Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Chromatographic Characterization of Carbowax-Modified Silica Gels: Influence of Polymer Loading and Pore Structure

A. M. El-Fadly[a]; S. Faramawy[a]; A. Y. El-NAGGAR[a]; A. M. Youssef[b]
[a] EGYPTIAN PETROLEUM RESEARCH INSTITUTE, NASR CITY, CAIRO, EGYPT [b] CHEMISTRY DEPARTMENT, MANSOURA UNIVERSITY, MANSOURA, EGYPT

To cite this Article El-Fadly, A. M. , Faramawy, S. , El-NAGGAR, A. Y. and Youssef, A. M.(1997) 'Chromatographic Characterization of Carbowax-Modified Silica Gels: Influence of Polymer Loading and Pore Structure', Separation Science and Technology, 32: 18, 2993 — 3005

To link to this Article: DOI: 10.1080/01496399708000791

URL: http://dx.doi.org/10.1080/01496399708000791

SEPARATION SCIENCE AND TECHNOLOGY, **32**(18), pp. 2993–3005, 1997

Chromatographic Characterization of Carbowax-Modified Silica Gels: Influence of Polymer Loading and Pore Structure

---

A. M. EL-FADLY, S. FARAMAWY,* and A. Y. EL-NAGGAR
EGYPTIAN PETROLEUM RESEARCH INSTITUTE
NASR CITY, CAIRO, EGYPT

A. M. YOUSSEF
CHEMISTRY DEPARTMENT
MANSOURA UNIVERSITY
MANSOURA, EGYPT

ABSTRACT

Two silica gels, untreated and thermally pretreated at 1000°C, were coated with different loadings (6, 15, 25 wt%) of Carbowax 20M. The surface of the coated silica gels was characterized by means of nitrogen adsorption measurements at −196°C and infrared spectroscopy. It was found that the coating reduces the surface dimensions of silica gel due to free entrance of polymer molecules occupying preferentially the micropores in the 5–60 Å range. Infrared spectroscopy indicated that the low polymer loading (6 wt%) is not sufficient to deactivate the surface of silica gels. Surface deactivation of unmodified and coated silica gels was also confirmed via thermodynamic parameters (ΔH and ΔS) which were calculated by the aid of inverse gas chromatography using *n*-hexane as a probe. The coated silica gels were evaluated as gas chromatographic stationary phases using two groups of nonpolar and polar solutes. The efficiency of chromatographic separation was discussed in terms of surface deactivation and pore structural changes brought about by different polymer loadings.

Key Words. Silica gel; Carbowax 20M; Pore analysis; Gas chromatography

---

* To whom correspondence should be sent at his present address: Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia.

INTRODUCTION

Inorganic adsorbents are widely used as stationary phases in chromatographic techniques GSC and HPLC (1–3). In this concern, silica gel gained more attention due to the ease of surface modification and the dependence of the surface characteristics on the methods of preparation (4–6). The surface of silica gel can generally be modified by heat or by special physical or chemical treatments, leading in each case to different adsorptive properties. These treatments may include hydrothermal treatment (2), silylation (7, 8), and incorporation of inorganic salts or organic compounds (9, 10).

Among several known methods for deactivation of diatomaceous support for GLC, coating with nonpolar polymers was used to form a highly stable nonextractable thin layer on the support surface (11, 12). Vogt and Aue (13) prepared and deactivated silica gels of different surface areas with nonextractable polymers of dimethyl silicon, straight chain hydrocarbon, and ethylene oxide types. They found that the thickness of nonextractable polymer layers increased significantly with decreasing surface areas of the support. Carbowax-modified supports, owing to low adsorptivity and poor wetting, could be used for the analysis of polar compounds (14).

In the present work, two silica gels of different surface reactivities have been deactivated by coating with different loadings of Carbowax 20M. The influence of surface deactivation and pore structural change, which may take place due to coating with different polymer loadings, on the chromatographic characteristics is the main goal of this study.

EXPERIMENTAL

Preparation of Silica Gels

Mesoporous silica gel was prepared by a conventional method described by De Boer (15). The prepared silica gel was crushed and sieved to select 80–100 mesh. The obtained silica gel was washed by 6 mol·L^{-1} HCl (16). A portion of the acid-washed silica gel was then thermally treated at 1000°C for 2 hours (i.e., calcination). The notations used for untreated and calcined silicas are (Si) and $(Si)_C$, respectively. The obtained silica gels, (Si) and $(Si)_C$, were coated with different loadings (6, 15, 25 wt%) of Carbowax 20M, which is polyethylene glycol with a high molecular weight of 20,000. It was supplied from Supelco. The Carbowax 20M was dissolved in the proper amount of chloroform and added to silica gel. The mixture was heated at 70°C in a rotary evaporator with stirring until there was complete evaporation of chloroform. The coated silica was dried at 100°C for 24 hours.

