Properties of Zirconate Modificates of Silica Gel as Examined by Inverse Gas Chromatography

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SUMMARY: In our work the silica gel was modified at three temperatures by the zirconium coupling agents. As a result one obtains monomolecular layer of the zirconate on the silica gel surface. The physico-chemical properties of this layer and its influence on the modificate properties may be characterized by inverse gas chromatography (IGC) and expressed by both solubility parameters and surface parameters. The influence of the temperature of the modification and the modifier structure on the modificate's properties was examined and discussed. In this paper we looked for the relationships between the solubility parameter δ_2, its components and surface parameters γ_s^d, K_A, K_D and S_C.

Introduction

To characterize the monolayer one needs to use the solubility parameter δ_2 being is the square root of the energy density[1]. For non volatile species DiPaola-Baranyi and Guillet[2] proposed to calculate this parameter using solute-solvent interaction parameter χ^∞. The solubility parameter characterizing non volatile compounds δ_2 can be calculated as a slope of the plot of the left-hand side of equation (1) versus the solubility parameters of the series of chosen test compounds δ_1

$$\frac{\delta_1^2}{RT} - \frac{\chi^\infty}{V_1^0} = \frac{2\delta_2}{RT}\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_S^\infty}{V_1^0}\right) \quad (1)$$

where V^0 is molar volume of test solutes. Using different types of the test compounds one can obtain the dispersive δ_d and specific δ_S component of the solubility parameter[3]. One can also calculate the corrected solubility parameter δ_T derived from equation proposed by Price[4]

$$\delta_T^2 = \delta_d^2 + \delta_s^2 \quad (2)$$

Inverse gas chromatography is also a useful technique in the determination of the free surface energy and acid-base properties of the examined materials. The dispersive component

 CCC 1022-1360/00/$ 17.50+.50/0

of the free surface energy γ_s^d can be calculated using experimentally determined ΔG_{CH_2} after transformation of the equation (3) [5)]

$$\Delta G_{CH_2} = N \cdot a_{CH_2} \cdot 2\left(\gamma_s^d \cdot \gamma_{CH_2}\right)^{1/2} \tag{3}$$

where: N denotes Avogadro number, a_{CH_2} - the surface covered by one methylene group and γ_{CH_2} - free surface energy of polyethylene.

The dispersive properties of the examined materials can also be determined with the use of Dong parameter $C'P_{DS}$. This parameter can be calculated as a slope of adsorption energy ΔG versus molar deformation polarisation of n-alkanes P_{DP} used as the test compounds.

The acid-base properties of the examined surface can be determined after calculating the specific component of adsorption energy ΔG^S. For each polar probe the specific component of adsorption energy ΔG^S can be calculated by subtracting adsorption energy ΔG_{probe} of the probe from adsorption energy $\Delta G_{n\text{-}alkane}$ of a hypothetical n-alkane having the same molar deformation polarisation P_{DP}. From the temperature dependence of the specific component of adsorption energy ΔG^S one may calculate the enthalpy of specific interactions ΔH^S. The acid-base properties can be determined with the use of ΔH^S and transformed equation (4)

$$-\Delta H^s = K_D \cdot AN^* + K_A \cdot DN \tag{4}$$

where: AN^* and DN denotes 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 and electron donor, respectively. The acid-base parameters are calculated for a series of test compounds as a slope of the plot of the left-hand side of the transformed equation versus AN^*/DN and DN/AN^*. The surface character may also be determined as the ratio of the K_D and K_A parameters: $S_C=K_D/K_A$.

Experimental Part

Modifications

Four zirconium coupling agents were used to modify silica gel. They were as follows:

- Zirconium IV, (neoalkoxy)tris(2-propenoato-O) (called NZ39),
- Zirconium IV, (neoalkoxy)tris(2-methyl-2-propenoato-O) (NZ33),
- Zirconium IV, (neoalkoxy)tris(dodecylbenzenesulfonato-O) (NZ09),
- Zirconium IV, (neoalkoxy)tris[(2-ethylenediamino)ethylato] (NZ44).

