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On the Salt-linkage Formations of Porous and Nonporous Silica Particles with Trimethylammonium Glycol Chitosan Iodide

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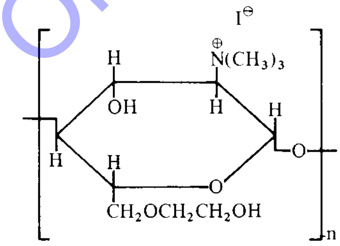
SUMMARY:

The stoichiometry of the salt-linkage formations of nonporous and porous silica particles with trimethylammonium glycol chitosan iodide (TGCI) was investigated by comparing the results of colloid titration and adsorption experiments with those of potentiometric titrations. The surface charge (Q) of colloidal silica as function of pH was evaluated by means of the colloid titration with TGCI. On the other hand, the density (D) of $\equiv SiO^{\ominus}$ groups of silica gel at different pH was also evaluated by the adsorption experiment of TGCI. These results obtained were compared with the Q vs. pH and D vs. pH curves which were obtained by the potentiometric titrations at various ionic strengths for colloidal silica and silica gel, respectively. It was concluded that the $\equiv SiO^{\ominus}$ groups on the surface of nonporous colloid silica form the salt-linkages stoichiometrically with $^{\oplus}N(CH_3)_3$-groups in TGCI, whereas the salt-linkage formation between $^{\oplus}N(CH_3)_3$-groups in TGCI and $\equiv SiO^{\ominus}$ groups of silica gel does not follow the stoichiometric relationship, since the salt-linkages of the $\equiv SiO^{\ominus}$ groups in the pores of the silica gel could be affected by the steric hindrance of the TGCI chain.

Introduction

The stoichiometry of polyion complex formation has been examined by various experimental methods. Most of the previous investigations though have dealt almost exclusively with the system composed of oppositely charged polyelectrolytes. Little attention has been paid to the complexation between ionic colloid particles and polyions.

The colloid titration, which was originated by Terayama[1)], is based on the polyion complex formation between polyacidic and polybasic ions. Thus, the stoichiometry of the complexation between polyanion and polycation in the titration system can be investigated by the analysis of the titration curve. We reported previously on the colloid titration behavior of poly(diallyldimethylammonium chloride)[2)], alternating



TGCI

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copolymer of maleic acid with methyl vinyl ether[3], poly(ethyleneimine)[4], and human carboxyhemoglobin[5]. In these studies, poly(vinyl alcohol-co-potassium vinylsulfate) (KPVS) and trimethylammonium glycol chitosan iodide (TGCI), [6-*O*-(2-hydroxyethyl)-2-(trimethylammonio)chitosan iodide], on which the polyelectrolyte properties[6] had been investigated, were used as standard titrants for the polybases and polyacids, respectively. The results obtained were compared with those of potentiometric titrations and discussed in terms of the stoichiometry of the complexation for each titration system.

It is now of interest to investigate the stoichiometry of the salt-linkage formation of the polyion with surface groups of the colloid particle. For this purpose, colloidal silica which is a nonporous and spherical particle of amorphous silica[7] was chosen in view of the available information[8] on the dissociation of surface groups ($\equiv$SiOH). TGCI was chosen as the polyion component, and the colloid titration with TGCI titrant was carried out for the silica sol. On the other hand, the adsorption experiment of TGCI on silica gel was also carried out in order to investigate the salt-linkage formation of the polyion with the porous particle. The results of colloidal silica and silica gel were compared with those of potentiometric titrations for both the samples of silica and discussed in terms of the stoichiometry of the salt-linkage formation between $^{\oplus}N(CH_3)_3$-groups attached to the TGCI chain and $\equiv SiO^{\ominus}$ groups situated on the surface or in the pores of the silica particle.

Experimental Part

The weight of colloidal silica and silica gel is reported as the weight of silica, i.e., the dry weight of both silica samples. The content of colloidal silica in the sol sample was determined as follows: the sol was evaporated to dryness and then dried at 120 °C for 4 h. The suspension of silica gel was prepared by weighing out the required quantity of silica gel dried at 120 °C for 4 h.

