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Carbenium ion pairs on silica: UV-spectroscopic and electrokinetic measurements of triarylmethylium/halide-aerosil in 1,2-dichloroethane

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Abstract: The interaction of carbenium ion pairs with silica is studied by means of UV-spectroscopy, electrokinetic and adsorption measurements using triphenylmethyl derivatives, $(RC_6H_4)_3CX$, (X = F, Cl, Br, SCN, OH; R = Cl, I, H, CH_3, $C(CH_3)_3$, OCH_3, $N(CH_3)_2$) in interaction with silica particles suspended in 1,2-dichloroethane. The adsorption of triarylmethyl-halides onto silica is accompanied by the heterolytic dissociation of the tertiary carbon-halogen bond. The degree of ionization depends on the basicity of the counter anion and acidity of the cation, respectively. The influences of both concentration and structure of triarylmethyl halides on the zeta-potential are discussed with regard to steric and electronic factor. The zeta-potential values of the adsorbates decrease significantly, as compared with the free silica surface, from a certain triarylmethyl halide concentration where ionization takes place, to a constant level which is characteristic of the carbenium ion pair. These constant zeta-potential values of the adsorbates depend on the basicity of the counter ion and the σ_p Hammett constants of the ring substitutents, with exclusion of sterically hindered substituents and salt derivatives, e.g., crystal violet and malachite green.

Key words: Cationic interfacial polymerization – zeta-potential – triarylmethyl halide – silica – carbenium ion pair

1. Introduction

In the solid state crystalline covalent triarylmethyl-halides are usually colorless. In solution, depending on the Lewis-acidity of the cation, the basicity of the counter ion and of both the polarity and acceptor strength of solvent ionization and dissociation may take place [1, 2] (Eq. 1). The ionization is accompanied by the appearance of a new, strong visible absorption due to the corresponding carbenium ion, and increase in conductivity.

$$R\text{–}X \overset{K_i}{\rightleftharpoons} R^+X^- \overset{K_d}{\rightleftharpoons} R^+ + X^- \qquad (1)$$

The lower the basicity of the counter ion and the acidity of the carbenium ion, respectively, the higher the degree of ionization (K_i) as demonstrated by Feigel and Kessler [3].

The influence of the solvent on the whole process is very complex due to the consecutive steps ionization-dissociation. However, the ionization is mainly determined by the acceptor strength of the solvent due to the solvation of negatively charged counter ions, and the dissociation by the overall polarity (may be the dielectric constant) of the surrounding medium. Solvents with donor properties stronger than acetonitrile (DN = 14.1; DN means the donor number of the solvent according to Gutmann [4]) react with carbenium ions possessing a $pK_{R^+} < 0$.

Advantageously, covalent arylmethyl-halides are adsorbed onto several inorganic solids with acceptor properties such as silica and alumina [5].

Depending on the kind of counter ion and cation the adsorption process is accompanied by the heterolytic ionization of the carbon halogen bond according to the following mechanism, evident for the interaction of triarylmethyl chlorides with silica (Eq. (2)) [5–7]:

$$\text{R–X} + \text{H–O-Silica} \overset{K_i}{\rightleftharpoons} \text{R}^+\text{X}^- \ldots \text{H–O-Silica} \quad (2)$$

The ionization is attributed to an electrophilic attack of the silanol groups upon the negatively polarized halogen atom of the arylmethyl derivative. Electrolytic dissociation of the triphenylmethylium halide-silica into the solvent phase cannot take place because of diffusion-controlled ion recombination of solvated halides with triphenylmethylium in solution [8]. In the case of triarylmethyl halides the adsorption mechanism is as mentioned above: increasing surface concentration of R–X only causes a gradual disappearance of the single valency vibration of silanol at 3740 cm^{-1}. New absorptions in the region of 960 cm^{-1} which would indicate the appearance of covalent Si–O–C bonds are not observed [9]. This result is supported in that triphenylmethylium hexachloroantimonate is not adsorbed onto silica in comparison with the tetrafluoroborate salt. It is known that hexachloroantimonate does not participate in hydrogen bonding complexes due to its non-nucleophilic property, in contrast to the tetrafluoroborate [10]. That means a coordination of the sterically hindered triphenylmethylium on the oxygen atom of silanol groups does not take place, and the adsorption occurs via ion pair intermediates. However, the existence of a chemisorbate of diphenylmethylium hexachloroantimonate with silica-aerosil is observed in a very low yield. The larger reactivity of the diarylmethylium is due to its easier sterical accessibility [11]. To elucidate the only ionization mechanism, according to Eq. (2), we have employed the triphenylmethyl derivatives as model compounds. According to Feigel and Kessler [3], we have applied their ionization scheme, derived for homogeneous solutions, and considered aerosil/1,2-dichloroethane as medium for ionization (solid line in Fig. 1) as reported previously [12].

