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Inverse phase gas chromatographic study on non-extractable modifiers for silica gel. II- solubility and surface parameters

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ABSTRACT

The silica gel was modified with non-extractable thin film of polyethylene glycol-20M, polyethylene glycol-4000 and linear polyethylene of low density. The pretreatment methods: hydrothermal treatment and calcinations at 800 and 1100°C were used to get on more homogenous surfaces more suitable for non-extractable thin film formations. Physicochemical characteristics of this layer and its influence on the modified silica gel properties were characterized by inverse phase gas chromatography via the calculation of both surface and solubility parameters. The influence of solubility and surface parameters on probes retentions were presented and discussed.

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KEYWORDS

Non-extractable thin film;
Silica;
Gas chromatography;
Surface;
Solubility.

INTRODUCTION

Inverse gas chromatography is an extension of conventional gas chromatography in which a nonvolatile material to be investigated is immobilized in column. This stationary phase is then characterized by monitoring the passage of volatile probe molecules of known properties as they carried through the column by inert carrier gas. IGC is now used to study synthetic and biological polymer, copolymers, polymer blends, glass and carbon fiber, coal, solid food, modified silicas, surfactants, petroleum pitches and heavy residues of oil distillation^[1].

The syntheses of a number of modified diatomaceous earth supports that carry non-extractable layers of polymers ranging in polarity from polyethylene to polydiethylene glycol succinate have been early de-

scribed^[2-4]. These modified supports were corollaries to a similar material based on carbowax-20M, which proved to be a well deactivated, fast and efficient phase in gas chromatography. The typical carbowax load was between 0.1 and 0.2%^[3].

The advantages of these column packings are that are reasonably selective, low bleed, highly inert, i.e. can used for separation trace levels of highly polar compounds^[5]. The non-extractable prefix result from the failure extraction of these polymeric coating with strong solvent in a Soxhlet for a long time, ca. month.

All results of earlier investigation^[6-8] indicated that the modifier structure influences both properties of the monolayer formed on the surface of silica gel and surface properties of the obtained adsorbent. In many cases, this extremely thin film (may be monolayer) al-

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lows fast and efficient chromatographic separation of high molecular weight polar compounds. Although the support appears well deactivated, surface forces can be assumed to contribute significantly to retention. The aim of the present article is the probe of these surface forces via inverse phase gas chromatographic characterization of a number of the pretreated silica supports modified by non-extractable PEG-20M, linear polyethylene and PEG-4000 by the calculation of thermodynamic quantities.

Theory

Properties of the monolayer may be determined by the solubility parameter δ_2 that is calculated from the slop of the plot of the left hand side of Eq.(1) versus δ_1 (the solubility parameter of test solutes):

$$\delta_1^2/RT - \chi_{s\infty}/V_1^\circ = (2\delta_2/RT) \cdot \delta_1 - (\delta_2^2/RT + \chi_{s\infty}/V_1^\circ) \quad (1)$$

Where R is the gas constant, T is the absolute temperature, V_1° is the molar volume of the probe solutes, χ^s is the solute-solvent interaction parameter proposed by Dipaola-Baranyi and Guillet^[9], $\chi_{s\infty}$ is the entropic term of χ^∞ .

Using different types of probe solutes it is possible to obtain the dispersive and specific component of solubility parameter^[10,11]. It was shown earlier that the solubility parameter (and its increments) could be successfully used for characterization of organic layer bonded to silica surface^[12]. Another way to express changes in modified supports in comparison to the raw one is to calculate surface parameters. These parameters express intermolecular interactions in adsorbent-adsorbate system and may be generally divided into dispersive and specific. Dispersive properties of the examined supports can be expressed by $C'P_{DS}$ parameter proposed by Dong et al.^[13] and written as:

$$RT \cdot \ln V_N + C = C \cdot P_{DS} \cdot P_{DP} \Delta G^S \quad (2)$$

Where C and C' are constants, ΔG^S is the specific component of adsorption energy (for n-alkanes $\Delta G^S=0$), P_{DS} and P_{DP} denote molar deformation polarization of the solid and probe, respectively.