Materials

Colloidal silica was prepared by polymerization-dehydration of monosilicic acid according to the method of Heston et al.[9]. This preparation method consists in increasing the size of silica particles by slow addition of monosilicic acid obtained by passing sodium silicate through an ion exchange resin (Dowex 50). Polymerization was performed in alkaline media (pH 9) at 90 °C for 8 h. The resulting sol was filtrated through a membrane filter with a pore size of 50 nm, and then passed through a mixed-bed of ion exchange resins (Dowex 1 and 50), in order to eliminate an excess of electrolyte. The diameter of the silica particles was 16 ± 4 nm, as established by electron microscopy (Fig. 1). Measurement of the surface area by BET nitrogen adsorption gave a value of 264 m^2/g. These values agree with those estimated from the empirical relationship[10] between diameter and surface area. On the other hand, the pH value (3,42) at the point of zero charge evaluated by potentiometric titration was also in agreement with that (pH 3,5 ± 0,2) reported in the literature[8].

Wako gel LC-5H with a grain size of 100 mesh was used as a sample of porous silica. The purification was performed in 2 M perchloric acid for 2 h with stirring. The silica gel was separated by centrifugation, washed with distilled water until the pH of the suspension reaches 5 – 6, and dried at 120 °C for 4 h. The surface area of silica gel was 386 cm^2/g, as established by the BET method.

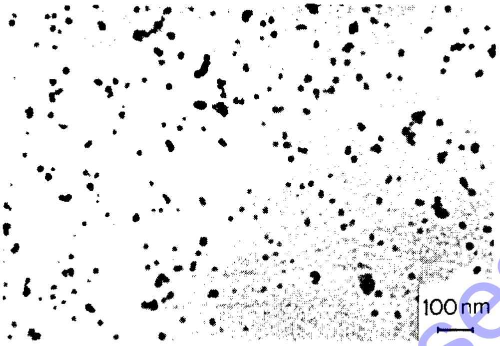

Fig. 1. Electron micrograph of colloidal silica measured with a Hitachi Transmission Electron Microscope (model H-500)

Trimethylammonium glycol chitosan iodide (TGCI) used here was colloid titration reagent available commercially from Wako Pure Chemical Industries, Ltd. The intrinsic viscosity was 0,230 dl/g, as determined by viscometric measurement in 1 M NaCl at 25 °C.

$(C_{11}H_{22}O_5NI)_n$ $(375{,}2)_n$	Calc.	N 3,73	C 35,2	H 5,92
	Found	N 3,31	C 30,1	H 5,57

The electrochemical and conformational properties are characterized in[6].

Colloid titration

The titration was carried out at 25 ± 0,1 °C in a nitrogen atmosphere using a Hirama Automatic Recording Titrator. The original sol was diluted with distilled water, and then the pH was adjusted to 3 – 8 with 0,1 – 1 M NaOH or HCl. The sample sol (50 ml) containing 0,02 – 0,4 g of silica was titrated with TGCI solution adjusted to the pH of the sample itself. In spite of the titration with the titrant of which the pH is the same as that of the sample, the pH of the titration system was more or less decreased by the addition of the titrant. Thus, the pH values at the initial and end points of the titration were always measured. The end point was determined by means of the measurements[2–5] of turbidity at 420 nm and conductivity (Fig. 2). The end point was also confirmed by the indirect titration method[1–3].

Adsorption experiment

The suspension (containing 0,1 – 1,8 g of silica in 40 ml of distilled water) was adjusted to the pH range of 3 – 10,5 by using 0,1 – 1 M NaOH or HCl. The suspension was stirred at 25 ± 0,1 °C in a nitrogen atmosphere until the pH was equilibrated. The TGCI solution adjusted to the pH of the suspension was added to the suspension from a microburet with a precision of 0,0005 ml, and then stirred at 25 ± 0,1 °C in a nitrogen atmosphere. After the adsorption equilibrium was established, the pH of the suspension was accurately measured. The amount of adsorbed TGCI was determined by colloid titration for the supernatant obtained by centrifugation of the sample suspension. The poly(vinyl alcohol-co-potassium vinylsulfate) (KPVS) solution (0,002485 mol/l) was used as a standard titrant for the colloid titration.