The ordinate of Fig. 1 expresses the electrophilicity of the carbenium ion as pK_{R^+}, and the abscissa can simply be viewed as a basicity scale of the counter ion expressed as the pK_s of the corresponding protonic acid. The dashed lines indicate the frontiers in which solvents arylmethyl halides are more ionic or more covalently present. Thus, the left area of a line (the dashed lines are taken from ref. [3]) indicates the covalent combination of R^+ and X^- (R–X) where K_i is smaller than one. For instance, triphenylmethyl-chloride is dissolved covalently in methylene dichloride but it is adsorbed ionically at the silica surface (the yellow triphenylmethylium absorption at 410 nm and 430 nm appears), compared with triphenylmethyl-isothiocyanate which is not ionized at silica. Hence, methylene dichloride or 1,2-dichloroethane are excellent suspending liquids for the application of triphenylmethyl chloride in conjunction with silica. Thus, the colored suspensions of triphenylmethylium halides in aerosil/1,2-dichloroethane becomes convenient for synthetic alternatives in comparison with carbenium salts in solution of haloalkanes, as for hydride ion acceptors [12] and as initiator for cationic interfacial polymerization of *p*-methoxystyrene [13].

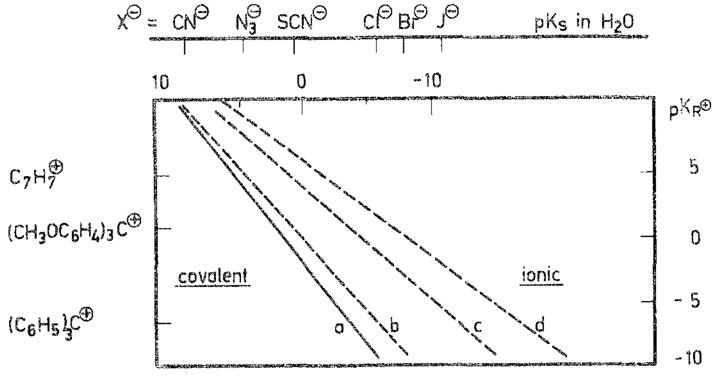

Fig. 1. Graphical search for cationoid compounds in which K_i (see Eq. (1)) approximates the value 1. For aerosil/1,2-dichloroethane as medium see line (a) (the lines for SO_2 (b), CH_3CN (c) and CH_2Cl_2 (d) are according to ref. [3])

The principle of interfacial initiation of cationic vinyl polymerization is demonstrated in Eq. (3).

$$\begin{array}{l} (\mathrm{RC_6H_4})_3\mathrm{CX} + \mathrm{HO\text{-}silica} \rightleftharpoons \\ \qquad \downarrow + \text{monomer} \\ \quad \text{no initiation} \\ (\mathrm{RC_6H_4})_3\mathrm{C^+X^-} \cdots \mathrm{H{-}O\text{-}silica} \\ \qquad \downarrow + \text{monomer} \\ \quad \text{interfacial initiation} \end{array} \qquad (3)$$

Advantageously, the counter ion is responsible for the coordination of both the initiating triphenylmethylium at the silica surface and of the propagating chain carrier after initiation. The propagating polymer cation (i.e., *p*-methoxystyrylium) allows an interaction with various surface groups leading to controlled grafting. For that reason triphenylmethylium halide-silica is suitable exclusively for interfacial initiation of various cationic polymerizable monomers leading to both composites and extractable polymer with narrow molecular weight distribution (MWD). The balance between these products is strongly dependent on the surface concentration of the initiating ion pair intermediate [13]. To get a better understanding of the behavior of triarylmethyl halide/aerosil adsorbates among initiation in organic liquids, the formation of an electrochemical double layer at the solid/liquid interface must be taken into account. According to the well-known Stern model two layers have to be considered:

a) a so called Stern layer close to the surface is immobile and
b) a diffuse layer allows a thermal motion of charge carriers, and is continuously in weak contact with the Stern layer.

The electrokinetic potential or zeta-potential is defined as the electric potential in the slipping plane between Stern layer and diffuse layer and can be measured by means of electrophoretic or electroosmotic procedures.