The silica gel (Fluka, 'Silica gel 60' 0.2-0.5 mm (35-70 mesh)) was modified in isopropanol solution at three temperatures: room temperature (~20°C), 50°C and 70°C. The zirconates were used in proportion to the silica gel 20:100 (weight parts). After 2 hours of modification the excess of the zirconates was extracted with isopropanol in Soxhlet apparatus. The content of zirconium in the monolayer was determined by X-ray fluorescence (OXFORD model ED^{2000}). The molecular coverage ratio varied from 1.8 to 2.5 μmol Zr/m^2.

IGC experiments

The conditions of IGC experiments were as follows: column stainless steel, 1 m, 3 mm I.D., measurement temperatures 120, 130 and 140°C, temperatures of injector and FID detector 160°C, carrier gas helium at flow rate 40 ml/min, gas chromatograph Chrom 5 (Kovo, Czech Republic). The amount of the column filling varied from 4.659 to 6.001 g and injection volumes from 0.1 to 1.0 ml of vapours of test compounds. The volatile test compound: n-alkanes from n-pentane to n-nonane, benzene, carbon tetrachloride, chloroform and methylene chloride. This narrow range of test solutes is connected with relatively high acidity of silica gel. The test solutes having basic character adsorb too strong and can not be used in IGC examination of silica gel. An example of such a selection of test compounds for IGC examination of different silicas can be found in literature[6].

Results and Discussion

The values of the solubility parameter δ_2 decreased after modification of silica gel with all the zirconium modifiers. The modification caused the increase of the values of the dispersive increment of the solubility parameter δ_d and the decrease of the values of its specific-polar increment δ_p (Table 1). The values of the corrected solubility parameter δ_T and the solubility parameter δ_2

decreased in order silica gel > silica gel modified with NZ39 > silica gel modified with NZ09 > silica gel modified with NZ33 > silica gel modified with NZ44 (for modification at 50°C and measurement at 130°C - see Table 1). Please note that the values of the solubility parameters for silica gel are only hypothetical and were calculated only for the sake of comparison. The values of the dispersive increment of the solubility parameter δ_d decreased in order NZ39 > NZ09 > NZ44 > NZ33 > silica gel while the values of the polar increment of the solubility parameter δ_p decrease in order silica gel > NZ33 > NZ09 > NZ39 > NZ44. As changes in the dispersive increment of the solubility parameter δ_d are very small we can not

determine how it can influence the values of the parameters δ_T and δ_2. However, we can observe the substantial influence of the polar increment of the solubility parameter δ_p on the parameters δ_T and δ_2.

The values of the dispersive component of the free surface energy γ_s^d and $C'P_{DS}$ decreased in order silica gel modified with NZ44 > silica gel modified with NZ09 > silica gel modified with NZ39 > silica gel modified with NZ33 > silica gel. The values of these parameters change in similar order to that found for the dispersive increment of the solubility parameter δ_d (measurements carried out at 120 and 140°C). The highest values of the dispersive parameters can be found after modification with NZ44 and NZ09 having alkyl and amino-alkyl groups.

Table 1. Solubility parameters [10^3*$(J/m^3)^{1/2}$] determined for the examined modified silica gel (IGC at 130°C).