Potentiometric titration

The titration was carried out at 25 ± 0,1 °C in a nitrogen atmosphere, using a Hitachi-Horiba pH meter (model F-5) and a microburet with a precision of 0,0005 ml. The titration of colloidal silica was performed with 0,1002 M HCl for the sample sol (50 ml) containing 0,7683 g of silica, 0,01 – 0,05 mol of NaCl to adjust ionic strength, and free NaOH used for sol stabilization. The

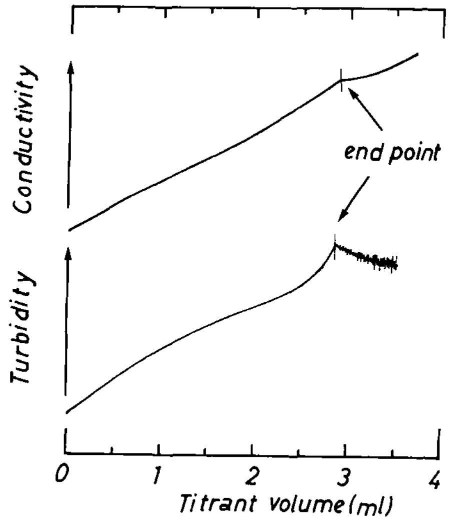

Fig. 2. Typical example of the end point determination of colloid titration with TGCI solution for sample sol (50 ml) containing 0,0816 g of silica (titration rate: 0,125 ml/min; concentration of TGCI: 0,004831 mol/l at the pH (6,91) of the end point). On the basis of these titration data, the amount (M_s) of $^{\oplus}N(CH_3)_3$— groups in TGCI bound to $\equiv SiO^{\ominus}$ groups was calculated to be $1{,}40 \cdot 10^{-5}$ mol

titration data was analyzed in the same manner as recently described by Komura et al.[8]. The result at ionic strength of 1,0 was confirmed by the titration method of Sears[11]. On the other hand, the titration of silica gel was also performed by the method of Nakagaki et al.[12]: the suspension (50 ml) containing 0,2 – 0,3 g of silica and 0 – 0,05 mol of NaCl was titrated with 0,1002 M HCl (in the region of pH < 5,3 – 6,2) and 0,1019 M NaOH (in the region of pH > 6,2 – 5,3).

Results and Discussion

An accurate information on the electrochemical property of TGCI was obtained to calculate the amount of $^{\oplus}N(CH_3)_3$— group (M_s in moles) which is bound by the salt-linkages to $\equiv SiO^{\ominus}$ groups of colloidal silica or silica gel. Fig. 3 shows the relation between pH and the degree of dissociation (α), which was obtained from the colloid titration curve of TGCI in[6] by the following equation[4]:

$$\alpha = (1/E_w)/(1/E_w^0) \tag{1}$$

where E_w represents the equivalent weight of TGCI, and E_w^0 (423) is the value of E_w at

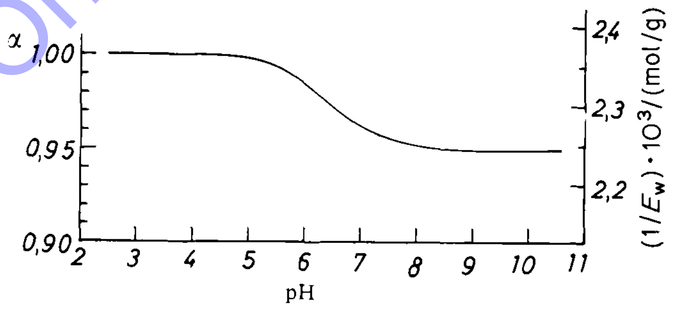

Fig. 3. Relationship between pH and the degree of dissociation (α) obtained from the colloid titration curve (see Fig. 7 in ref.[6]) represented by plotting the reciprocal of the equivalent weight (E_w) of TGCI against pH

$\alpha = 1$ and determined by the nitrogen content (3,31%). The result in Fig. 3 indicates that the dissociation of the TGCI ion is kept constant in the region of pH < 5 and pH > 8, while it varies slightly in the neutral region. This dissociation behavior was supported by the results[6)] of electrophoresis. The change in the α value in the neutral region seems to be due to incomplete quaternization of primary amino groups in glycol chitosan[2,6)]. The content of the residual amino groups[a)] in TGCI was 5,13%, as estimated by the difference in the α values in the acidic and basic regions.

