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Physico-chemical characterization of chemically bonded stationary phases including metal complexes by inverse gas chromatography

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Abstract

The solubility parameter δ_2 and dispersive force parameters were estimated for a group of chemically bonded stationary phases. Selected physico-chemical parameters were determined by means of inverse gas chromatography. The influence of the structure of the liquid phases examined on their properties was evaluated and discussed.

1. Introduction

The retention mechanism of components of mixtures to be separated by complexation gas chromatography is based on at least two systems. In one case, they are organic complexes formed by analyte molecules and stationary phases with electron-donor or electron-acceptor properties. Aromatic or unsaturated compounds with several electron-withdrawing substituents, such as NO_2, Cl or CN, are efficient electron acceptors. Tetracyanoethylene or 1,3,5-trinitrobenzene may serve as examples. Such compounds when supported on a support, dissolved in an inert stationary phase or chemically bound to a silica surface are employed in GC, TLC and HPLC [1].

The other group consists of packings where metal cations are the main factor responsible for the chromatographic separation. Electron-deficient species, such as many metal cations, have at least one empty valence orbital available for extra coordination. As a result, they are capable of complexing appropriate electron-donating species. A typical example is Ag^+, cation which has been widely used since 1962 for the separation of unsaturated compounds. Most frequently it is employed in the form of $AgNO_3$ dissolved in glycol or squalane [2]. The stabilities of complexes formed by alkenes and silver depend on the anion of the silver salt ($BF_4^- > ClO_4^- \gg NO_3^-$). Other factors influencing the stability of a complex of a metal cation and solute molecules are valency, electronic structure and radius of the central metal ion. A significant role is also played by steric effects and the basicity of molecules to be separated on a column. In addition to unsaturated hydrocar-

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bons, other soft bases containing N, O or S heteroatoms (n-donors) have been separated on complexing stationary phases in GC [3–5]. In addition to silver, various complexing metal ion compounds containing, e.g., Hg^{2+}, Cu^{2+}, Pd^{2+}, Ni^{2+} and Co^{2+} have also been investigated.

In order to eliminate the effect of the liquid stationary phase (which acts as a solvent for a metal salt) and to increase the packing stability, metal cations are bound to a silica surface with the help of suitable silanes having their hydrocarbon chain terminated with an appropriate functional group, e.g., diphenylphosphine, thiol, cyano, amino [6–8]. One such group is β-diketone, the complex-forming properties of which were used in this study in order to bind Cu(II), Ni(II) and Pd(II) cations to a SiO_2 surface.

These compounds have not so far been characterized with respect to physico-chemical parameters often used in the description of the properties of commercial stationary phases, surfactants and extractants [9–14]. One of the most interesting parameters used in characterization of polymers [14–17], commercial stationary phases [18–20] and surfactants [21–24] is the solubility parameter δ_2, defined by Hildebrand and Scott [25] and introduced into inverse gas chromatographic experiments by DiPaola-Baranyi and Guillet [15,26].

In an inverse gas chromatographic (IGC) process, a volatile diluent injected on to the column has a tendency to be absorbed by the liquid phase, i.e. the examined compound (product). This tendency is a function of the solute–solvent interaction parameter κ and is measured in terms of retention, e.g., specific retention volume V_g. The interaction parameter was usually obtained at the limit of zero concentration of the solute and was calculated as follows:

$$\kappa_{12}^{\infty} = \ln\left(\frac{273.15R}{P_1^0 V_g M_1}\right) - \frac{P_1^0}{RT}(B_{11} - V_1^0) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1^0}{V_2^0}\right) \quad (1)$$

where M_1, P_1^0, B_{11}, V_1^0, ρ_1 and V_g^0 are the molecular mass, saturated vapour pressure, second virial coefficient, molar volume and specific retention volume of the solute, respectively, ρ_2 and V_2^0 are the density and molar volume of the stationary phase, respectively, T is the column temperature and R is the gas constant.

The solubility parameter δ_2 of the liquid phase was calculated from the following equation:

$$\frac{\delta_1^2}{RT} - \frac{\kappa_{12}^{\infty}}{V_1^0} = \frac{2\delta_2}{RT} \cdot \delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\kappa_S^{\infty}}{V_1^0}\right) \quad (2)$$

where δ_1 is solute solubility parameter and κ_S^{∞} is entropic term of the interaction parameter. On plotting the left-hand side of Eq. 2 versus δ_1 one obtains a straight line with slope proportional to δ_2 of the polymer. Most often excellent linearity of Eq. 2 was found [14]. However, in some instances deviations from a straight line were reported [21–24,27].