Characterization of Surface Textures

The surface textures of the unmodified silica gels and the coated ones were studied with the adsorption isotherms of N_2 at $-196°C$ using a conventional volumetric apparatus. Specific surface areas and pore volumes were calculated from the isotherms by applying the BET equation (17). The porosity was detected through the corrected modless method (18).

Infrared Spectroscopy

Unmodified and coated silica gels were analyzed using infrared spectroscopy. The instrument used was a Perkin-Elmer model 1430 spectrophotometer. The sample was prepared as a thin disk with KBr. The weights of the sample and KBr were kept constant.

Gas Chromatography

The unmodified silica gels, (Si) and $(\mathrm{Si})_C$, and those coated with different polymer loadings were tested by gas chromatography. This was with the aim of investigating their efficiencies for separating nonpolar and polar solutes. The solid material was packed in a stainless steel column (7 ft × 4 mm id) by charging under vacuum. The packed column was activated at 200°C for 10 hours in a stream of pure nitrogen gas at a flow rate of 40 $\mathrm{mL{\cdot}min^{-1}}$. The gas chromatograph used was a Pye Unicam 4550 equipped with FID. Nitrogen gas was used as a carrier at a flow rate of 15 $\mathrm{mL{\cdot}min^{-1}}$. The analysis was carried out at different temperatures depending on the column efficiency, resulting in the optimum separation of the studied solutes.

RESULTS AND DISCUSSION

Influence of Coating with Polymer on Surface Characteristics of Silica Gels

Two silica gels, (Si) and $(\mathrm{Si})_C$, were used as solid supports and coated with different loadings of Carbowax 20M. The resulting materials were characterized by means of nitrogen adsorption and infrared spectroscopic techniques in order to show the influence of polymer treatment on pore structure and deactivation of silica gel surfaces.

The adsorption–desorption isotherms of nitrogen at $-196°C$, obtained on the supports and the coated silica gels, were of type II of Brunauer's classification (17). The isotherms exhibited hysteresis loops at P/P_0 ranging between 0.25 and 0.95. The adsorption data are summarized in Table 1, including specific surface area (S_{BET}), total pore volume (V_p), estimated from the saturation values of adsorption isotherms, and average pore radius (r_p), assuming the cylindrical pore model.

The results indicate that surface area and total pore volume decrease by increasing the polymer loading. This is due to an increase of the polymer fraction occupying the pore volume of silica gel. Vogt and Aue (13) proved that the nonextractable polymers (e.g., OV-101, polyethylene, and Carbowax 20M) reduce the pore diameter of silica gels by 2 to 10%, occupying 4 to 30% of the pore volume.

In a rough approximation, the percentage of pore volume occupied by polymer, α%, could be derived from the pore volumes of a coated silica gel and a solid support (V_{P1} and V_{P2}, respectively) according to the following equation:

$$\alpha\% = (V_{P2} - V_{P1}) \times 100/V_{P2} \tag{1}$$

The values of α% are also given in Table 1. It is obvious that α% increases with polymer loadings. For each polymer loading, the fraction of pore volume occupied by polymer for the calcined silica, $(Si)_C$, exceeds that for the untreated silica gel, (Si). This could be directly linked with the finding that the pore volume of (Si) is larger than that of $(Si)_C$. The same weight and, therefore, also volume of Carbowax added to both types of silica gel may consume a larger part of the pores in particles with a lower pore volume.

TABLE 1

N_2 Adsorption Data of Silica Gels Coated with Different Loadings of Carbowax 20M

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	V_p ($mL \cdot g^{-1}$)	r_p (Å)	S_t ($m^2 \cdot g^{-1}$)	N_{OH}/100 Å^2 [a]	α (%)
(Si)	295.3	0.7673	51.97	295.8	15.13	—
$(Si)_{6P}$	260.9	0.7208	55.25	255.8	—	6.0
$(Si)_{15P}$	196.4	0.6045	61.56	191.2	—	21.0
$(Si)_{25P}$	124.4	0.5038	70.78	133.3	—	34.0
$(Si)_C$	269.8	0.5697	42.23	271.2	2.04	—
$(Si)_{C\text{-}6P}$	238.4	0.5225	44.90	245.6	—	8.0
$(Si)_{C\text{-}15P}$	179.4	0.4044	50.02	183.4	—	29.0
$(Si)_{C\text{-}25P}$	98.8	0.3023	61.17	106.7	—	47.0

[a] N_{OH}/100 Å for (Si) and (Si)C was estimated and presented in Ref. 19.