Relationships relating to donor-acceptor properties of solids and electrokinetic phenomena have been shown by Fowkes [14], and Labib and Williams [15], Cremer [16] and by the authors [17, 18]. The objective of this study is to prove that zeta-potential measurements can be applied to describe the behavior of triphenylmethylium halide/silica adsorbates in organic liquids, such as 1,2-dichloroethane. In the following, the influences of the counter ion and the influence of the substituents of the phenyl rings on the zeta-potential are discussed.

2. Experimental and materials

The zeta-potential of the solid-liquid interface was determined by means of electrophoretic methods. The zeta-potential is calculated by the Hückel equation [19]:

$$\zeta = -\frac{3 * U_E * \eta}{2 * \varepsilon_r * \varepsilon_0} \qquad (4)$$

with

η – viscosity of the solvent (liquid)
ε_r – relative dielectric constant of the liquid
ε_0 – permittivity of vaccum
U_E – electrophoretic mobility $U_E = \dot{V}_p/E$
V_p – particle velocity
E – electric field strength.

The electrophoretic mobility was determined by means of a REPAP-zeta-potential equipment. The closed measuring cell includes two Pt-electrodes with a distance of 0.9 cm.

The distance between the glass windows was 0.1 cm. An electric field of 100 V/cm was applied. The solid-liquid systems were prepared as described in ref. [13]. Every zeta-potential value was averaged from 10 independent measurements. The error of the reported values is in the order of $< 5\%$.

The triphenylmethyl derivatives were obtained by the reaction of the triphenylmethyl alcohols with the corresponding acetyl halide according to [20]. They were purified by recrystallization from hexane and stored under argon. The purity of all reagents was confirmed by elemental analysis.

1,2-Dichloroethane, purified by standard procedure and dried over $\mathrm{CaH_2}$, was freshly distilled before use.

Silica was used as the commercially available product Aerosil 300, (DEGUSSA Frankfurt/Main). It was stored in closed vessels. Before use, it was dried under vaccum for 6 h at 673 K. The silica was kept in Schlenk vessels, and a stock solution of triaryl-methyl/halide in 1,2-dichloroethane was added under inert conditions. The suspension was degassed and the solid particles were dispersed by ultrasonic treatment.

The adsorption measurements were carried out at conditions as described above. The surface concentration in the dependence on the concentration of the solution was determined by two independent methods, elemental analysis of the solid adsorbates after drying, and by UV measurements of the supernatant solutions.

3. Results and discussion

3.1. *UV/Vis-measurements*

UV/Vis-measurements of the transparent aerosil/1,2-dichloroethane suspension allows a clear decision about whether ionization takes place or not, if the concentration of carbenium is larger than 10^{-6} mol/g of the solid. We have investigated the surface promoted carbenium ion-pair formation considering more than 20 relevant compounds. The qualitative results are compiled in Table 1.

The comparison of the UV/Vis-maxima of the carbenium measured on the silica surface with those obtained from solutions of adequate hexachloroantimonates gives a straight line with a slope of one (corr = 0.999). This result points out that the electronic structure of every substituted triphenylmethylium ion is the same one in solution as in the ion pair intermediate occurring at the silica surface. Obviously, the counter ion shields the acidic surface groups. In the case of the triphenylmethane dyes, crystal violet and malachite green, additional influences due to specific interactions of silanol upon the dimethylamino groups in the UV-spectra are not observed [24]. However, in the case of alumina and titan dioxide as surfaces the behavior is quite different and will be reported in a following paper [25]. The results in Table 1 are in accordance with Fig. 1, and will

Tabel 1. UV-spectroscopic results of the interaction of various triarylmethyl derivatives (4-RC_6H_4) (4$R'C_6H_4$) (4$R''C_6H_4$)CX with silica-aerosil in 1,2-dichloroethane suspensions at 293 K

