Study on adsorption of nonionic and cationic polymers on silica gel by using total organic carbon analysis

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The adsorption behaviour of poly(ethylene oxide) and trimethylammonium glycol chitosan iodide from water onto silica gel is reported. A total organic carbon analytical method was employed to determine precisely the small quantity of polymer remaining after the attainment of adsorption equilibrium. The adsorption isotherms and the curves of equilibrium adsorption against pH were obtained and compared with the ionization properties of the silanol groups investigated by potentiometric titration. The results obtained are discussed in terms of the adsorption mechanism for nonionic and cationic polymers.

Keywords Adsorption behaviour; poly(ethylene oxide); silica gel; analysis; total organic carbon; ionization; titration; mechanism

INTRODUCTION

Numerous studies have dealt with the adsorption phenomena of water-soluble polymers on hydrophobic colloids. The amount of adsorbed polymer was estimated by two different methods[1]: one is by direct measurement and the other is an indirect method based on the concentration of polymer remaining in the adsorption system. Typical examples of the direct measurement are the general weighing method, radiotracer analysis[2], and infra-red spectroscopy[3]. The residual polymer concentration is determined by chemical analysis, e.g. the Kjeldahl method[4], and also by the measurement of the physical quantities dependent on polymer concentration, e.g. conductance[5], refractive index[6], turbidity[7], etc.

Recent years have seen dramatic developments in an analytical method using total organic carbon (TOC) in aqueous solution[8]. At present using the TOC analytical technique, it has become possible to determine rapidly and precisely small quantities of organic matter in dilute solutions. The principal advantage is that the analytical result is free from the interference of salts in aqueous solution, since the organic matter in the solution is converted to carbon dioxide gas in a combustion furnace and detected by the appropriate methods (e.g. gas chromatography and infra-red spectroscopy). Thus, the TOC method is thought to be suitable for the determination of the adsorbed amount of water-soluble polymers, although this has not been adopted in adsorption experiments reported previously.

Silica dispersion is an especially suitable system for studies on the adsorption phenomena of water-soluble polymers, because the surface chemistry has been more thoroughly investigated than any other solid. Previously we reported on the electrostatic interaction of trimethylammonium glycol chitosan iodide (TGCI) with charged silanol groups ($\equiv SiO^-$) on the surface of colloidal silica[9]. Compared with polyelectrolyte, the adsorption of nonionic polymers on silica has been studied extensively[10-13]. In previous studies, however, little attention has been paid to the difference in the adsorption mechanism for ionic and nonionic polymers.

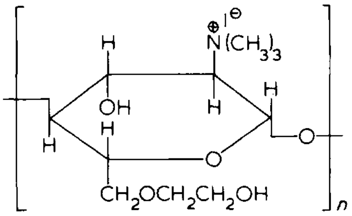
The purpose of the present study is to test the suitability of the TOC method for the determination of the adsorbed amount of water-soluble polymer and to clarify the adsorption mechanism for cationic and nonionic polymers.

Poly(ethylene oxide) (PEO) and TGCI were used as the sample polymers. The adsorption isotherms and pH dependence of equilibrium adsorption were obtained and compared with the dissociation properties of the silanol groups evaluated by potentiometric titration method. The results are discussed in terms of the interactions of the silanol groups on the surface and in the pore of the silica gel with the trimethylammonium groups in TGCI and the ether groups in PEO.

EXPERIMENTAL

Materials

The PEO samples were obtained from two commercial products with different molecular weights, by fractional precipitation using benzene as the solvent and isooctane as the precipitant[14]. The weight-average molecular weights ($\overline{M}_w$) for the fractions used here were 2.14×10^4 and 5.02×10^6, as estimated by viscometric measurement[15]. TGCI was the same sample as used in previous studies[9,16]. The structural formula is expressed as follows:



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The equivalent weight (423) was determined from the nitrogen content and from the result of colloid titration. The degree of polymerization (about 400) was estimated roughly by an osmometric method. The results of the elemental analysis for both polymers were: H, 9.16%; C, 54.42% for PEO, and H, 5.57%; C, 30.10%; N, 3.31% for TGCI.

Wako gel Q-63 with a grain size of 325 mesh was used as the adsorbent. The purification was carried out 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 suspension reached 5–6, and dried at 120°C for 4 h. The surface area of the silica gel was 554 m^2 g^{-1}, as established by the BET method.