For pore structure analysis, the *t*-curves of Sing et al. (20) on nonporous hydroxylated silica were used for all the studied samples. V_l–t plots were constructed, where V_l is the volume of N_2 adsorbed ($mL \cdot g^{-1}$) and t is the statistical thickness (Å). Straight lines, passing through the origin, were obtained, and the specific surface areas (S_t) were calculated from the slopes. The reasonable agreement between S_{BET} and S_t is the main criterion for the correct choice of the *t*-curve used in the analysis (Table 1).

The analysis of the pores in each case was carried out using a computer program written in FORTRAN IV language (21) for the IBM computer

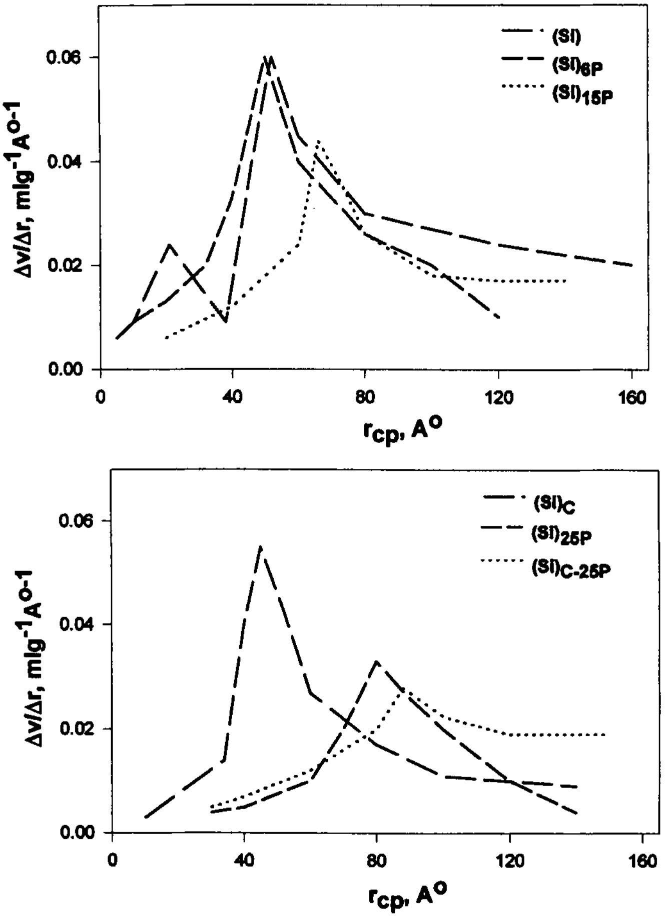

FIG. 1 Pore size distribution curves of silica supports and coated silica gels.

assuming a cylindrical pore (cp) model. The pore size distribution curves, shown in Fig. 1, represent the distribution of pore volumes ($\Delta V/\Delta r$) as a function of the most frequent hydraulic pore radii (r_{cp}, Å).

For the unmodified support (Si), the distribution curve shows a fraction of micropores and the most frequent hydraulic pore radius is observed at ~50 Å. This indicates that most of the surface is located in the mesopores region. The most frequent hydraulic pore radius of the calcined silica, $(Si)_C$, is shifted to a narrower region (~45 Å). This shift to a narrower pore region is in agreement with the lower value of the mean pore radius (r_p), calculated according to the BET model, of the $(Si)_C$ silica.

With respect to the silica gels treated with Carbowax 20M, the most frequent hydraulic pore radii are generally shifted to a wider pore region (55–85 Å) as compared with the silica supports. The fraction of micropores (r_{cp} = 5–60 Å) decreases markedly as the polymer loading increases. These findings can be attributed to the polymer preferentially occupying these micropores, as is clarified in Fig. 2.