The procedure proposed by Voelkel and coworkers [21–24] allowed the calculation of the increments of the solubility parameter corresponding to dispersive (δ_d), polar non-hydrogen bonding (δ_p) and hydrogen bonding (δ_h) interactions. There have been numerous reports of the examination of the properties of surfactants and extractants by IGC [11,14,21–24,28–36]. The parameters used therein may be divided into two groups: (i) empirical parameters (e.g., polarity index) and (ii) parameters having a strong physical meaning (e.g., thermodynamic functions of solution, Gibbs excess function of solution, criterion A). The advantages and restrictions in using these parameters have been discussed [11]. A number of empirical relationships were evaluated between the surfactant properties and their polarity parameters [14].

The importance of the dispersive forces in solute–solvent intermolecular interactions in GC experiments has been reported [13,37–42]. The proposed dispersive force parameters have been used for the characterization of the properties of commercial stationary phases and surface-active species [13,32,37–42].

The criterion A was proposed by Sevcik and Lowentap [39] and defined as

$$A = \frac{t'_{Rn-1} t'_{Rn}}{t'_{Rn} - t'_{Rn-1}} \quad (3)$$

where t'_{Rn+1}, t'_{Rn} and t'_{Rn-1} are the adjusted retention times of n-alkanes having $n+1$, n and $n-1$ carbon atoms, respectively, used as test solutes. It was proposed to describe the dispersive properties of stationary phases. An increasing value of A corresponds to decreasing polarity of the liquid phase.

The partial excess Gibbs function of solution per methylene group, $\Delta G^E(CH_2)$, represents the ability of the stationary phase to interact with solutes by means of intermolecular interactions other than dispersive interactions.

Roth and Novak [41] proposed to calculate $\Delta G^E(CH_2)$ from the retention data for two consecutive members of homologous series:

$$\Delta G^E(CH_2) = RT \ln[(V^0_{gn} P^0_n)/(V^0_{gn+1} P^0_{gn+1})] \quad (4)$$

where V_g is the specific retention volume, P^0 is the saturated vapour pressure and the subscripts n and $n+1$ refer to the two consecutive homologues.

Commercial stationary phases are usually characterized by McReynolds' constants [43] calculated in the standard way using the retention indices of benzene, 2-butanol, 2-pentanone, pyridine and 1-nitropropane. The sum of the values for these test solutes is represented by $\Sigma_{i=1}^{5} \Delta I_i$.

The aims of this investigation were (i) to characterize the examined stationary phases by the solubility parameter, dispersive force parameters and thermodynamic parameters of solution and (ii) to determine the influence of the molecular structure of the compounds on the parameters considered.

2. Experimental

2.1. Preparation of packings

Preparation of packing with bonded trichlorooctylsilane

Dry silica was immersed in a solution consisting of 3 ml of trichlorooctylsilane and 80 ml of water-free xylene. The mixture was heated at boiling point and stirred in an evaporator for 12 h. The packing was then washed with xylene and transferred into a Soxhlet apparatus, where it was subjected to extraction with the same solvent. The next stage was an end-capping reaction using hexamethyldisilazane (HMDS). The reaction proceeded in xylene. After the above stage, the packing was extracted and dried.

Preparation of packing with bonded 3-(3-trimethoxysilylpropyl)pentane-2,4-dione (TMSPP)

Silica was dried under vacuum at 180°C for 12 h, then a solution of silane (10 ml) in water-free xylene (250 ml) was added and the mixture obtained was boiled under reflux for 15 h. The system was protected from moisture. Unreacted silane was extracted with xylene and then with hexane in a Soxhlet extractor. Finally the packing was dried.

Preparation of packings with TMSPP-bonded $CuCl_2$, $PdCl_2$, $Cu(acac)_2$, $Ni(acac)_2$ and $Ni(hfac)_2$

A packing with bonded silane (TMSPP) was covered with a saturated, water-free solution of the appropriate salt in tetrahydrofuran (THF). The reagent system was allowed to stand for 7 days at room temperature, being protected from any access of moisture during that period. The excess of salt was then removed by extraction with THF in a Soxhlet extractor. After the extraction, packings were dried *in vacuo*.