Authors^[13] proved that $RT \ln V_N$ is proportional to P_{DP} . This dependence is linear and the slope of the line is equal $C'P_{DS}$. Parameter $C'P_{DS}$ is a measure of ability of a surface being characterized to undergo dispersive interactions and is known as the Dong parameter. The specific component of adsorption energy ΔG^S was also calculated by subtracting from adsorption energy

of polar probe adsorption energy of a hypothetical n-alkane having the same value of boiling point. ΔG^S is calculated for all polar probes at four temperatures which allows us to calculate the specific component of enthalpy of adsorption ΔH^S required in calculating acid-base properties of the examined surface^[14]. The specific component of enthalpy of adsorption ΔH^S is further correlated to parameters characterizing surface ability to specific interactions^[15]:

$$-\Delta H^S = K_D \cdot AN + K_A \cdot DN \quad (3)$$

Where AN and DN are the acceptor and donor number of the test solute, K_A and K_D reflect the ability of the examined surface to act as electron acceptor or donor, respectively. Parameters K_A and K_D are calculated from the transformed Eq.(4):

$$(-\Delta H^S)_i / AN_i = K_A (DN_i / AN_i) + K_D \quad (4)$$

Where index 'i' means parameters of the different test compounds.

EXPERIMENTAL

Preparation of silica supports

1. Pretreatment methods

Acid washing

Parent silica 90-120mesh was acid washed with hot 6 N HCl as described earlier. This operation was done in a 250ml beaker by simply slurring the support with hot acid in the beaker. Until the color became yellow, the acid was occasionally replaced. Usually no more than three or four washing were required to remove all traces of yellow color. The support was then washed with several portions of distilled water to remove excess acid and neutrality. The acid washed support was then oven dried at 150°C overnight.

2. Hydrothermal treatment

Portions (10g of each) of the acid-washed silica gels were well covered with distilled water (10ml) in a glass insert tube and hydrothermally treated at temperature 250°C in a high-temperature bomb, much as described earlier^[16], i.e. the bomb was lowered into a large drying furnace preset at 250°C for 24h. Then removed from the furnace with due caution, and left to cool down in a safe place. The treated silica gels were acid washed as before in order to remove any traces of metals originat-

ing from the bomb.

3. Calcination

A 10g of acid washed silica in a 25 ml crucible placed into a muffle furnace and the temperature was preset at 800°C for 6h.

Treatment method

1. Preparation of support non- extractable thin film carbowax 20M packing

For preparation of non-extractable very thin film of carbowax 20M on the silica support, 0.20g of the carbowax-20M was dissolved in 50ml of chloroform, and then added to 10g of the acid washed or pretreated support to prepare 5% coated support after solvent evaporation. The heat treatment process (support bonding) was done in a 100ml volumetric pipette connected to the injector of sigma-3B gas chromatograph at 270°C for 16h according to Moseman procedure^[3]. The non-support-bonded Carbowax-20M was extracted from the silica gel support by refluxing in chloroform for 10 h until two successive washes yield no visible yellow color^[3].

2. Preparation of support-non-extractable thin film carbowax 4000 packing

The packing was prepared as described above with the difference; the temperature of heat treatment was kept at 220°C for 16h^[17].

3 Preparation of support- non-extractable thin film linear polyethylene packing

The packing was prepared as described above with the difference, the temperature of heat treatment was kept at 260°C for 16h, and toluene is used as the extraction solvent^[3].