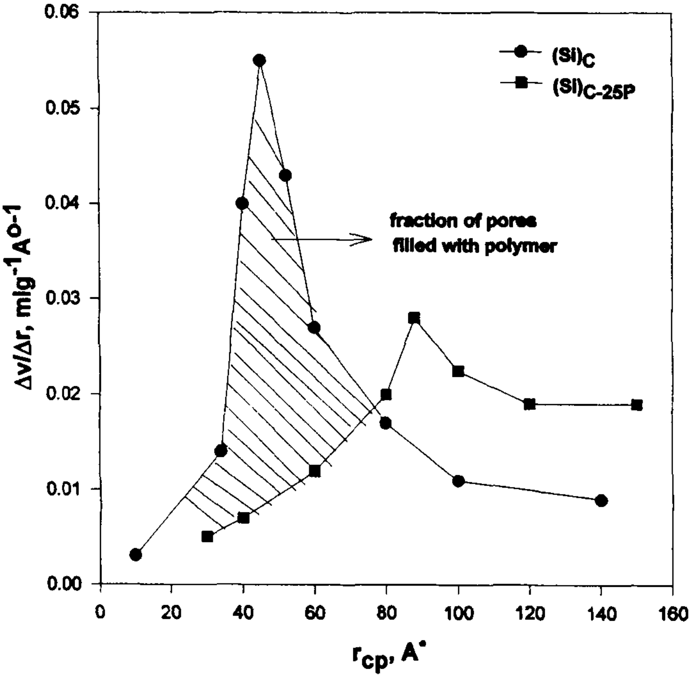

FIG. 2 Effect of coating with polymer on the porosity of silica gel.

The silica gels were subjected to infrared spectroscopy in order to investigated the effect of polymer loading on the —OH's of silica gel. The spectra of the studied samples are shown in Fig. 3. The infrared spectra of the silica gels show absorption bands at the 3419–3744 cm^{-1} range due to surface —OH's (22, 23). It is clear that the intensity of this absorption band decreases with increasing polymer loading. This may indicate more interaction of the polymer with the surface hydroxyls. It has been shown that silanol groups available on a fully hydroxylated silica gel interact with ether oxygens present in a Carbowax layer (24). From the spectra of $(Si)_{6P}$ and $(Si)_{C\text{-}6P}$, it seems that low polymer loading (viz., 6 wt%) is not enough to deactivate the surface of the silica supports.

Chromatographic Characterization

Thermodynamic Parameters

Thermodynamic parameters, including heat of adsorption (ΔH) and entropy (ΔS), may be useful in interpreting the deactivation of the silica surfaces as a result of coating by different polymer loadings. The heat of solution can be estimated by the following equation given by Green and Pust (25):

$$t_m = (LAB/F)e^{-\Delta H/RT} \tag{2}$$

where t_m = retention time (minutes), L = length of column (cm), A = internal area of the column (cm^2), B = constant, F = flow rate ($mL \cdot min^{-1}$), R = universal gas constant, and T = temperature of column (K).

By plotting log t_m versus $(1/T) \times 10^3$, a linear relationship was obtained and the heat of adsorption (ΔH), in $kJ \cdot mol^{-1}$, could be calculated from the slope of the straight line. The free energy (ΔG) and entropy of adsorption (ΔS) are expressed in $kJ \cdot mol^{-1}$ and $J \cdot mol^{-1}$, respectively, according to the equations (26):

$$\Delta G = RT \log Vg \tag{3}$$

$$\Delta S = (\Delta H - \Delta G)/T \tag{4}$$

where Vg is the retention volume (mL).

ΔH and ΔS for silica gels coated with polymer are given in Table 2. These parameters were calculated with the aid of retention data of n-hexane which was used as a probe for inverse gas chromatography. The effect of polymer loading can be illustrated by considering the silica gel supports, (Si) and $(Si)_C$. Both thermodynamic parameters decrease as the polymer loading increases. This is due to the deactivation of the silica surface, leading to less interaction with the solute.