Material	δ_T	δ_d	δ_p	δ_2
unmodified silica gel	16.7±0.2	13.0±0.1	10.5±0.3	16.2±0.1
silica gel modified with NZ 33 at 20°C	14.8±0.2	13.3±0.1	6.3±0.5	15.6±0.1
silica gel modified with NZ 33 at 50°C	14.9±0.3	13.1±0.1	7.1±0.7	15.6±0.1
silica gel modified with NZ 33 at 70°C	15.0±0.3	13.1±0.1	7.2±0.7	15.6±0.1
silica gel modified with NZ 39 at 20°C	15.5±0.1	13.4±0.1	7.7±0.2	16.2±0.1
silica gel modified with NZ 39 at 50°C	15.2±0.2	13.7±0.1	6.6±0.5	15.9±0.1
silica gel modified with NZ 39 at 70°C	14.8±0.2	12.9±0.1	7.2±0.4	15.6±0.1
silica gel modified with NZ 09 at 20°C	14.7±0.2	13.5±0.1	5.9±0.8	15.5±0.1
silica gel modified with NZ 09 at 50°C	15.1±0.2	13.4±0.1	7.1±0.2	15.7±0.1
silica gel modified with NZ 09 at 70°C	15.1±0.2	13.3±0.2	7.1±0.4	15.8±0.1
silica gel modified with NZ 44 at 20°C	13.5±0.2	13.3±0.1	2.6±0.1	14.5±0.1
silica gel modified with NZ 44 at 50°C	14.2±0.1	13.3±0.1	5.0±0.1	15.2±0.1
silica gel modified with NZ 44 at 70°C	14.4±0.1	13.8±0.1	4.3±0.3	15.1±0.1

The values of the parameter K_A with exception of NZ39 decreased after modification in the following order: silica gel modified with NZ39 > silica gel > silica gel modified with NZ09 >

silica gel modified with NZ33 > silica gel modified with NZ44 (Fig.1.). This order can be compared with

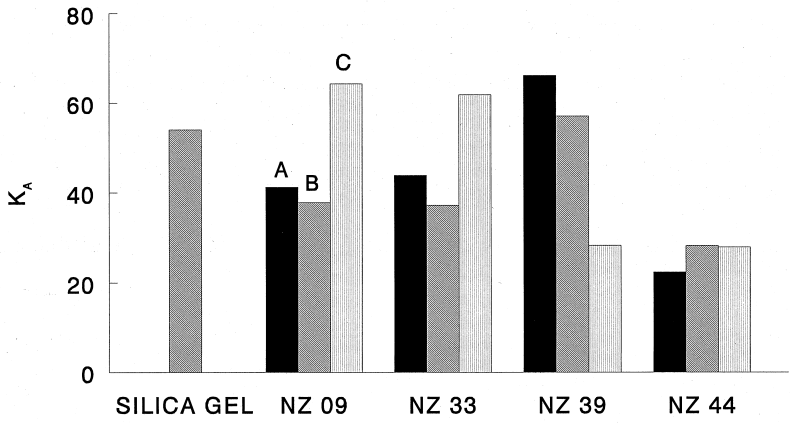

Fig.1. The influence of the silica gel modification on the values of the K_A parameter A - modification temp. 20°C, B - modification temp. 50°C, C - modification temp. 70°C.

changes of the values of the polar increment of the solubility parameter δ_p. The values of the parameter K_D changed as follows silica gel modified with NZ44 > silica gel modified with NZ39 ≈ silica gel modified with NZ33 > silica gel modified with NZ09 > silica gel (Fig.2.) and the values of

the parameter S_C changed similarly: silica gel modified with NZ44 > silica gel modified with NZ39 > silica gel modified with NZ33 ≈ silica gel modified with NZ09 > silica gel (Fig.3.). We can clearly observe the influence of the modifier structure on the modified silica gel properties. The modifiers having basic groups caused an increase in the S_C values of the modified silica gel. We can observe some deviations from changes described above (see Fig.1. and Fig.3.) for the values of parameters K_A and S_C. However, it does not change the conclusion that we must use modifier NZ44 if we want to obtain the modified silica gel with properties which differ most from the raw silica gel.

