream of dry pure nitrogen (*in situ* method)[12]; then the yield grafted supports were washed by chloroform to remove the residual of reagent. The silanized supports were dried at 110°C before being packing into chromatographic columns. Silanized chromosorbs P and G were prepared in the same manner, to use as reference supports.

Polymer Condensation

A suitable amount of bentonite granules (S = 12 m^2/g) were coated by rotary evaporation technique with 3% of silicone SE-52 and heated under a slow flow of dry pure nitrogen at 280°C for 24 h, then extracted with chloroform in a Soxhlet apparatus of 48 h for removing the excess of non-bonded silicone SE-52, then the extracted material was dried at 110°C before being packed into chromatographic column. Grafted chromosorbs P and G were prepared in the same manner, to use as reference supports.

Supports Characterization

The gas chromatographic characteristics of packing were evaluated using "inverse gas chromatographic method" and plotting the relationship between variation of the logarithm of retention volume of CH_2Cl_2 as an auxiliary solute and the reciprocal of the absolute temperature in the range 40–100°C, Fig. 1, 2.

Gas Chromatographic Analysis

We used the obtained supports in separating several mixtures of aromatic compounds (benzene, toluene, ethylbenzene and cumene) and some normal hydrocarbon compounds (pentane, hexane, heptane and octane). Nitrogen was used as carrier gas at flow rate 40 mL/min.; the inject port temperature: 200°C. Our prepared supports were compared with commercial silanized or grafted by SE-52 chromosorbs G and P by the same manner as our grafted supports; the corresponding chromatograms are presented in Figs. 3–9.

RESULTS AND DISCUSSION

By studying the changes in superficial structure of silanized bentonite in the above mentioned three cases using "inverse gas chromatographic method", we found differences between retention volumes for CH_2Cl_2 in three cases for columns (50 cm × 4 mm); the first one packed with bare bentonite (S = 112 or 12 m^2/g), curve (a) in Fig. (1, 2), the second packed with dimethylchlorosilane (DMCS) silanized bentonite; curve (b) in Figs. 1, 2 and the third one packed with silicone SE-52 grafted bentonite (S = 12 m^2/g), curve (c) in Fig. (2). The differences in retention volumes between the bare bentonite and the grafted bentonite are due to the new superficial structure of supports, see Figs. 1, 2.

The packed column with DMCS grafted bentonite (112 m^2/g) is suitable for separating the mixture of aromatic compounds: benzene, toluene, ethylbenzene and cumene, and the mixture of normal hydrocarbons C_5–C_8, see Fig. 3. The packed column with DMCS silanized bentonite (12 m^2/g) shows a good separation for a mixture of aromatic compounds: benzene, toluene, ethylbenzene and cumene, and the mixture of normal hydrocarbons C_5–C_8, and the packed column with silicone SE-52 grafted benotonite (12 m^2/g) show a good separation for mixture of aromatic compounds: benzene, toluene, ethylbenzene and cumene with

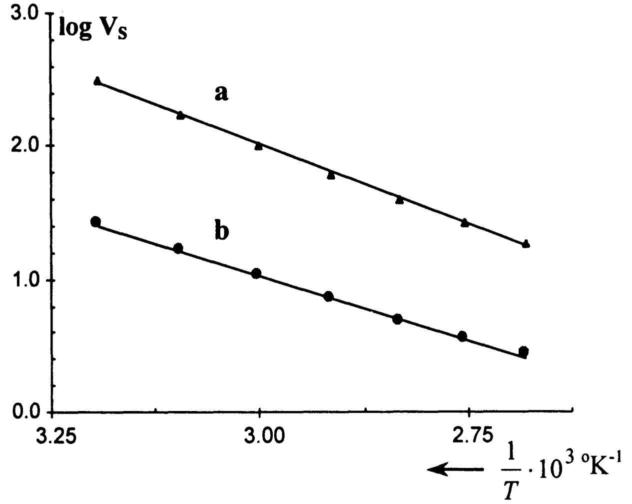

Fig. 1. Variation of log V_s with 1/T (increasing in the direction of the arrow) for CH_2Cl_2 as a test solute on (50 cm × 4 mm) packed columns by bentonite (S = 112 m^2/g): a = bara bentonite, b = DMCS silanized bentonite