IGC experiments

Conditions of inverse phase gas chromatographic experiment were as follows: column stainless steel, 1m×3mm i.d., measurements temperatures ranged from 90-170°C, temperatures FID detector and injector 160°C; carrier gas nitrogen at flow rate 30 ml/min., gas chromatograph Perkin-Elmer sigma 3 B. the volatile test compound were four groups: (i) n-alkanes: C₅-C₁₀; (ii) Alkylated-aromatics: benzene, toluene, ethylbenzene, p-xylene, o-xylene and iso-propylbenzene; (iii) halo-

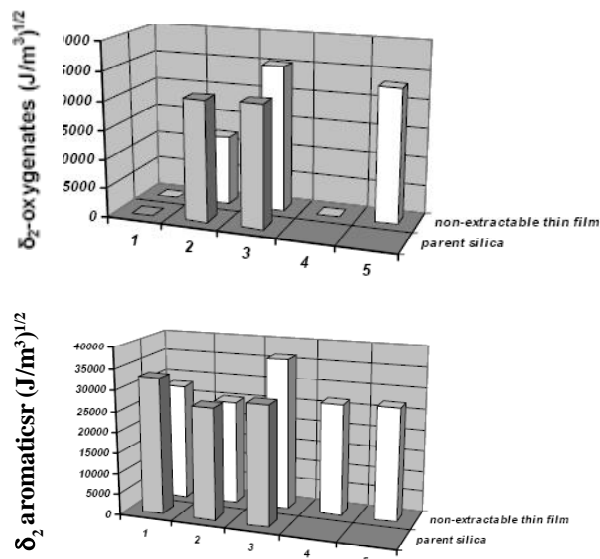


Figure1: Values of the polar increment of solubility parameter.

Parent silicas: (1) Si_p; (2) Si_{C1100}; (3) Si_{hydrothermal}; Non-extractable thin film modified silicas: (1) PEG-20M-Si_p (2) PEG-20M-Si_{C800} (3) PEG-20M-Si_{Hydrothermal} (4) PE-Si_{Hydrothermal} (5) PEG-4000-Si_{Hydrothermal}

TABLE 1 : Designations of the investigated modified silicas

Modified Support	Designation
Parent raw silica	Si _p
Calcined silica at 1100°C	Si _{C1100}
Hydrothermal treated silica	Si _{Hydrothermal}
Polyethylene glycol-20M bonded parent silica	PEG-20M-Si _{Hydrothermal}
Polyethylene glycol-20M bonded calcined silica at 800°C	PEG-20M-Si _{C800}
Polyethylene glycol-20M bonded Hydrothermal treated silica	PEG-20M-Si _{Hydrothermal}
Linear-polyethylene bonded Hydrothermal treated silica	PE-Si _{Hydrothermal}
Polyethylene glycol-4000 bonded Hydrothermal treated silica	PEG-4000-Si _{Hydrothermal}

genated-aromatics: chlorobenzene, bromobenzene and (vi) oxygenates: methanol, ethanol, n-propanol, n-butanol, acetone, 2-butanone and 3-methyl-2-pentanone and diethylether. The amount of injected compound from 0.1 to 1µl of the test compound.

RESULTS AND DISCUSSION

Solubility parameter

Values of the dispersive and polar components of the solubility parameter were calculated using n-alkanes and aromatics and oxygenated probes, respectively, for

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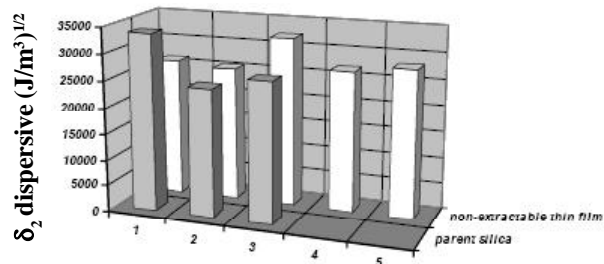


Figure 2: Values of the dispersive increment of solubility parameter

the non-extractable thin film-modified silica supports given in TABLE 1.