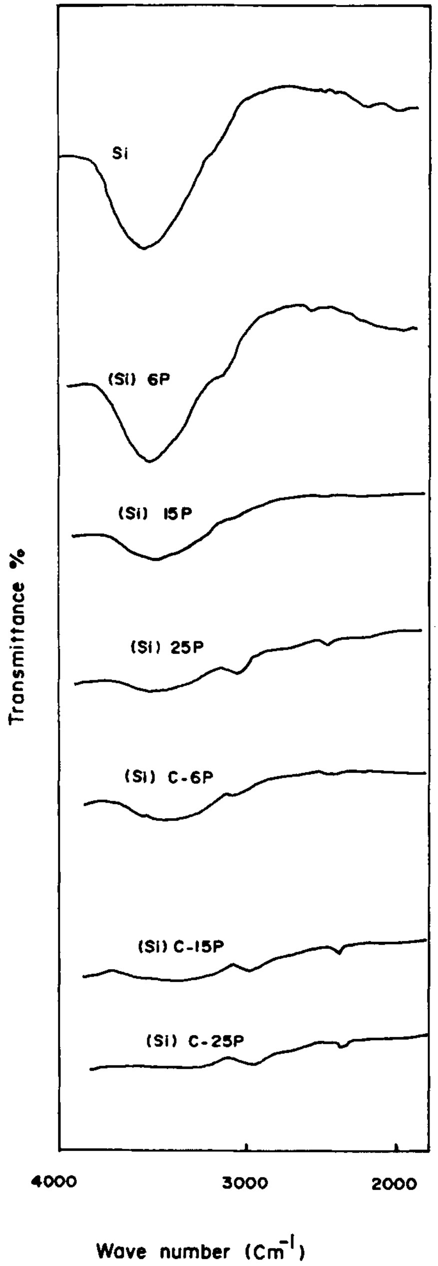

FIG. 3 Infrared spectra of the unmodified and coated silica gels.

TABLE 2
Thermodynamic Parameters (ΔH and ΔS) and Uniform Criteria (Δ) for the Studied Silica Gels

Sample	$-\Delta H$ (kJ·mol^{-1})	$-\Delta S$ (J·mol^{-1})	Δ	
			n-Alkanes	*n*-Alcohols
(Si)	11.34	121	0.366	0.000
$(Si)_{6P}$	9.61	62	0.374	0.000
$(Si)_{15P}$	9.33	56	0.459	0.237
$(Si)_{25P}$	8.19	43	0.480	0.275
$(Si)_C$	17.27	64	0.278	0.000
$(Si)_{C\text{-}6P}$	8.24	35	0.299	0.191
$(Si)_{C\text{-}15P}$	6.73	33	0.405	0.348
$(Si)_{C\text{-}25P}$	7.62	39	0.344	0.292

For $(Si)_{C\text{-}25P}$ silica gel, $-\Delta H$ and $-\Delta S$ values exceed those obtained in the case of $(Si)_{C\text{-}15P}$. Accordingly, one may conclude that the surface of the calcined silica will reach a maximum deactivation by coating it with 15 wt% of polymer. This can be explained in terms of the diffusional limitations of *n*-hexane which may take place by increasing the polymer loading to 25 wt%. The increase of polymer loading may be reflected in the crowd of polymer molecules occupying the pore of the silica. This is evidenced by a high α% value of 47 for $(Si)_{C\text{-}25P}$ coated silica gel.

Gas Chromatographic Separation

GC separations of the coated silica gels have been studied in terms of separation efficiency, peak shape, and duration of analysis. The separation has been tested using solutes of different polarities, namely *n*-alkanes (C_6–C_9) and *n*-alcohols (C_1—OH to C_4—OH). The efficiency of separation could be verified using the uniform criterion (Δ) which is calculated according to the following equation (27):

$$\Delta = n_K \tau K_{\mathrm{eff}}/t \tag{5}$$

where n_K = number of peaks in the chromatogram, τ = base width of narrowest peak, K_{eff} = separation factor for the worst separated pair of components, and t = duration of analysis. Table 2 shows the uniform criteria for model systems comprising the various classes of solutes. For instance, coating with a polymer gives different separation efficiencies depending on the polarities of the solutes.