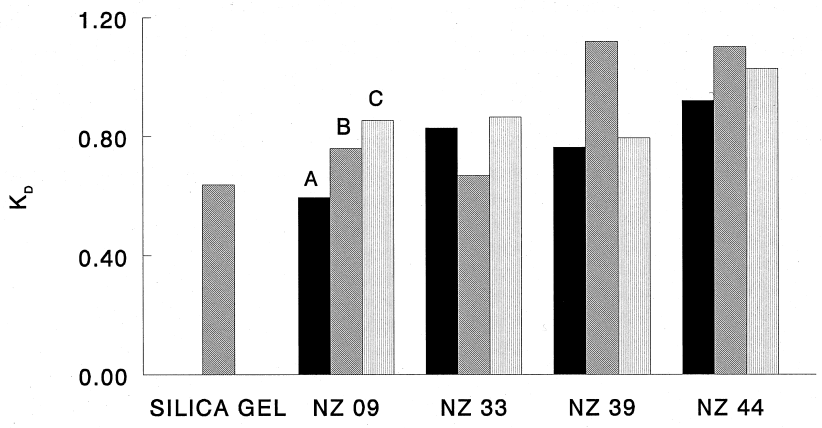

Fig.2. The influence of the silica gel modification on the values of the K_D parameter A - modification temp. 20°C, B - modification temp. 50°C, C - modification temp. 70°C.

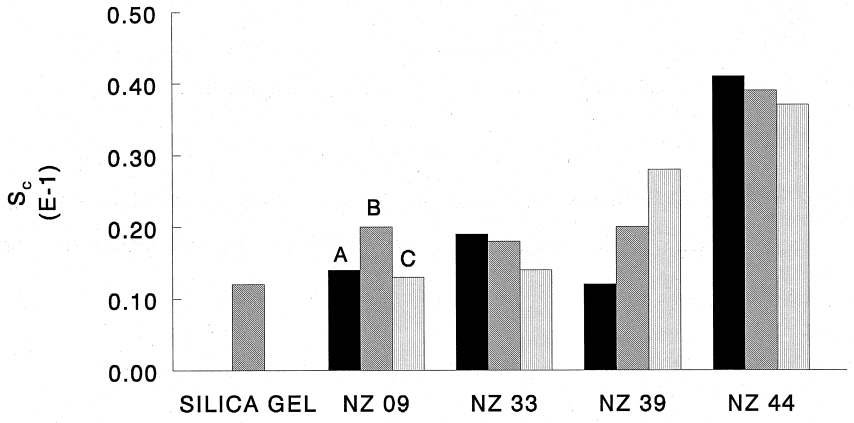

Fig.3. The influence of the silica gel modification on the values of the S_C parameter A - modification temp. 20°C, B - modification temp. 50°C, C - modification temp. 70°C.

Table 2. Surface parameters determined for the examined modified silica gel (IGC at 130°C).

Material	γ_s^d [mJ/m^2]	$C'P_{DS}$ [J/cm^3]
unmodified silica gel	28±0.4	425±3
silica gel modified with NZ 33 at 20°C	29±11	430±67
silica gel modified with NZ 33 at 50°C	26±0.3	414±0.4
silica gel modified with NZ 33 at 70°C	26±0.2	412±2
silica gel modified with NZ 39 at 20°C	31±1	446±3
silica gel modified with NZ 39 at 50°C	32±1	459±0.3
silica gel modified with NZ 39 at 70°C	27±1	414±4
silica gel modified with NZ 09 at 20°C	30±1	444±7
silica gel modified with NZ 09 at 50°C	29±3	435±2
silica gel modified with NZ 09 at 70°C	29±3	437±21
silica gel modified with NZ 44 at 20°C	31±1	442±4
silica gel modified with NZ 44 at 50°C	37±1	509±1
silica gel modified with NZ 44 at 70°C	39±2	528±18

The influence of the temperature on the modification process is not clear (Table 2). Only for silica gel modified with NZ44 we can observe that the increase of temperature of the modification process caused an increase of the values of δ_T, γ_s^d and $C'P_{DS}$ parameters reflecting ability to dispersive interactions.

It is also to emphasise that, if we expect the polar properties bound the nature of the terminal function of the zirconate pending groups, the other properties of modified silica gel remain relatively constant.

Acknowledgements

The authors thank Kenrich Petrochemicals Inc. (USA) for the delivery of the modifiers.

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