This approximately agrees with that (3,46%) determined by elemental analysis. Thus, the effect of pH on the molarity of the TGCI solution was corrected by the curve of α vs. pH, when the M_s value was evaluated by the results of the colloid titration and the adsorption experiment.

The dependence of M_s on the weight (W) of silica was at first investigated by the results of the colloid titrations at various pH. As is shown in Fig. 4, the plots of M_s vs. W are expressed by straight lines passing through the origin, indicating the quantitative formation of salt-linkage between $\equiv SiO^{\ominus}$ groups on the surface of colloidal silica and $^{\oplus}N(CH_3)_3$— groups in TGCI. That is to say, it is found that the amount of TGCI which is bound by the salt-linkage to colloidal silica is proportional to the weight of silica.

To compare the results of the colloid titration with those of the potentiometric titration, the surface charge (Q) expressed in moles of $\equiv SiO^{\ominus}$ groups per 1 g of silica, was obtained as function of pH from both titration data. The estimation of the Q value by the colloid titration was based on the slopes of the straight lines shown in Fig. 4. Furthermore, the estimation of the Q value by the potentiometric titration was carried out according to[8)]. The results are summarized in Fig. 5. It is observed that the Q values by means of both titrations increase with increasing the pH values. This is in contrast to the fact[13)] that the amount of poly(vinyl alcohol), (PVA), adsorbed on various silica particles decreases with increasing pH. Thus, the adsorption mechanism of TGCI appears to be obviously different from that of a non-electrolyte polymer such as PVA: the former is due to the salt-linkage between $\equiv SiO^{\ominus}$ groups on the colloidal silica and $^{\oplus}N(CH_3)_3$— groups in TGCI, while the latter[13)] is interpreted by an interaction of the polymer with $\equiv SiOH$ groups and/or Si-O-Si bonds on the silica particle. On the other hand, the Q vs. pH curve obtained by the colloid titration is found to be in agreement with that by the potentiometric titration at high ionic strength. On the basis of this finding, it can be indicated that the salt-linkage formation between $\equiv SiO^{\ominus}$ and $^{\oplus}N(CH_3)_3$— groups approximately follows a stoichiometric relationship. In the acidic region, however, the Q value is slightly overestimated by means of the colloid titration. As has been mentioned in the Experimental Part, the pH of the colloid titration system was decreased by the addition of the TGCI solution adjusted to the pH of the sample. Therefore, and overestimation of Q in the

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[a)] In the region of pH < 5, the residual amino groups are completely protonated and could form the salt-linkages with $\equiv SiO^{\ominus}$ groups. Thus, the M_s value at this pH region is given by the sum of the mole numbers of $^{\oplus}N(CH_3)_3$— groups and of the residual amino groups.