Merck grade reagents of anhydrous potassium biphthalate and anhydrous sodium bicarbonate were used as the standard samples for the calibration of the TOC analyser. The water used for preparing both standard solutions was distilled under reduced pressure in a stream of nitrogen just before use to avoid the absorption of carbon dioxide gas.

Adsorption experiment

The sample suspension was prepared by weighing out the required quantity of silica gel. The silica gel concentrations (g dl^{-1}) for the adsorption experiments of TGCI and PEO were 1.00 and 0.10, respectively. The suspension (50 ml) was adjusted to pH 3–11 with 0.1–1 N HCl or NaOH. After the pH was equilibrated, the polymer solution adjusted to the pH of the suspension, was added from a microburette to within ±0.005 ml, and then stirred at 25±0.1°C under nitrogen until the adsorption equilibrium was established. The residual polymer concentration was determined by TOC analysis for the supernatant obtained by centrifugation. The residual TGCI concentration was also confirmed by the colloid titration method[17,18].

The TOC analysis was carried out using a Beckman TOC analyser (model 915-B) provided with two analytical channels for detecting both total carbon (TC) and inorganic carbon (IC). The TC channel is equipped with a combustion tube packed with cobalt oxide catalyst. The IC channel is equipped with a combustion tube packed with quartz chips wetted with phosphoric acid. The combustion tubes in the TC and IC channels were kept at 950°C and 150°C, respectively. The TC and IC components in sample solution (50 μl) were converted to carbon dioxide gas which was conveyed by a continuous flow (200 ml min^{-1}) of purified air to an infra-red detector set at the wave number of 2349 cm^{-1}.

The colloid titration was carried out by using 0.00252 N potassium poly(vinyl alcohol) sulphate solution as the standard titrant. The end point was determined by a turbidity titration method, using a Hirama Automatic Recording titrator. The detailed titration technique was described previously[17,18].

Potentiometric titration

The titration was carried out at 25±0.05°C in a nitrogen atmosphere, using a Beckman digital pH meter (model 4500) and a microburette to within ±0.0001 ml. Two titrations were carried out to obtain a titration curve: one with the suspensions containing 5 g silica gel in 50 ml of distilled water and of 0.5 N NaCl solution, and the other (blank) with the same solvents in the absence of silica gel. One normal HCl and NaOH solutions were used as the titrants for the titrations in the pH regions below and above 5.1–5.8, respectively. The amount of charged (and/or cation-exchanged) silanol groups was calculated from the difference in the titrant volumes required to reach the same pH in the sample and blank.

RESULTS AND DISCUSSION

Determination of polymer concentration

For the determination of the adsorbed amount of water-soluble polymers by TOC analysis, it is necessary to examine the accuracy in the measurement of polymer concentration. The calibration of TOC instrument was first carried out to determine accurately the polymer concentration. Anhydrous potassium biphthalate and anhydrous sodium bicarbonate were used as the standard samples for TC and IC analytical channels, respectively. The recorder deflection (*Rd*) was reproducible to ±1.1% on repeated runs, as established at full range of the detector and at the carbon concentration range of 10–70 mg l^{-1}. The value of *Rd* for the TC channel was observed to be proportional to the carbon concentration, but the result of the IC analysis showed that there is a detectable amount of IC. The *Rd* value for the IC channel does not vary with the carbon concentration, indicating that the IC content is independent of the phthalate concentration. The result for IC could be due to the contamination of carbon dioxide gas into the standard solution from the atmosphere, although the standard solution was prepared carefully by using distilled water which is free from carbon dioxide gas (see Experimental section). Thus, it is necessary to eliminate the effect of carbon dioxide gas in order to determine accurately the polymer concentration. This problem is solved by the use of the TOC value obtained by subtracting IC from TC, since it can be assumed that the TOC value is directly proportional to the polymer concentration.

In order to confirm this assumption, the calibration curves of *Rd* vs. carbon content were obtained by using the phthalate and carbonate standard samples (*Figure 1*). It is found that the *Rd* value for TC analysis for the phthalate standard is in fair agreement with that for IC analysis for the carbonate standard. Furthermore, the difference between the *Rd* values for TC and IC analyses for the phthalate standard (or the difference between the *Rd* values for IC analyses for the carbonate and phthalate standards) is directly proportional to the carbon content, and their relationship is represented by a straight line passing through the origin. These results indicate that the TOC value is not affected by the IC component in sample solution.