2.2. Apparatus

All chromatographic measurements were carried out on a GCHF 18.3 gas chromatographic manufactured by Chromatron (Berlin, Germany), equipped with a flame ionization detector and a digital thermometer (Slandi, Warsaw, Poland) for measuring the column temperature. Argon was used as the carrier gas. The packings were placed in stainless-steel columns (1 m × 0.3 cm I.D.) and conditioned at 150°C for 12 h. Sample volumes were 0.01 μl of solute vapour.

Injection was repeated at least three times. The peaks were sharp and symmetrical.

Elemental compositions (C, N, H) of the investigated packings were determined on a Perkin-Elmer (Norwalk, CT, USA) Model 240 elemental analyser. Surface-area measurements were performed on a Grawimat Sorptometer (Sartorius, Gottingen, Germany). Results of the physico-chemical measurements are given in Table 1.

2.3. Calculations

The solubility parameter was calculated according to the procedure of DiPaola-Baranyi and Guillet [15], i.e. from Eq. 2. Criterion A and $\Delta G^{E}(CH_2)$ were calculated from Eqs. 3 and 4, respectively. In the calculation of $\Delta G^{E}(CH_2)$, C_5–C_{10} n-alkanes were used as test solutes. $\Delta G_s^m(CH_2)$ was calculated according to the procedure of Risby and co-workers [42–45], also with the use of n-alkanes as test solutes.

The examined compounds were not characterized by McReynolds' $\Sigma_{i=1}^{5} \Delta I_i$ values. However, Kováts retention indices for several test solutes were calculated and are discussed in the following section.

3. Results and discussion

Values of all parameters obtained for the examined stationary phases are summarized in Table 2. The solubility parameters δ_2 are in the range $(10.2–15.8)\cdot 10^3$ $(J/mol)^{1/2}$ at the lowest temperature, i.e., they are similar to those reported earlier for silicone stationary phases (ca. 13.2 units for OV-101) [19], but lower than those of broad and narrow distributed oligooxyethylene derivatives of cetyl alcohol (15.0–17.8 units) [21] or oligooxyethylates containing highly fluorinated hydrophobes (18.2–19.4 units [22]. However, the solubility parameter generally decreases with increasing temperature of the experiment and the comparison of results obtained at different temperatures may be dubious. Even in our case the temperatures of the experiments varied slightly. As no linear relationship was found between the solubility parameter and the temperature of the experiment, we cannot

Table 1
Physico-chemical characteristics of the investigated packings

Packing	Elemental analysis (%)				Surface area (m^2/g)	Surface concentration of silane ($\mu mol/m^2$)
	C	H	Cl	M (metal)		
I[a]	2.41	0.43	–	–	65	4.87
II[b]	2.54	0.61	–	–	75	3.33
III[c]	2.84	0.78	0.27	0.49	82	3.33
IV[d]	2.94	0.75	0.25	0.75	81	3.33
V[e]	2.08	0.44	–	0.1	71	2.41
VI[f]	2.46	0.74	–	0.11	74	2.88
VII[g]	1.84	0.33	–	1.73	71	2.04

[a] $(CH_2)_7CH_3$.
[b] $(CH_2)_3CH(COCH_3)_2$.
[c] $(CH_2)_3CH(COCH_3)_2 \cdot CuCl$.
[d] $(CH_2)_3CH(COCH_3)_2 \cdot PdCl$.
[e] $(CH_2)_3CH(COCH_3)_2 \cdot Cu(acac)$ (acac = acetylacetonate).
[f] $(CH_2)_3CH(COCH_3)_2 \cdot Ni(acac)$.
[g] $(CH_2)_3CH(COCH_3)_2 \cdot Ni(hfac)$ (hfac = hexafluoroacetylacetonate).

Table 2
Solubility parameter δ_2, dispersive force parameters and retention indices for the investigated packings