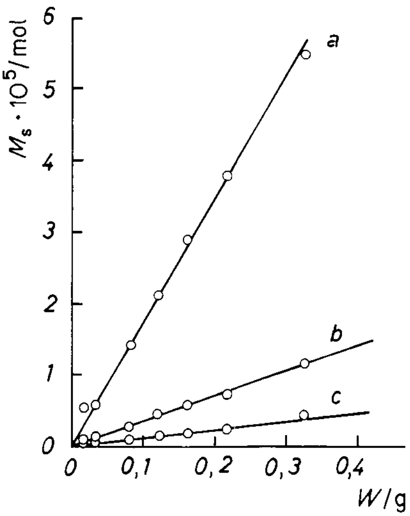

Fig. 4

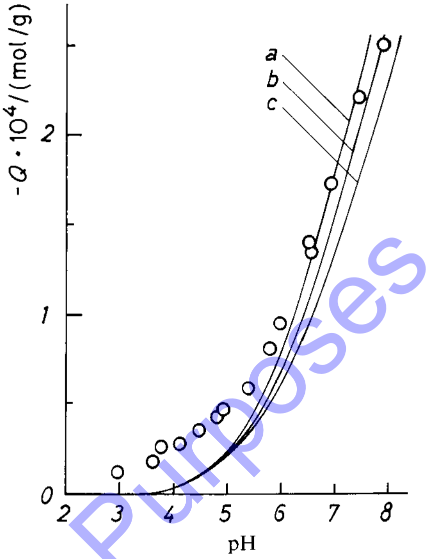

Fig. 5

Fig. 4. Linear relationship between M_s and W for colloidal silica at different pH of the end point; pH values: a, 6,91; b, 4,48; c, 2,98. W denotes the silica weight in 50 ml of the sample sol

Fig. 5. Surface charge (Q) of colloidal silica as function of pH determined by means of colloid titration (circles) and of potentiometric titrations (full lines) at different ionic strengths: 1 (a), 0,5 (b), and 0,2 (c)

acidic region could be understood by the assumption that the proton is released from the surface of colloidal silica by the reaction with TGCI:

$$\equiv \mathrm{SiOH} + {}^{\oplus}\mathrm{N(CH_3)_3}\text{—} \rightarrow \equiv \mathrm{SiO}^{\ominus}\text{---}{}^{\oplus}\mathrm{N(CH_3)_3}\text{—} + \mathrm{H}^{\oplus}$$

In order to confirm this assumption, the amount of protons (R_{H^+} in moles) which is released from colloidal silica by the salt-linkage with the TGCI ion, was evaluated by means of the difference in pH values at the initial and end points of the colloid titration. The R_{H^+} was then calculated by (see Appendix):

$$R_{H^+} = \frac{(V_0 + V_t)}{1000\,W}\left[(C^i_{OH^-} - 2C^e_{OH^-}) + (C^e_{H^+} - C^i_{H^+})\right] \qquad (2)$$

where W represents the weight of silica in V_0 ml of sample sol used for the titration, V_t is the titrant volume at the end point, $C^i_{OH^-}$ and $C^e_{OH^-}$ are the molarity of hydroxyl ions at the initial and end point of the titration, respectively, and $C^i_{H^+}$ and $C^e_{H^+}$ are the molarity of protons at the initial and end points, respectively. The relationship between R_{H^+} and pH at the end point is shown in Fig. 6, together with the curves of ΔQ vs. pH. Here, the ΔQ value represents the difference in Q obtained by the colloid and potentiometric titrations, respectively (see Fig. 5). In the acidic region (pH < 5 – 6), the curve of R_{H^+} vs. pH is observed to be in fair agreement with that of ΔQ vs. pH within the accuracy of the pH-measurement. The variation of R_{H^+} in the neutral region could be due to errors in the pH-measurements and/or to an interaction of protons with the residual amino groups in TGCI. In any event, it is evident that the overestimation of the Q value by the colloid titration is related, at least in the acidic region, to the reaction of $\equiv$SiOH with $^{\oplus}$N(CH$_3$)$_3$— as mentioned above.

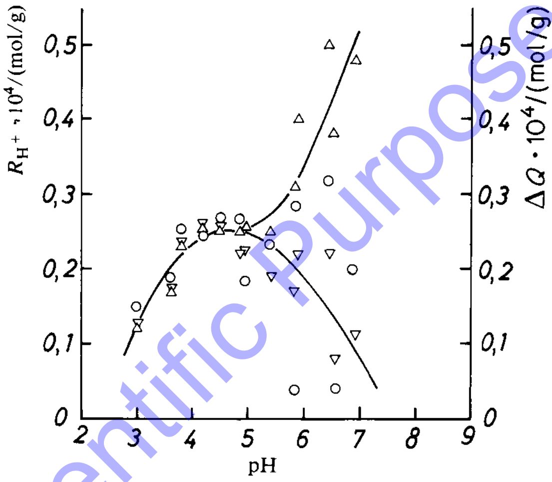

Fig. 6. Comparison of the R_{H^+} vs. pH curve (○) with the ΔQ vs. pH curves (▽, △) obtained by the difference between the Q values estimated by colloid titration and by potentiometric titrations at ionic strengths: 0,2 (▽) and 1,0 (△)