Changes in values of these parameters depend on the structure of non-extractable polymeric layer and pre-treatments. Careful inspection of the data in figure 1 leads to the following observations: (i) the hydrothermal treatment cause the decreasing the value of δ_d component as result of decreasing surface area from 331 to 144.6m²/g; (ii) the values of the dispersive component δ_d of the solubility parameter are lower for the PEG-20M-Si_p and PEG-20M-Si_{C800} supports compared to unmodified Si_p and (iii) the values of the dispersive component δ_d of the solubility parameter are higher for the non-extractable-thin film-modified hydrothermal pretreated silica supports compared to unmodified Si_{Hydro}. Where, these modified hydrothermal pretreated silica supports can be arranged as: PEG-20M-Si_{Hydrothermal} > PEG-4000-Si_{Hydrothermal} > PE-Si_{Hydrothermal} according to δ_d value increment. This difference can be attributed to the chemical structure of the polymer and in particular, to its conformation structure on the surface of silica. However, the changes in the values of δ_d are not considerable.

The difference between the parent and hydrothermal pretreated silica supports with respect to the effect of thin bonded film on δ_d value may be rendered to the difference in their surface texture characteristic, i.e. porosity, surface area, pore size, ...etc of both supports which effected the conformation, continuity of thin bonded layer and polymer deposition in surface irregularities. In case of highly active heterogeneous parent silica surface, it would appear that the polymer progressively saturate the more active sites by preferential adsorption, causing the probes to access the less energetic free sites^[18], the amount of polymer is not enough

to form continuous film on this surface type. While the same polymer amount may form a continuous film on the more inert and smooth surface of Si_{Hydrothermal} support, causing probes to access the bonded film^[19]. The modified silica support may contain different active sites. Values of the polar component of solubility parameter for examined silica supports with respect to oxygenated probes δ_{p-ox} differ considerably from each other (Figure 2). Values of δ_{p-ox} parameter are lower for the modified silica gel than for unmodified. The oxygenated probes not eluted from Si_p, PEG-20M-Si_p and PE-Si_{Hydrothermal} supports, which give an indication about the free highly energetic sites with respect to these modified silicas. Ketones only eluted on PEG-Si_{C800} support, which has the lowest δ_{p-ox} value. For PEG-20M-Si_{Hydrothermal}, PEG-4000-Si_{Hydrothermal} the value of δ_{p-ox} parameter is higher than for unmodified Si_{Hydrothermal} and Si_{C1100}. These two modified supports have the highest the values of δ_{p-ox} parameter, indicating that these two modified supports are the most suitable for separation the oxygenated solutes. Non-elution of the oxygenated probes from PE-Si_{Hydrothermal} support indicating on the existence of hydrogen bonds between PEG-20M and PEG-4000 oxygen atoms and the free silanols on hydrothermal treated silica surface^[20].

Values of the polar component of solubility parameter for examined silica supports with respect to aromatic probes δ_{p-arom} not differ considerably from each other (Figure 2). Values of δ_{p-arom} component of solubility parameter for the modified silica supports are lower for the modified silica supports than for unmodified, with the exception of PEG-20M-Si_{Hydrothermal} support. This gives an indication about the nature of the interactions between the modifiers and aromatic-energetic sites of silica surface. The modified silicas can be arranged as PEG-20M-Si_{Hydrothermal} > PEG-4000-Si_{Hydrothermal} \approx PEG-20M-Si_p > PE-Si_{Hydrothermal} \approx Si_{Hydrothermal} > PEG-20M-Si_{C800} according to δ_{p-arom} value increment. The δ_{p-arom} difference values for the calcined and hydrothermal treated supports give an indication about the ability of hydrogen bonding between surface silanols and oxygen atoms of PEG-20M depend on the availability of these groups on mesopores hydrothermal treated surface compared to the collapsed calcined surface. The similarity in δ_{p-arom} values for PE-Si_{Hydrothermal} and unmodified form gives an indication about such modifica-