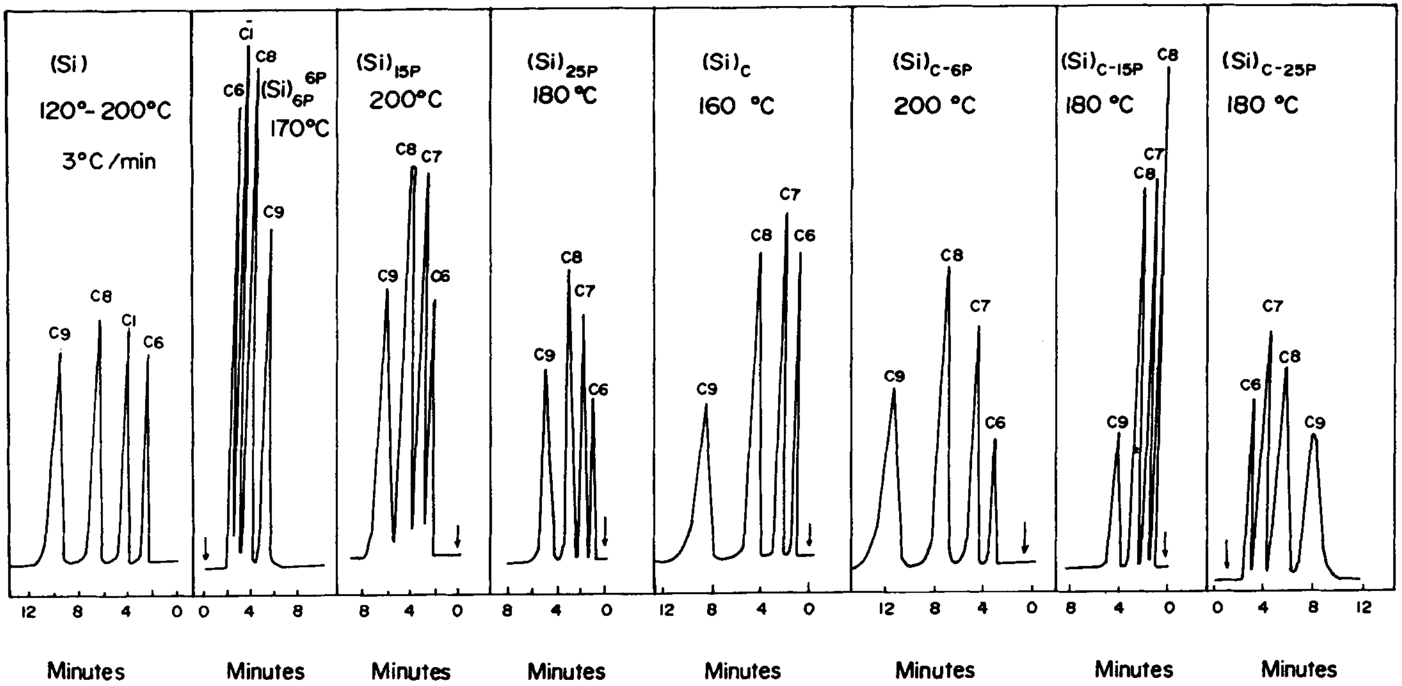

FIG. 4 Gas chromatographic separation of a mixture of *n*-alkanes by the studied silica gels.