As was shown in Fig. 5, the result of the colloid titration for colloidal silica suggested that the polar groups on the surface of nonporous colloid particles form stoichiometrically salt-linkages with polyelectrolyte ions. However, if the polar groups were situated in pores of the porous particle, it could be considered that no salt-linkage formation follows a stoichiometric relationship because of the steric hindrance of the polymer chain. To obtain information about the salt-linkage formations of $^{\oplus}$N(CH$_3$)$_3$— groups in TGCI with $\equiv$SiO$^{\ominus}$ groups of porous silica, the adsorption experiment of TGCI on silica gel was carried out at a different pH.

Fig. 7 shows the dependence of M_s on W for silica gel. It is found that the plots of M_s vs. W at various pH are expressed by straight lines passing through the origin. This is similar to the results of colloidal silica (see Fig. 4) and indicates the quantitative formation of the salt-linkage between $^{\oplus}$N(CH$_3$)$_3$— and $\equiv$SiO$^{\ominus}$ groups. In the case of silica gel, however, the slope of the straight line is smaller than that of colloidal silica. This could be related to two contributions; one is the difference in the amount of $\equiv$SiOH groups for silica gel and colloidal silica used here, and the other is the effect of steric hindrance on the salt-linkage formations of $^{\oplus}$N(CH$_3$)$_3$— groups with $\equiv$SiO$^{\ominus}$ groups in the pores of silica gel.

In order to investigate further the salt-linkage formation between silica gel and TGCI, the density (D) of $\equiv$SiO$^{\ominus}$ groups, expressed in moles per 1 g of silica, was

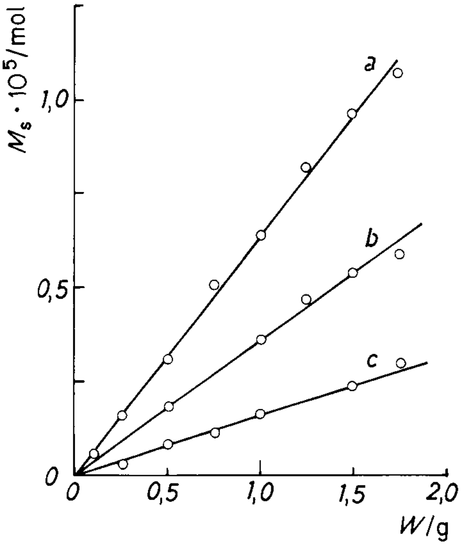

Fig. 7. Linear relationship between M_s and W for silica gel at different pH of the adsorption equilibrium; pH values: 4,61 (a); 7,09 (b); 8,60 (c). W denotes the silica weight in 50 ml of the suspension

evaluated by means of the adsorption experiment and the potentiometric titration[a]. Figs. 8 and 9 show the curves of D vs. pH by the adsorption experiment and the potentiometric titration, respectively. The D values by both estimation methods exhibit a rapid increase in the basic region because the protons dissociate from $\equiv$SiOH groups of the silica gel with the increase in basicity. This behavior of silica gel is similar to that of colloidal silica (see Fig. 5). However, the D value from the adsorption experiment is smaller than that from potentiometric titration, whereas the Q value from colloid titration approximately agrees with that by the potentiometric titration. From the comparison of the Q vs. pH curves with the D vs. pH curves at the region of pH < 8 (see Figs. 5 and 9), it is found that there is no remarkable difference in the amount of $\equiv$SiOH groups for colloidal silica and silica gel. Thus, the difference between the D values by the adsorption experiment and the potentiometric titration can be understood by the effect of the steric hindrance of TGCI chain on the salt-linkage formation between silica gel and TGCI: the $\equiv$SiOH groups situated in the pores and on the surface of the silica gel are dissociated by $OH^{\ominus}$, but the dissociated $\equiv SiO^{\ominus}$ groups in the pores do not form salt-linkages with $^{\oplus}N(CH_3)_3$— groups in TGCI because of the steric hindrance of the polymer chain.