Compound R	R′	R″	X	Ionization	$\tilde{\nu}_{max}$/cm^{-1} on silica	$pK_{R^+} - pK_s$ a)
$-N(CH_3)_2$	$-N(CH_3)_2$	$-N(CH_3)_2$	Cl	b)	16950	15.4
$-N(CH_3)_2$	$-N(CH_3)_2$	-H	Cl	b)	16000	12.9
$-N(CH_3)_2$	$-OCH_3$	-H	Cl	b)	19160	10.8
$-OCH_3$	$-OCH_3$	-H	Cl	+	19800	4.9
$-OCH_3$	$-CH_3$	-H	Cl	+	20680	3.7 c)
$-OCH_3$	-H	-H	Cl	+	20920	2.6
$-OCH_3$	-Cl	-H	Cl	+	20520	0.65 c)
$-C(CH_3)_3$	$-C(CH_3)_3$	$-C(CH_3)_3$	Cl	+	21720	− 0.80
$-C(CH_3)_3$	-H	-H	Cl	+	21840	− 0.40
-H	-H	-H	Cl	+	22900	− 0.63
-H	-H	-H	Br	+	22800	0.87
-H	-H	-H	F	+	23000	−10.03
-H	-H	-H	NCS	−	−	− 7.66
-H	-H	-H	N_3	−	−	−11.6
-H	-H	-H	OH	−	−	−20.63
-Cl	-H	-H	Cl	+	22200	− 1.43 c)
-I	-H	-H	Cl	+	20500	− 1.35 c)
-Cl	-Cl	-Cl	Cl	?	−	− 1.74
$(4-CH_3OC_6H_4)_2CH-Cl$				+	20100	+ 0.29
$(4-CH_3C_6H_4)_2CH-Cl$				−	−	− 4.4
$(C_6H_5)_2CH-Cl$				−	−	− 7.3

a) The pK_{R^+} values of the carbenium ions and pK_s values of the counter ions were taken from refs. [21, 22] and [23], respectively

b) These compounds are salts

c) The pK_{R^+}-values involved were estimated by a Linear Free Energy-relationship according to ref. [25b]

be discussed in connection with the electrokinetic data in chapter 3.2. Advantageously, the following can be used as a rule (excluding the fluoride ion where HF_2^- formation may take place): if the difference of $pK_{R^+} - pK_s$ is lower than around − 1.5, no ionization on silica occurs. According to [26] a more detailed study describing quantitatively the very complex mechanism will be reported [27].

3.2. Electrokinetic measurements

The interpretation of experimental results of electrokinetic phenomena of bare solids in pure weakly polar liquids such as benzene or 1,2-dichloroethane are still controversially discussed, ref. [15, 18]. However, the experimental results are evident, and the zeta-potential of bare aerosil in 1,2-dichloroethane is negative ($\zeta = -98$ mV). This indicates that silica surface serves as an electron acceptor towards 1,2-dichloroethane, ref. [18]. As a consequence, the adsorption of donor molecules decreases the acceptor strength of the surface and the zeta-potential becomes more positive. Accordingly, the adsorption of triphenylmethyl halides causes an increase in the negative zeta-potential of the aerosil due to nucleophilic attack of the negatively polarized halogen atom upon the acidic silanols.

3.2.1. Influence of the counter ion

The zeta-potentials of aerosil as function of the triphenylmethyl halide concentration (mol per g silica) are shown in Fig. 2.

The course of the zeta-potential versus concentration plots can be separated into three different sections according to Fig. 2.

1) In the first section, where $0 < \gamma < \gamma_{min}$, the zeta-potential is determined essentially by the interface between the measured aerosil and 1,2-dichloroethane. Insufficient triphenylmethyl halide is adsorbed to influence the measured zeta-potential. According to ref. [13], the γ_{min} concentrations agree very well with the lowest initiator concentration which can effect cationic interfacial polymerization of *p*-methoxystyrene by $(C_6H_5)_3C^+X^-$-silica initiation.
2) In the second section between γ_{min} and γ_{max}, the negative zeta-potential increases significantly with increasing triphenylmethyl halide concentration because ionization is enhanced. That means the carbenium-ion intermediate formed on the surface determines the zeta-potential.

   In contrast, the adsorption of $(C_6H_5)_3COH$ and $(C_6H_5)_3CNCS$ on silica does not change the zeta-potential, which implies that no ionized species can be observed (see Table 1) [6].
3) In the third section above γ_{max} the zeta-potential reaches a constant level which is determined by the $(C_6H_5)_3C^+X^-$-silica adsorbate. The silica surface is shielded by carbenium ion pairs above γ_{max}, and a further increase in the overall $(C_6H_5)_3CX$-concentration does not change the zeta-potential. This agrees very well with the efficiency of composite yield by