Liquid phase[a]	Temperature (°C)	δ_2 $[10^3 (J/m^3)^{1/2}]$	Criterion A	$\Delta G_S(CH_2)$ (J/mol)	$\Delta G^E(CH_2)$ (J/mol)	Retention index		
						Benzene	Thiophene	Furan
I	120.8	13.920	1.634	−1245.0	1422.4	612.5	605.3	457.8
	130.8	13.791	1.563	−1114.1	1576.9	592.4	609.9	459.4
	140.8	13.675	1.528	−983.1	1634.0	603.4	613.1	458.4
II	120.4	14.615	1.717	−1473.1	1199.3	682.1	683.9	524.0
	130.6	14.288	1.681	−1337.7	1265.2	681.6	695.1	544.5
	140.1	14.793	1.616	−1227.9	1396.4	674.1	691.3	529.9
III	124.7	15.789	1.690	−1390.6	1205.0	737.8	724.9	556.0
	137.3	15.489	1.656	−1521.1	1296.6	716.1	714.1	537.1
	146.2	16.359	1.656	−1620.8	770.8	760.6	761.9	665.4
IV	126.4	15.396	1.709	−1380.4	1202.7	678.3	690.8	528.9
	136.1	15.254	1.629	−1348.7	1324.7	676.2	695.8	544.2
	145.5	15.653	1.590	−1220.0	1421.5	676.2	690.1	539.9
V	120.6	13.631	1.826	−1734.3	894.4	671.8	676.9	521.4
	130.3	13.531	1.736	−1589.3	1052.5	689.1	689.2	524.8
	140.3	13.934	1.669	−1439.8	1177.8	687.2	692.5	549.1
VI	120.6	10.187	1.816	−1628.4	968.2	703.1	710.6	571.8
	130.4	10.002	1.703	−1490.7	1147.5	698.2	684.7	519.4
	140.4	10.537	1.658	−1350.3	1240.9	710.6	714.5	564.6
VII	120.7	10.470	1.816	−1628.2	968.5	703.7	710.6	571.8
	130.4	10.269	1.703	−1491.9	1147.5	698.2	684.7	519.4
	140.5	10.802	1.658	−1350.0	1241.2	710.6	714.5	564.6

[a] Numbers as in Table 1.

extrapolate our results to a temperature of 90°C and compare the δ_2 values for compounds examined in this work with those reported earlier for other liquid phases. We may only qualitatively judge that δ_2 values for chemically bonded phases at lower temperatures, e.g., at room temperature, would be slightly higher than those for other classes of compounds.

Eq. 2 is linear and the correlation coefficient in all instances was above 0.97. This means that despite the relatively low molecular mass of the liquid phases no significant deviations from linearity of the basic relationship was observed. Therefore, estimation of increments of the solubility parameter was impossible. However, such deviations may appear if one extends the list of test solutes, i.e., by using typical polar test solutes such as alcohols, ketones, pyridine or nitropropane.

For the stationary phases examined the lowest (δ_2) values were obtained for two Ni-containing materials, i.e., $Ni(hfac)_2$ and $Ni(acac)_2$, and the highest values were found for these phases modified by $PdCl_2$ and $CuCl_2$. This means that the lowest polarity (as measured by δ_2) is exhibited by chemically bonded phases in which metal ion is screened by the relatively large organic part of the molecule. Higher values were found for acetylacetonate derivatives having a copper atom as the complexing centre (Fig. 1).

The criterion A for non-polar stationary phases is high, i.e., usually slightly above 2 units [32, 41]. An increase in the polarity of the liquid phase causes a decrease in this parameter. The highest values of criterion A were found for phases modified by $Cu(acac)_2$, $Ni(acac)_2$ and $Ni(hfac)_2$ and the lowest one for a C_8 liquid phase.

The partial molar excess Gibbs free energy of solution per methylene group, $\Delta G^E(CH_2)$, re-

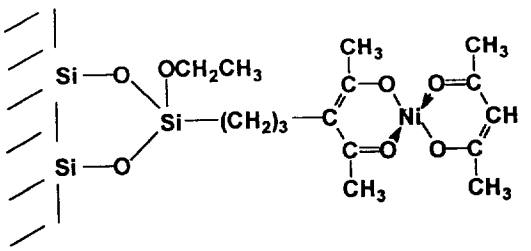

Fig. 1. Schematic diagram of packing.

flects the resistence of the liquid phase to dissolve the non-polar methylene fragment. The values of this parameter increases with increase in the polarity of the liquid phase. A stationary phase modified by $Cu(acac)_2$ seems to be the least polar and C_8 the most polar phase.

The partial molar Gibbs free energy of solution per methylene group increases with increase in the polarity of the stationary phase. The lowest value -1.628 kJ/mol was found for phases having $Ni(hfac)_2$ and $Ni(acac)_2$ and these two stationary phases should be indicated as the least polar [according to $\Delta G_s^m(CH_2)$].