On the basis of the results obtained here, it may be concluded that the stoichiometric relationship for salt-linkage formation appears not only in the case of oppositely charged polyions, but also in the case of the polyion and ionic colloid if the polar groups of the colloid are located on the nonporous surface.

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[a] It was pointed out that amorphous silica was dissolved in alkaline media. However, the D values obtained here were uncorrected by the weight loss of silica gel because the solubility of silica (including monomeric silicic acid and silicate ions) at 25 °C was generally believed to be less than 0,005 g/100 ml in the range of pH < 11[14, 15].

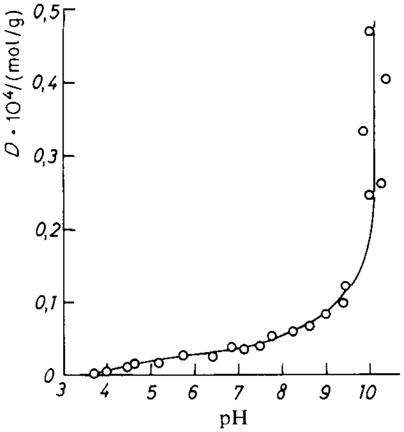

Fig. 8

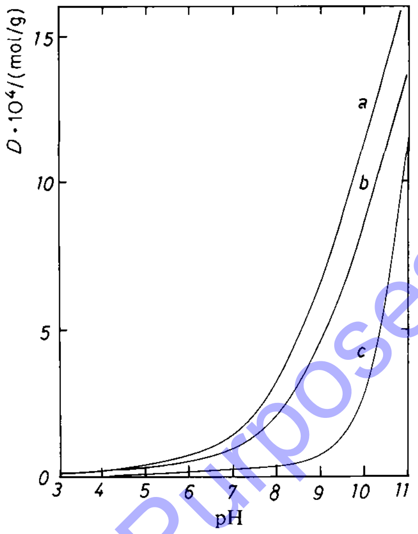

Fig. 9

Fig. 8. Density (D) of $\equiv SiO^{\ominus}$ groups of silica gel as function of pH obtained by the adsorption experiment

Fig. 9. Density (D) of $\equiv SiO^{\ominus}$ groups of silica gel as function of pH obtained by potentiometric titrations at different ionic strengths: 1,0 (a), 0,5 (b) and 0 (c)

Appendix

Let us consider that the amount-of-substance concentrations of proton and hydroxyl ion in the titration system vary from $C^i_{H^+}$ and $C^i_{OH^-}$ at the initial state to $C^e_{H^+}$ and $C^e_{OH^-}$ at the end point since the protons are released from $\equiv$SiOH groups on the colloidal silica by the salt-linkage with $^{\oplus}N(CH_3)_3$— groups in TGCI. In the course of the titration, a part of the released protons was neutralized with hydroxyl ions, and the other remains in the system, if an interaction between proton and TGCI ion is negligible. Thus, the total concentration ($r^t_{H^+}$) of the released protons can be obtained by subtracting $C^i_{H^+}$ from the sum of the neutralized proton ($C^i_{OH^-} - C^e_{OH^-}$) and of the remainder ($C^e_{H^+} - C^e_{OH^-}$) which was corrected by the molarity of protons resulting from the dissociation of water molecules:

$$r^t_{H^+} = (C^i_{OH^-} - 2C^e_{OH^-}) + (C^e_{H^+} - C^i_{H^+}) \qquad \text{(A-1)}$$

The amount of the released protons ($r^m_{H^+}$ in moles) in the sample sol (V_0 in ml) is given by:

$$r^m_{H^+} = \frac{V_0 + V_t}{1\ 000}\, r^t_{H^+}$$

$$= \frac{V_0 + V_t}{1\ 000}\,[(C^i_{OH^-} - 2C^e_{OH^-}) + (C^e_{H^+} - C^i_{H^+})] \qquad \text{(A-2)}$$

where V_t represents the titrant volume at the end point. Eq. (2) in the text is easily obtained by dividing $r^m_{H^+}$ by the weight (W) of silica in the sample sol.

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