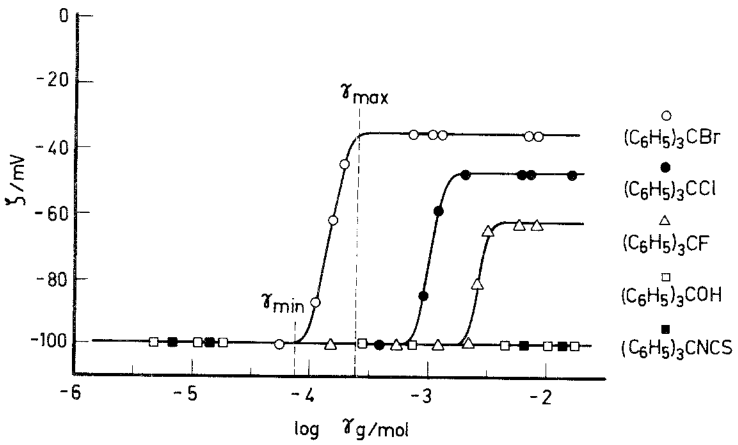

Fig. 2. Zeta-potential of triphenylmethylium halide-silica adsorbates versus the overall triphenylmethyl halide concentration of the suspension in 1,2-dichloroethane.
□ $(C_6H_5)_3COH$, ■ $(C_6H_5)_3CNCS$, △ $(C_6H_5)_3CF$, ● $(C_6H_5)_3CCl$, ○ $(C_6H_5)_3CBr$

triphenylmethylium halide-silica initiation, where higher initiator concentrations than γ_{max} do not enhance the polymer yield grafted onto the surface, see ref. [13].

The zeta-potential level above γ_{max} shows the following order for the various triphenylmethyl derivatives:

$$SCN^- = OH^- \ll F^- < Cl^- < Br^- .$$

This order agrees very well with corresponding scales concerning the hardness of anions according to Pearson [28] and Gutmann [29]. The decrease in the necessary γ_{min} concentration which is responsible for the equilibrium between covalent and ionic species is confirmed by the lowering of the carbon halide bond strength for heterolytic dissociation [2, 3]. The order of γ_{min} values of the various triphenylmethyl halides is the same one as for the order of the differences of zeta-potential values between γ_{min} and γ_{max}.

It becomes obvious that carbenium interfacial processes are only possible in the case of $(C_6H_5)_3C^+F^-$-, Cl^--, and Br^--silica intermediates [12].

3.2.2. *Influence of the substituents of the ring*

Electronic factors

The zeta-potential as function of the overall concentration of various substituted $(RC_6H_4)_3C^+Cl^-$ compounds adsorbed on the silica are plotted in Fig. 3.

The curves exhibit the same shape as observed in the case of the halide derivatives which indicates principally a similar mechanism. Variation of the substituents of the ring changes both the zeta-potential level above γ_{max}, and the γ_{min} concentration range. Increasing stabilization of the carbenium ion due to donor substituents with $-\sigma_p$ Hammett constants, such as $-CH_3$, $-OCH_3$, or $-N(CH_3)_2$, decrease the zeta-potential level at γ_{max} and the γ_{min} concentrations in comparison with the unsubstituted compound. Both results agree with the lowering of the heterolytic dissociation barrier of the carbon halogen bond. That means, the ion pair formation on the surface influence the zeta-potential values beginning at γ_{min}, and the increased stability of the carbenium ion leads to a weaker interaction with the corresponding chloride/silica. Thus, the increased stability of the carbenium ion leads to a decrease in the negative charge density in the electrochemical double layer. The formation of ionic aggregates in the course of adsorption of triarylmethyl halides on silica can be demonstrated by adsorption measurements. Representative adsorption isotherms are shown in Fig. 4. This behavior relates to Freundlich isotherms, and shows that with increasing triarylmethyl/halide concentration the concentration on the surface increases continuously, too.