Generally, in all instances, despite the parameters considered, investigated phases containing large organic molecules were selected as those exhibiting the lowest polarity. A C_8 chemically bonded phase was ordered by δ_2 (Table 3) as slightly more polar than those modified by $Cu(acac)_2$. However, C_8 is the most polar when judged on all the dispersive force parameters. If this difference is not taken into account, the arrangement of the examined stationary phases is similar with the use of all the parameters considered: $Ni(hfac)_2 \approx Ni(acac)_2 \approx Cu(acac)_2 < TMSPP \approx C_8 < CuCl_2 \approx PdCl_2$.

n-Alkanes used as test solutes interact with the stationary phase only by dispersive interaction. In such a case the strongest relationships are observed for a C_8 chemically bonded phase. Here the dispersive interactions are predominant as no steric effects characteristic of complexes and free β-diketonate groups are observed. The solubility parameter δ_2 was calculated with the use of retention data for *n*-alkanes, aromatics and polar solutes, and strong specific interactions were taken into account. Therefore, the ordering based on δ_2 differs from the others where dispersive force parameters were considered.

Straight-line relationships (Figs. 2 and 3a) were found between dispersive force parameters and the surface concentration of silane (SC):

$$\Delta G^E(CH_2) = 2.192 - 3.988 \times 10^{-4} SC$$
$$R = 0.987$$
$$\Delta G_s^m(CH_2) = 1.104 - 4.237 \times 10^{-4} SC$$
$$R = 9.979$$
$$\text{Criterion } A = 1.1983 - 0.075SC$$
$$R = 0.905$$

The relationship between δ_2 and surface concentration is characterized by a low value of the correlation coefficient, $R = 0.7$ (Fig. 3b).

The application of ligands containing a β-diketonate group allowed a comparison of their specific interaction ability with typical electron donors. In fluorinated acetylacetonates, substitution of the hydrogen atom in the methyl group causes a decrease in the σ-donor and π-donor abilities of ligands. The small differences between stationary phases with $Ni(hfac)_2$ and

Table 3
Influence of modifying agent on investigated parameters

Parameter	Order
Criterion *A*	$Cu(acac)_2 < Ni(acac)_2 = Ni(hfac)_2 < TMSPP < PdCl_2 < CuCl_2 < C_8$
$\Delta G^E(CH_2)$	$Cu(acac)_2 < Ni(acac)_2 = Ni(hfac)_2 < TMSPP < CuCl_2 < PdCl_2 < C_8$
$\Delta G_s^m(CH_2)$	$Cu(acac)_2 < Ni(acac)_2 = Ni(hfac)_2 < TMSPP < PdCl_2 < CuCl_2 < C_8$
δ_2	$Ni(acac)_2 < Ni(hfac)_2 < Cu(acac)_2 < C_8 < TMSPP < PdCl_2 < CuCl_2$