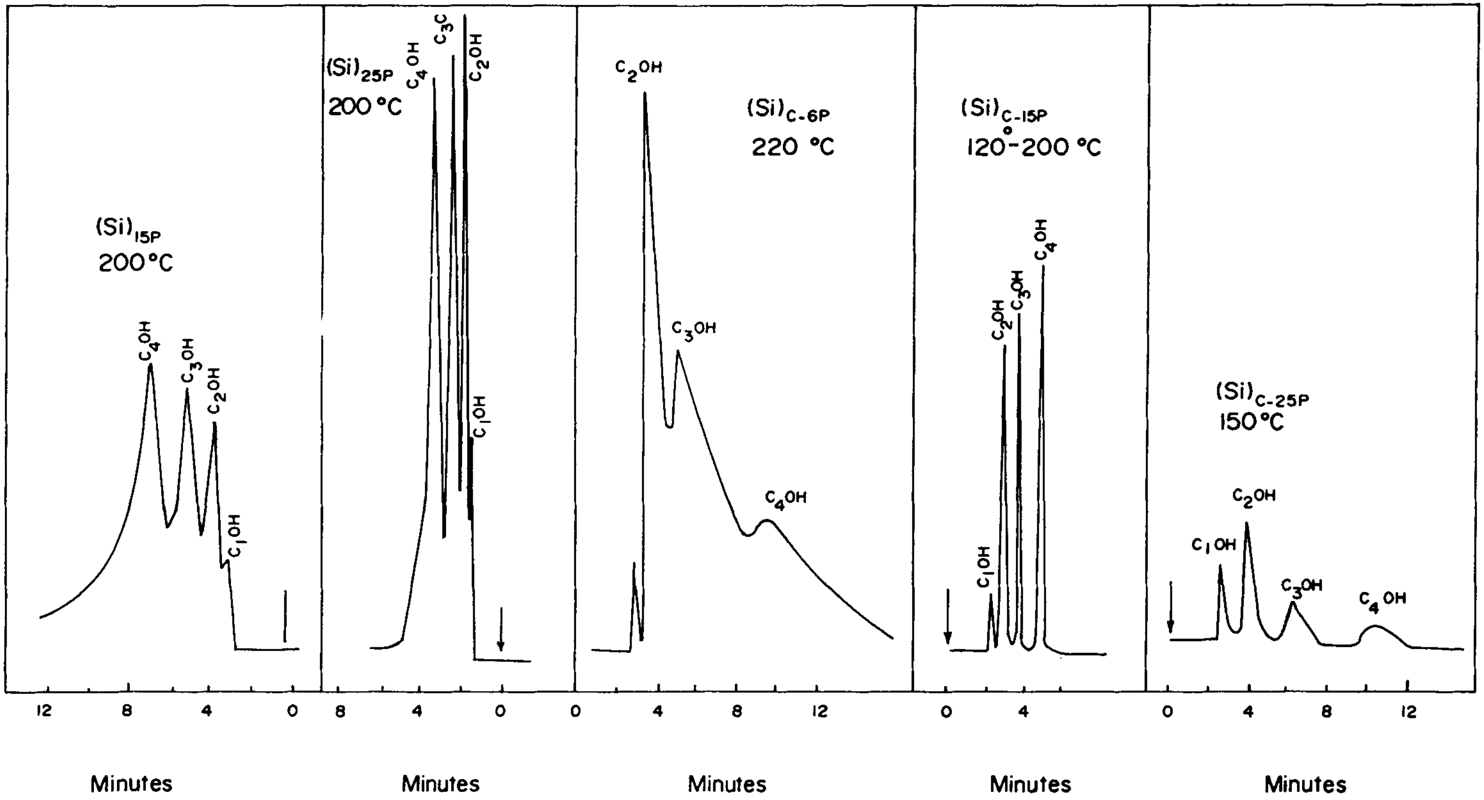

FIG. 5 Gas chromatograms of *n*-alcohols using modified silica gels as stationary phases.

Separation of **n*-Alkanes.*** Silica gels, either unmodified or coated with different polymer loadings, separate a mixture of *n*-alkanes (Fig. 4). For (Si)-coated silica gels, increasing the polymer loading increases the separation efficiency (Δ) of *n*-alkanes. This is due to the deactivation of the silica surface as proved by the results of infrared spectroscopy and thermodynamic parameters.

With respect to $(Si)_C$-coated materials, the highest efficiency (Δ = 0.405) was observed for $(Si)_{C\text{-}15P}$. This could be directly linked with the maximum deactivation of the silica surface brought about by coating with 15 wt% of Carbowax 20M, as previously discussed.

Separation of **n*-Alcohols.*** Figure 5 illustrates the separation of *n*-alcohols (C_1—OH to C_4—OH) using the various studied silica gels containing different loadings of polymer. The silica gels (Si), $(Si)_C$, and $(Si)_{6P}$ are not able to elute any detectable amounts of alcohols. This is due to the high surface reactivity of the unmodified silica gels. The reactivity of the surface arises from the occurrence of surface hydroxyls which may interact with —OH's of alcohols via hydrogen bonding. However, the coating of the silica gel with 6 wt% of Carbowax 20M, $(Si)_{6P}$, is not sufficient to deactivate the surface.

The coated silica gels containing 15 and 25 wt% of Carbowax 20M [$(Si)_{15P}$ and $(Si)_{25P}$, respectively] separate the alcohols, but the separation seems to be unacceptable for a quantitative analysis. Also, the $(Si)_{C\text{-}6P}$ silica gel elutes and separates the alcohols, but the chromatogram is not good (Fig. 5).

Only two packing materials of the calcined silica, $(Si)_{C\text{-}15P}$ and $(Si)_{C\text{-}25P}$, separate the *n*-alcohols with acceptable separation efficiencies (Δ = 0.348 and 0.292, respectively). It should be recalled here that $(Si)_{C\text{-}15P}$ revealed the maximum surface deactivation as evidenced by the lowest values of $-\Delta H$ and $-\Delta S$. The highest separation efficiency obtained at a short duration of analysis for the polar solutes could be considered as additional evidence for the high degree of deactivation of the $(Si)_C$ surface by coating it with 15 wt% of the polymer.