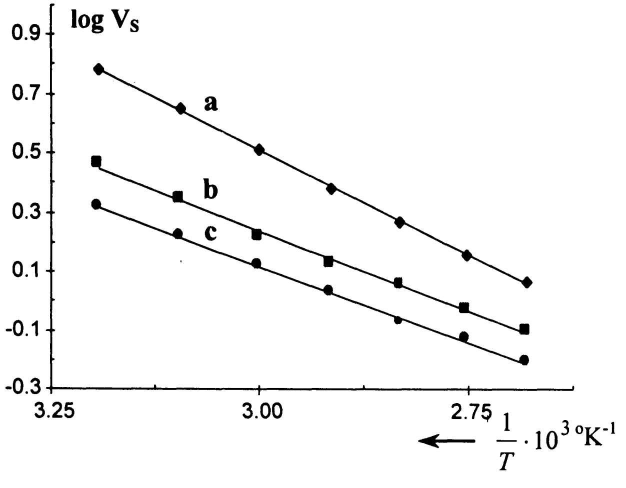

Fig. 2. Variation of log V_s with 1/T (increasing in the direction of the arrow) for CH_2Cl_2 as a test solute on (50 cm × 4 mm) packed columns by bentonite (S = 12 m^2/g): a = bara bentonite, b = DMCS silanized bentonite, c = SE-52 grafted bentonite

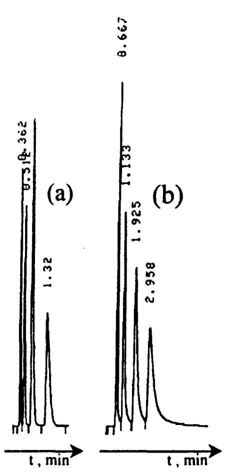

Fig. 3. Separation mixture of: a = C_5–C_8 at 100°C, b = aromatic compounds at 115°C, using DMCS silanized bentonite (S = 112 m^2/g)

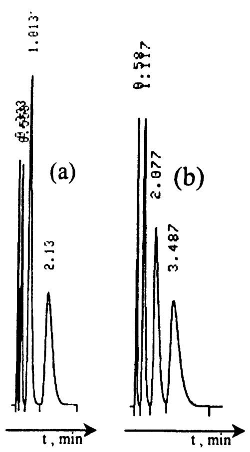

Fig. 4. Separation mixture of: a = C_5–C_8 at 75°C, b = aromatic compounds at 90°C, using DMCS silanized bentonite, (S = 12 m^2/g)

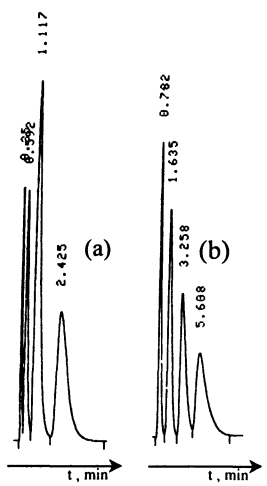

Fig. 5. Separation mixture of: a = C_5–C_8 at 75°C, b = aromatic compounds at 90°C, using SE-52 grafted bentonite, (S = 12 m^2/g)

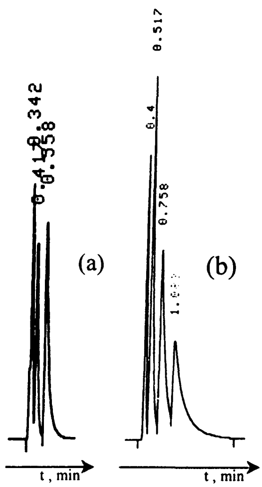

Fig. 6. Separation mixture of: a = C_5–C_8, b = aromatic compounds at 45°C, using DMCS silanized Chromosorb P.

a sharp symmetric peaks with short retention times, Fig. (4, 5). In all separations, we obtained a completely separated peaks, with a high sensitivity and reproducibility, compared with packed column by silanized or grafted by SE-52 chromosorbs G and P, see Fig. (6–9).