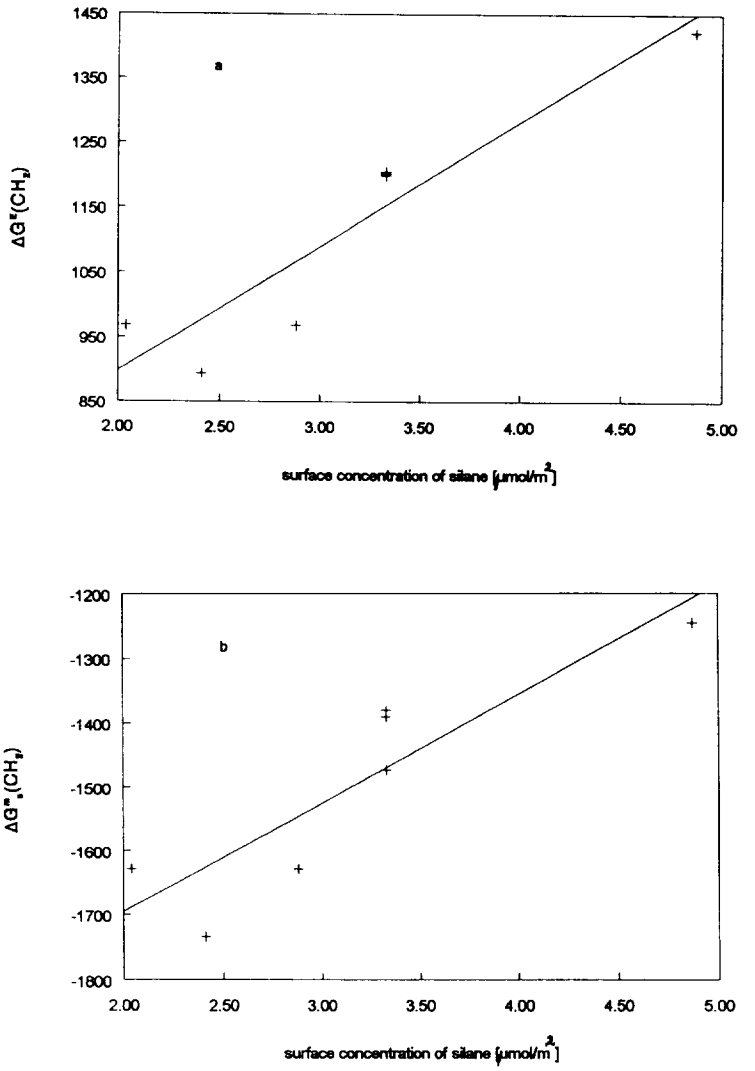

Fig. 2. Relationships between Gibbs functions of solution and surface concentration of silane (*SC*): (a) $\Delta G^{E}(CH_2)$ vs. *SC*; (b) $\Delta G_s^m(CH_2)$ vs. *SC*.

$Ni(acac)_2$ as judged by dispersive force parameters are probably caused by transformations occurring during the reaction of nickel salts with the TMSPP surface. One of hexafluoroacetylacetonate groups in $Ni(hfac)_2$ is replaced by an acetylacetonate group bonded to the silica surface. Therefore, only six instead of twelve fluorine atoms are present in the final complex. This causes lower than expected differences in the physico-chemical properties of both types of chemically bonded stationary phases.

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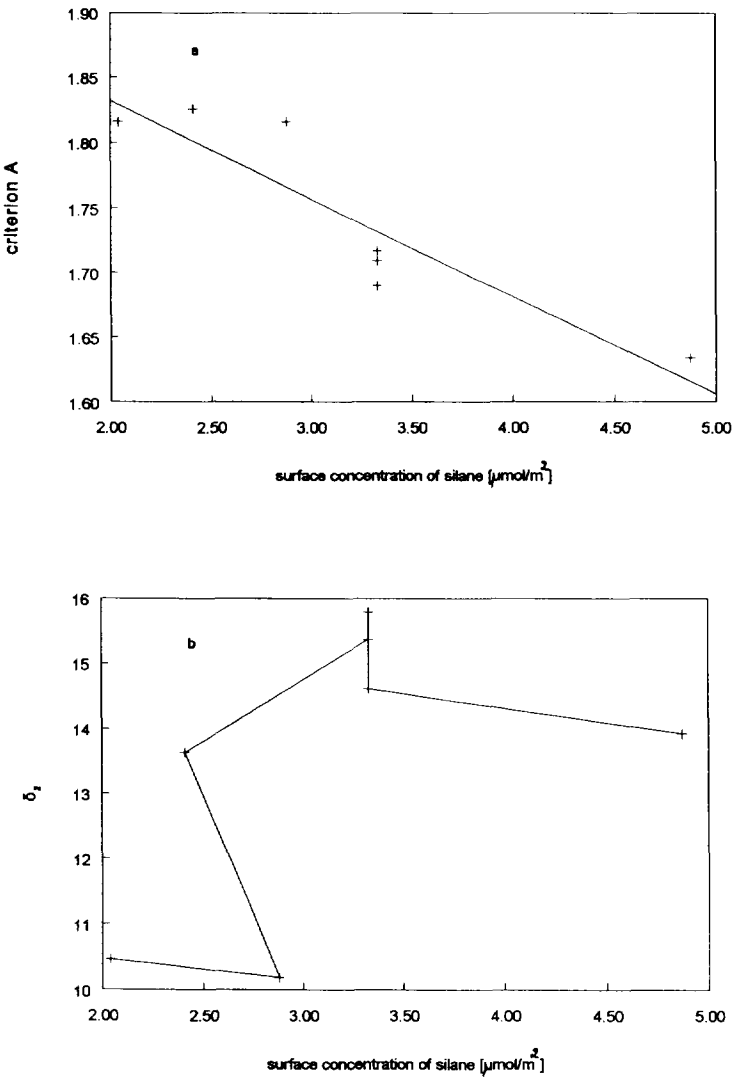

Fig. 3. Relationships between physico-chemical parameters and surface concentration of silane (*SC*): (a) criterion *A* vs. *SC*; (b) δ_2 vs. *SC*.

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