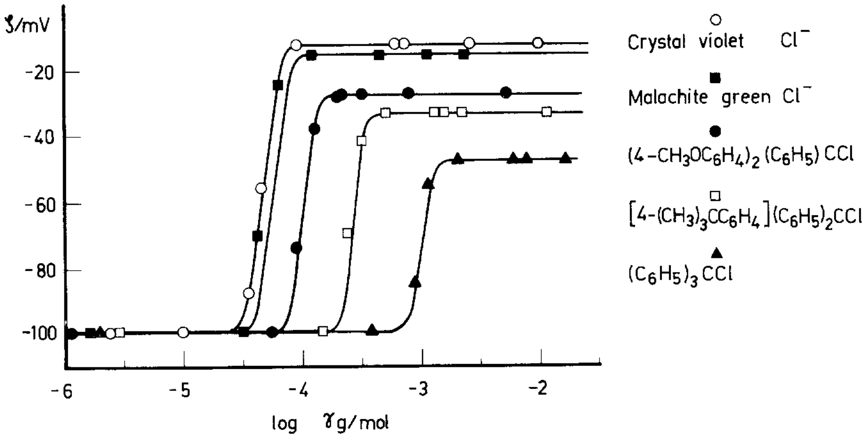

Fig. 3. Zeta-potential of various substituted triarylmethylium chloride-aerosil adsorbates versus the overall triarylmethyl chloride concentration of the suspension in 1,2-dichloroethane. ▲ $(C_6H_5)_3CCl$, □ $[4\text{-}(CH_3)_3C\text{–}C_6H_4][C_6H_5]_2CCl$, ○ $[4\text{-}(CH_3)_2N\text{–}C_6H_4]_3C^+Cl^-$, ● $[4\text{-}(CH_3OC_6H_4)]_2[C_6H_5]CCl$, ■ $[4\text{-}(CH_3)_2N\text{–}C_6H_4]_2[C_6H_5]_2C^+Cl^-$

We conclude, therefore, that depending on the ionization barrier of the triarylmethyl halide both are changed, the negative charge density in accordance with the zeta-potential, and the quantities of **carbenium ion pairs** only formed by the adsorption. The immediate influence of the substituents on the ring on both, the zeta-potential values above γ_{max} and the heterolytic dissociation of the carbon halogen bond can be demonstrated by comparison of the σ_p Hammett constants, which represent the electronic behavior of substituents [30], with the zeta-potential. The relationship of the zeta-potentials versus σ_p constants, a linear free energy relationship, is shown in Fig. 5.

A linear relationship is only obtained for triarylmethyl halides in the range from $-\sigma_p > 0.5$ to $\sigma_p < 0.5$, and only in this range does the silica cause a heterolytic dissociation of the carbon chlorine bond which is accompanied by a significant change of the UV/Vis-spectrum. Chlorides involving cations having a $pK_{R^+} > 1$ (Table 1) are salts, i.e., crystal violet and malachite green. Thus, the equilibrium between covalent species and ionic species is not affected by silica, and the adsorption mechanism is another one. Analogously, arylmethyl chlorides involving a cation having a $pK_{R^+} < -8$ only undergo a very weak ionization on silica (Table 1). The appearance of triarylmethylium ion pairs on silica surfaces is similar to the Winstein scheme, which is well known from analogous behavior in homogeneous systems [31]. Hence, the following mechanism for the interaction of triarylmethyl halides

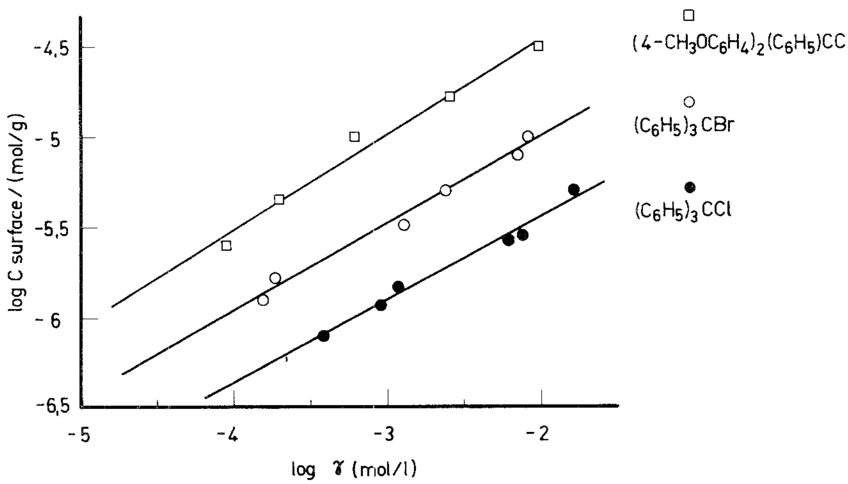

Fig. 4. Adsorption isotherms of selected triarylmethyl derivatives from 1,2-dichloroethane on aerosil-silica at 293 K
● $(C_6H_5)_2CCl$, ○ $(C_6H_5)_2CBr$,
□ $[4\text{-}(CH_3OC_6H_4)]_2[C_6H_5]CCl$