Figure 2 shows the calibration curves of *Rd* vs. TOC for TGCI and PEO, together with the scales of the polymer concentration obtained from the carbon content by elemental analysis. In this figure, the full line represents the calibration curve of TOC for the phthalate standard (see *Figure 1*). Excellent agreement is observed in the TOC calibration curves between TGCI and PEO, and also they fit in with that of the standard sample.

From the results mentioned above, it is clear that the measurement of the polymer concentration by the TOC method can be made even at the concentration of a few mg l^{-1}, thus indicating that this method is suitable for the determination of the amount of adsorbed polymer.

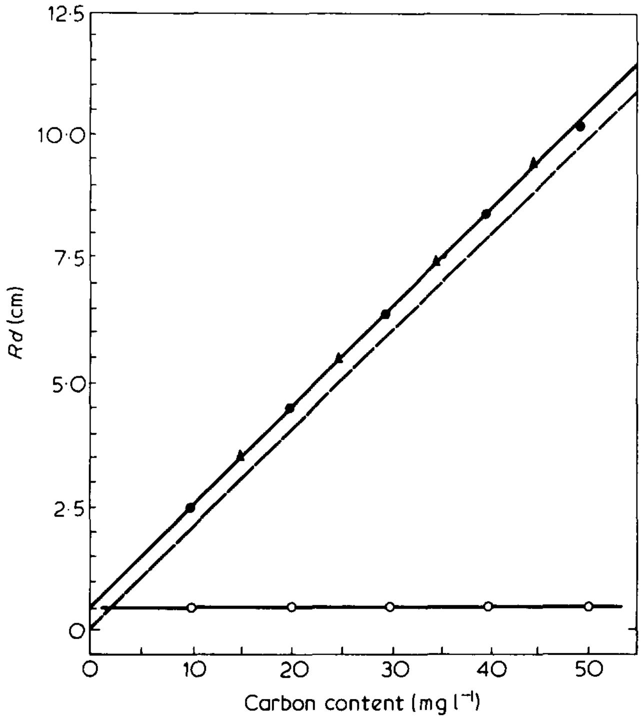

Figure 1 Calibration curves of *Rd* vs. carbon content: ●, TC for anhydrous potassium biphthalate; ○, IC for anhydrous potassium biphthalate; ▲, IC for anhydrous sodium bicarbonate. Broken line denotes the relation between *Rd* and TOC obtained by subtracting *Rd* value for IC analysis from that for TC analysis

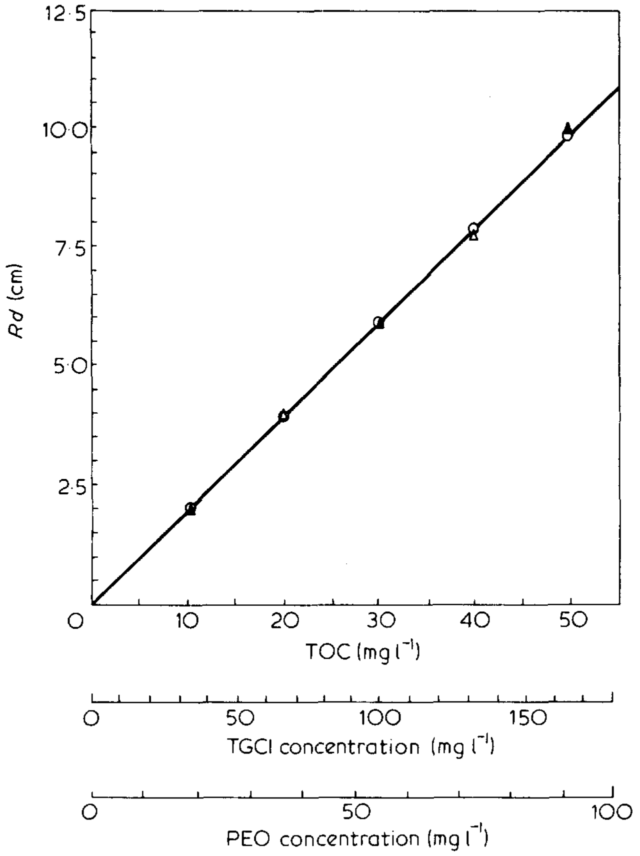

Figure 2 Calibration curves of *Rd* vs. TOC for TGCl (○) and PEO (▲, $\bar{M}_w$ = 5.02 x 10^6; △, $\bar{M}_w$ = 2.14 x 10^4). Full line denotes the calibration curve for anhydrous potassium biphthalate (see broken line in *Figure 1*). Scales of polymer concentration in mg l^{-1} were determined by elemental analysis