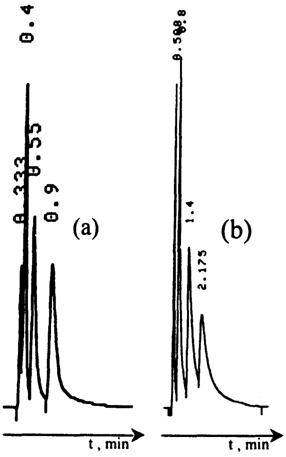

Fig. 7. Separation mixture of: a = C_5–C_8, b = aromatic compounds at 45°C, using SE-52 grafted Chromosorb P.

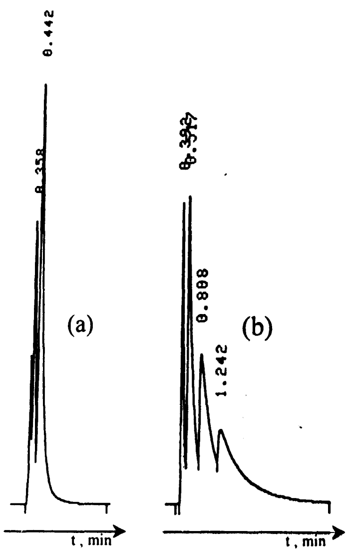

Fig. 8. Separation mixture of: a = C_5–C_8, b = aromatic compounds at 45°C, using DMCS silanized Chromosorb G.

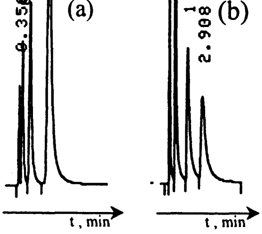

Fig. 9. Separation mixture of: a = C_5–C_8, b = aromatic compounds at 45°C, using SE-52 grafted Chromosorb G.

Conclusion

The three prepared supports show good separated peaks of all constituents of tested mixtures, with a good reproducibility and high sensitivity. The quality of the new supports is comparable with commercial supports chromosorbs G and P, but with lower cost. Our best results are due to the good purification of Algerian bentonite.

REFERENCES

1. P. Komadel, J. Stuck and B. Cicel, *Geol. Grapathica—Clays*, **1**, 11 (1993).
2. U. Menys, U. Roth and C. Troeltsch, *Eur. Pat. Appl. Ep.*, 4 pp. (1997).
3. A.V. Musheghyan, O.A. Kamalyan and G.G. Grigorean, *Chem. Anal.*, **39**, 309 (1994).
4. T.M. Roshchina, K.B. Gurevich and A.Y. Fadeev, Int. Conf. Filled Polym. Fillers, pp. 151–154 (1997).
5. Y. Ono and E. Suzuki, Jpn. Kokai Tokyo JP04, 92, 338, 393 (1992).
6. E. Suzuki, M. Okamoto and Y. Ono, *Sekiyu Gakkaishi*, **37**, 103 (1994).
7. M.M. Daniewski and W.A. Aue., *J. Chromatogr.*, **147**, 119 (1978).
8. A.A. Ramadan, S. Antakli and A.A. Sakur, *Qatar Univ. Sci. J.*, **14C**, 175 (1994).
9. B.D. Skrbic and J. Dj. Cvejanov, *Chromatographia*, **37**, 215 (1993).
10. Y. Takayama and K. Bunseki, *J. Chromatogr.*, **28**, 579 (1979).
11. C.R. Vogt and W.A. Aue, *J. Chromatogr. Sci.*, **16**, 268 (1978).
12. A.A. Sakur, Ph.D. Thesis, Aleppo Univ., Syria, 189 pp. (2000).
13. A.A. Ramadan, A.R. Kourini and M. Lahmek, *R.J. Aleppo Univ.*, **8**, 83 (1986).
14. D. Carrol and H.C. Starkey, *Clays Clay Miner.*, **19**, 321 (1971).
15. X. Chin and J. Huang, *Kuangchan Zonghe Liyonge*, **3**, 28 (1993).
16. O. Hadjadj-aoul, R. Belabbes, S. Charchari, M. Belkadi, Y. Combret and J.C. Combret, *Chromatographia*, **50**, 728 (1999).

(*Received*: 7 March 2003; *Accepted:* 20 August 2003) AJC–3148