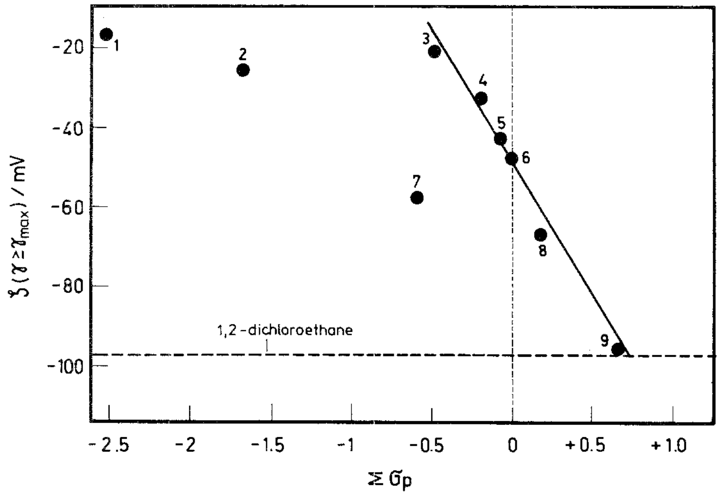

Fig. 5. Relationship of the constant zeta-potential values of the adsorbates of substituted triarylmethyl derivatives on silica versus the sum of the corresponding *p*-Hammett constants
1 = $[4\text{-}(CH_3)_2N\text{-}C_6H_4]_3C^+Cl^-$
2 = $[4\text{-}(CH_3)_2N\text{-}C_6H_4]_2[C_6H_5]_2C^+Cl^-$
3 = $(4\text{-}CH_3OC_6H_4)_2(C_6H_5)CCl$
4 = $(4\text{-}CH_3C_6H_4)_3CCl$
5 = $[4\text{-}(CH_3)_3CC_6H_4)](C_6H_5)_2CCl$
6 = $(C_6H_5)_3CCl$
7 = $[4\text{-}(CH_3)_3CC_6H_4)]_3CCl$
8 = $(4\text{-}IC_6H_4)(C_6H_5)_2CCl$
9 = $(4\text{-}ClC_6H_4)_3CCl$

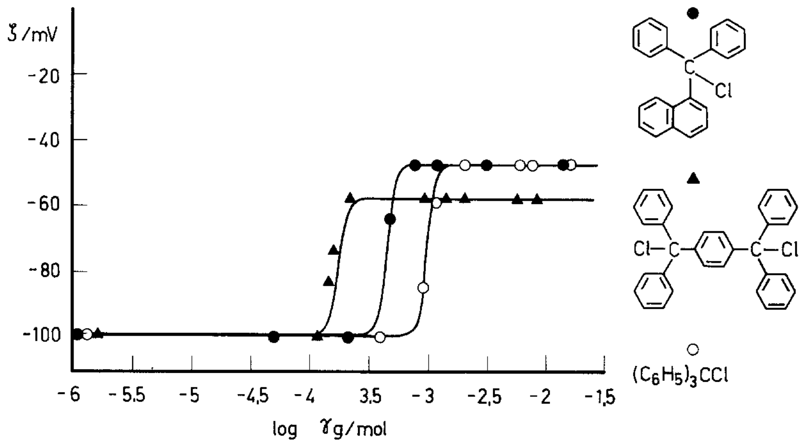

Fig. 6. Zeta-potentials of substituted triarylmethyl chlorides involving sterically bulky substituents versus the overall concentration of the suspension in 1,2-dichloroethane; the curve for $(C_6H_5)_2CCl$ is shown for comparison.
▲ $[(C_6H_5)_2CCl\text{–}C_6H_4\text{–}CClC_6H_5]_2$,
○ $(C_6H_5]_3CCl$,
● $[1\text{-}(C_{10}H_7)(C_6H_5)_2]CCl$

with silica-OH is suggested:

$$\text{silica-OH} + X\text{–}C(C_6H_4R)_3 \underset{\text{desorption}}{\overset{\text{adsorption}}{\rightleftharpoons}} \text{silica-OH } X\text{–}C(C_6H_4R)_3 \qquad (5a)$$

polarisation $\downarrow\uparrow$ depolarisation

$$\text{silica-OH} + X\text{–}C(C_6H_4R)_3 \rightleftharpoons \text{silica-OH} \cdots\cdots X^{\delta-}\text{–}C^{\delta+}(C_6H_4R)_3 \qquad (5b)$$

ionisation $\downarrow\uparrow$ recombination

$$\text{silica-OH} + X\text{–}C(C_6H_4R)_3 \rightleftharpoons \text{silica-OH} \cdot\cdot X^- \cdots\cdots C^+(C_6H_4R)_3 \qquad (5c)$$

Steric factors

As seen from Fig. 5, tris (4-tert. butylphenyl)methyl chloride does not fit in the linear relationship of the σ_p Hammett constants and the zeta-potentials. Similar zeta-potential plots have been obtained for diphenyl-1-naphthyl-methyl chloride and $(C_6H_5)_2CCl\text{–}C_6H_4\text{–}CCl(C_6H_5)_2$. The plots of zeta-potential versus the concentration of the respective triarylmethyl chlorides in comparison to $(C_6H_5)_3CCl$ are shown in Fig. 6.