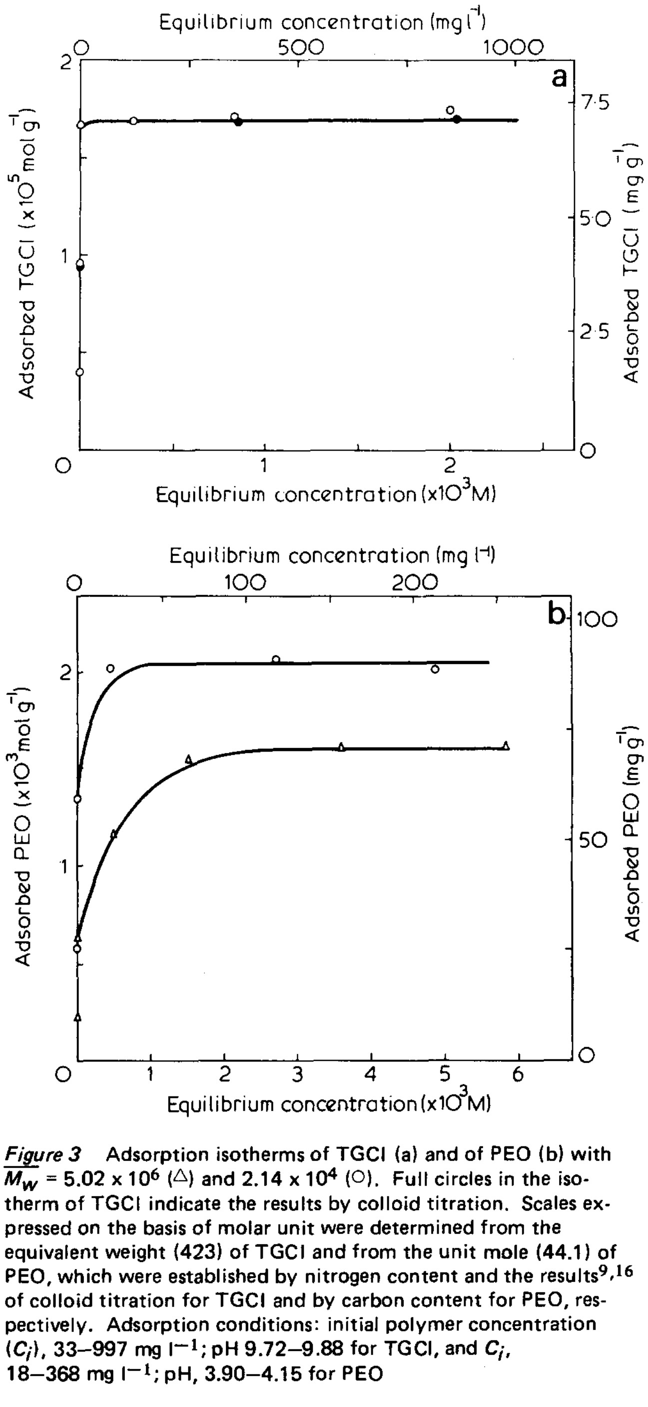

Figure 3 Adsorption isotherms of TGCl (a) and of PEO (b) with $\bar{M}_w$ = 5.02 x 10^6 (△) and 2.14 x 10^4 (○). Full circles in the isotherm of TGCl indicate the results by colloid titration. Scales expressed on the basis of molar unit were determined from the equivalent weight (423) of TGCl and from the unit mole (44.1) of PEO, which were established by nitrogen content and the results[9,16] of colloid titration for TGCl and by carbon content for PEO, respectively. Adsorption conditions: initial polymer concentration (C_i), 33–997 mg l^{-1}; pH 9.72–9.88 for TGCl, and C_i, 18–368 mg l^{-1}; pH, 3.90–4.15 for PEO