For each polymer loading, the calcined silica is much better than the untreated silica gel as a GC solid support used for the separation of alcohols. This is due to deactivation of the surface and reduction of the pore dimensions of silica gel by calcination treatment.

CONCLUSIONS

From the results obtained, one may conclude the following.

- A fraction of Carbowax 20 M interacts with the surface hydroxyls of silica gel whereas the remaining portion preferentially occupies micropores in the 5–60 Å range.

- The chromatographic separation of the nonpolar solutes (*n*-alkanes) is influenced by the deactivation of the silica surface due to coating with a proper polymer loading (viz., 15 wt% in the case of calcined silica).
- Decreasing the reactivity of the surface and reducing the pore dimensions of silica gel, as for a GC solid support, improve the efficiency of the Carbowax 20M-modified silica gels for separation of polar solutes (*n*-alcohols).

REFERENCES

1. S. P. Boudrea and W. T. Cooper, *Anal. Chem.*, *16*, 41 (1989).
2. S. Kapila and W. A. Aue, *J. Chromatogr.*, *78*, 35 (1973).
3. A. Namura, J. Yamada, K. Tsuonda, and K. Fukushina, *Anal. Sci.*, *5*, 335 (1989).
4. H. Halpaap, *J. Chromatogr.*, *78*, 63 (1973).
5. A. N. Kiselev, N. V. Kovaleva, and Yu. S. Nikitin, *Ibid.*, *58*, 19 (1971).
6. A. N. Kiselev, *Ibid.*, *49*, 84 (1970).
7. J. J. Pesek and J. A. Graham, *Anal. Chem.*, *49*, 133 (1977).
8. P. Van Der Voort, I. G. D'Hamers, K. C. Vtancken, and E. F. Vansant, *J. Chem. Soc., Faraday Trans.*, *87*, 3899 (1991).
9. M. M. Kopecini, S. K. Milonjic, and R. J. Laub, *Anal. Chem.*, *52*, 1032 (1980).
10. C. Gaget, D. Morel, and J. Serpinet, *J. Chromatogr.*, *244*, 209 (1982).
11. W. A. Aue, C. R. Hastings, and S. Kapila, *Ibid.*, *77*, 299 (1973).
12. M. M. Daniewski and W. A. Aue, *Ibid.*, *47*, 119 (1978).
13. C. R. Vogt and W. A. Aue, *J. Chromatogr., Sci.*, *16*, 268 (1978).
14. J. A. Jonsson, L. Mathiasson, and Z. Suprynowicz, *J. Chromatogr.*, *207*, 69 (1981).
15. J. H. De Beor, *Faraday Discuss.*, p. 52 (1971).
16. W. A. Aue, S. Kapila, and K. O. Gerhatdt, *J. Chromatogr.*, *78*, 228 (1973).
17. S. Brunauer, P. H. Emmett, and E. J. Teller, *J. Am. Chem. Soc.*, *60*, 309 (1938).
18. R. Sh. Mikhail, S. Brunauer, and E. E. Bodor, *J. Colloid Interface Sci.*, *26*, 45 (1968).
19. S. Faramawy, A. M. El-Fadly, A. Y. El-Naggar, and A. M. Youssef, *Surf. Coat. Technol.*, In Press (1997).
20. J. D. Carruther, P. A. Cutting, M. R. Harris, S. A. Mitchell, and K. S. W. Sing, *Chem. Ind.*, p. 1772 (1968).
21. R. Sh. Mikhail, S. A. Selim, and A. Goned, *Egypt. J. Chem.*, *18*, 957 (1975).
22. J. H. De Boer, *Physical and Chemical Aspects of Adsorbents and Catalysts*, Academic Press, New York, NY, 1970.
23. J. L. M. Van De Venne, J. P. M. Rindt, and G. J. M. Coenerr, *J. Colloid Interface Sci.*, *74*, 287 (1980).
24. P. K. Her, *The Colloid Chemistry of Silica and Silicates*, Cornell University Press, Ithaca, NY, 1955, p. 58.
25. S. A. Green and H. Pust, *J. Phys. Chem.*, *62*, 55 (1958).
26. Z. Kessaissa, E. Papirer, and J. B. Donnet, *J. Chromatogr.*, *196*, 481 (1980).
27. T. G. Andronikashvili, G. A. Tsitsishviti, T. K. Kvernadze, and N. G. Okudzhava, *Ibid.*, *406*, 145 (1987).

Received by editor February 20, 1997
Revision received May 1997