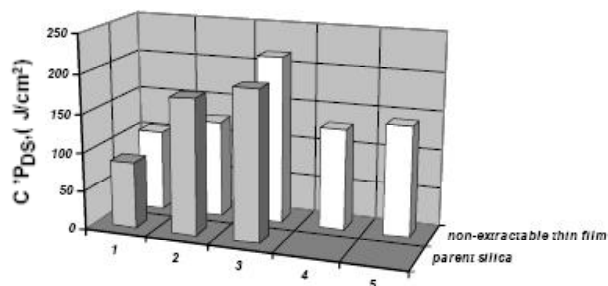
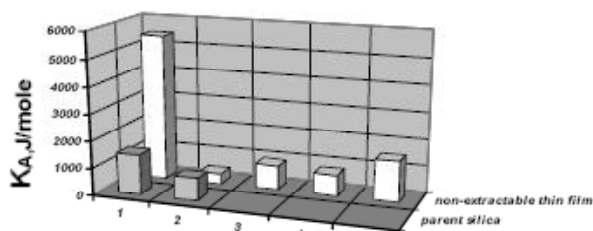
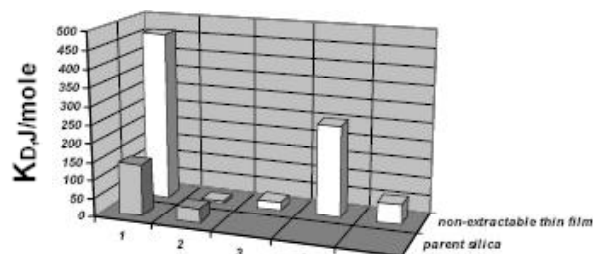


Figure 3: Values of Dong parameter

Figure 4: Values of K_A parameterFigure 5: Values of K_D parameter

tion process not depend only on modifier-shielding of surface silanols but also on the interactions between the functional groups of the given modifier and surface silanols^[20].

Surface parameters

The surface of the modified silica gel was characterized with the use of the Dong parameter and parameters K_A , K_D reflecting the ability of the examined surface to act as electron acceptor or electron donor, respectively. Also, the structure and the conformation of thin bonded film determine properties of the modified silica gel as well.

For all modified silicas, it can be observed the higher values of $C' P_{DS}$ parameter than the raw silica gel (Figure 3). PEG-20M-Si_{Hydrothermal} modified support has the highest value of the $C' P_{DS}$ parameter while PEG-20M-Si_p modified support has the lowest value. The thin

bonded modified silicas can be ordered as: PEG-20M-Si_{Hydrothermal} > PEG-4000-Si_{Hydrothermal} > PE-Si_{Hydrothermal} > PEG-20M-Si_{C800} > PEG-20M-Si_p according to the increase in the value of $C' P_{DS}$ parameter. The difference between the values of this parameter for the PEG and PE modifiers can be rendered to the hydrogen bonding formation between the oxygen of the ethylene oxide unit and surface silanols groups. The difference between the values of this parameter for the PEG-20M and PEG-4000 modifiers can be rendered to the number of hydrogen bonding. The higher value of $C' P_{DS}$ parameter for PEG-20M-Si_{Hydrothermal} than for PEG-20M-Si_{C800} and PEG-20M-Si_p can be explained in the term of the roughness or irregularities of the solid surface which determine the conformation of thin bonded film.

On the other hand, all polymeric modified samples have the lower value of $C' P_{DS}$ parameter than the raw hydrothermal treated form except for PEG-20M-Si_{Hydrothermal} modified support. The difference may rendered to the long chain length of PEG-20M compared to the other modifiers. For most of the modified supports, it is observed that lower K_A values than for the unmodified silica gel, except for PEG-20M-Si_p and PEG-4000-Si_{Hydrothermal}. PEG-20M-Si_{C800} has the lowest K_A and K_B values due to removal of the silanol active sites and the formation of modified siloxane linkages by calcinations treatment. The lower values of these parameters for hydrothermal treated form than the raw silica gel due to the removal silanol groups by the effect of water pressure while increased values for PEG-4000-Si_{Hydrothermal} compared to un-coated Si_{Hydrothermal} may to due the conformation of the thin film on the solid surface. The higher values of the K_A and K_B for PEG-20M-Si_p indicating increase the surface activity of silanols groups by thin film of such roughness surface. The higher value of K_D for PE-Si_{Hydrothermal} due to double bonds of polyethylene thin film.

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Full Paper

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