The charge stabilizing effect of the donor substituents, tertiary butyl and 1-naphthyl, respectively, is seen from the shift of $\gamma_{\min}$ to lower concentrations which agrees with the items described in the previous chapter. Obviously, sterically hindering substituents disturb the formation of ionic layers as seen from the representative zeta-potential levels above $\gamma_{\max}$ in comparison to $(C_6H_5)_3CCl$.

4. Conclusion

The occurrence of carbenium ion pairs at the silica surface can be studied with the help of model compounds such as triarylmethyl derivatives on silica surfaces by means of UV/Vis-spectroscopy, electrokinetic measurements and adsorption measurements. It could be demonstrated that zeta-potential measurements are suitable for elucidation of the electronic behavior of carbenium ion pairs on silica surfaces in 1,2-dichloroethane suspension.

The following results can be summarized:

1) The zeta-potential of triarylmethyl halide silica adsorbates depends on the triarylmethyl halide concentration in the solid liquid system.
2) The negative zeta-potential increases from a certain concentration on a constant level which is characteristic of the ion pair linked to the surface groups.

The interrelation between electrokinetic data and structural parameters can be demonstrated by means of the σ_p Hammett constants in a Free Energy relationship. It is evident that zeta-potential measurements in liquids of moderate polarity are convenient for detecting structure-reactivity relationships of surface mediated carbenium ion pair species.

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References

1. Freedman HH (1973) Carbonium Ions 4:1501
2. Schneider S, Mayr H, Plesch PH (1987) Ber Bunsenges Phys Chem 91:1369
3. a) Feigel M, Kessler H, Leibfritz D, Walter A (1979) J Amer Chem Soc 101:1943; b) Kessler H, Feigel M (1982) Acc Chem Res 15:2
4. Gutmann V (1970) Angew Chem 82:858
5. Leftin HP (1968) Carbonium Ions. John Wiley & Sons Vol 1:363
6. Ulbricht A, Spange S, Heublein G (1988) J prakt Chem 330:325
7. Arnett EM, Cassidy KF (1988) Rev Chem Intermed 9:27
8. Dorfmann LM, Sujdak RJ, Jones RL (1976) J Amer Chem Soc 98:4875
9. Spange S, Heublein B (1992) J Macromol Sci-Chem A29:987
10. Spange S, Dreier R, Opitz G, Heublein G (1989) Acta polymerica 40:55
11. Spange S, Simon F, Schütz H, Schramm A, Winkelmann H (1992) J Macromol Sci A29:997
12. Spange S, Schmiede B, Walther R (1992) GIT Fachzeitschrift für das Laboratorium 36:736
13. Spange S, Heublein G, Simon F (1991) J Macromol Sci – Chem A28:373
14. Fowkes FM (1987) J Adhesion Sci Techn 1:7
15. Labib ME, Williams R (1984) J Coll Interf Sci 97:356
16. Cremer M (1986) Proc XVIII FATIPEC Congr Venice 28:609
17. Spange S, Hortschansky P, Heublein G (1989) Acta Polymerica 40:602
18. Spange S, Simon F, Heublein G, Jacobasch HJ, Börner M (1991) Polym Coll Sci 269:173
19. Debye P, Hückel E (1924) Physik Z 25:204
20. Organic Synthesis, John Wiley & Sons, New York, London (1963) 3:841, 842
21. Ritchie CD (1986) Can J Chem 64:2239 (see references therein)
22. Schade C, Mayr H (1988) Tetrahedron 44:5761
23. Pearson R, Sobel H, Songstad (1968) J Am Chem Soc 90:319
24. Lueck HB, Rice BL, McHale JL (1992) Spectrochim Acta A 48:819
25. a) Spange S, Fandrei D (in press); b) Fandrei D (1992) Diplomarbeit, Jena University
26. Kittelmann U, Unger K, Kreis W (1980) Progr Colloid Polym Sci 67:19
27. Spange S, Walther R (1992) unpublished results
28. Pearson RG (1966) Science 151:172
29. Gutmann V, Mayer U (1968) Monatshefte Chem 99:1386
30. Hammett LP (1974) Physikalische Organische Chemie, Weinheim
31. Winstein S, Robinson GC (1958) J Amer Chem Soc 80:858

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