Adsorption isotherms

The amount of adsorbed polymer and equilibrium polymer concentration were determined from the analytical results of TOC for the polymer solutions before and after the adsorption by using the calibration curve in *Figure 2*. To avoid the absorption of carbon dioxide gas, the supernatant obtained by centrifugation of the suspension was acidified by the addition of one drop of 6 N HCl. The change in the sample volume (less than 1%) by this treatment can be tolerated with the experimental error of TOC analysis. The amount of adsorbed TGCl was further confirmed by the colloid titration method.

Figure 3 shows the adsorption isotherms for TGCl and PEO. The results of the colloid titration for TGCl are represented by black circles. From the results for PEO, it is observed that the equilibrium adsorption for the sample

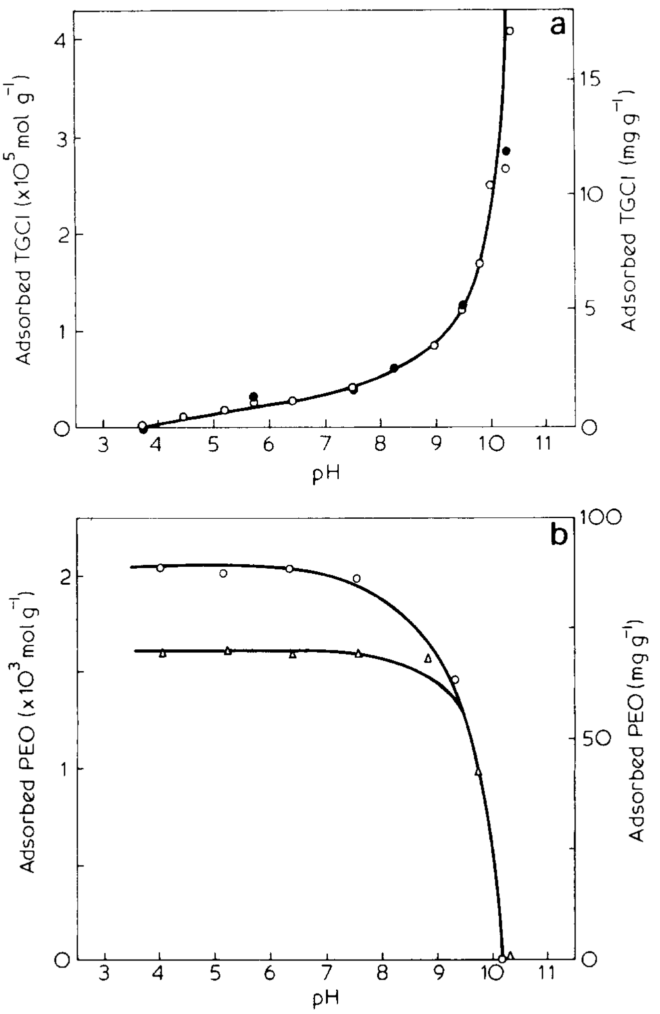

Figure 4 Curves of equilibrium adsorption vs. pH for TGCl (a) and for PEO (b) with $\overline{M}_w$ = 5.02 x 10^6 (△) and 2.14 x 10^4 (○). The results (●) for colloid titration are included in the curve of TGCl. C_i: 997 mg l^{-1} for TGCl; 276 mg l^{-1} for PEO

with $\overline{M}_w = 2.14 \times 10^4$ is larger than that for the sample with $\overline{M}_w = 5.02 \times 10^6$. This is in contrast to the adsorption behaviour[19] or PEO on nonporous silica particles such as Aerosil: the adsorbed amount is found to increase with the molecular weight. However, the absorbent used here is silica gel which is a well known porous particle with different pore sizes. Taking this fact into account, the result obtained can be understood by the explanation that the high molecular weight PEO is more difficult to penetrate in the pores of silica gel than the low molecular weight PEO because of the steric hindrance effect of the polymer chain.

In addition to these results, from the comparison of the isotherms for TGCl and PEO a remarkable difference is observed in equilibrium adsorption between both polymers. As will be discussed below, this result can be related to the difference in the adsorption mechanisms for cationic and nonionic polymers.

Curves of equilibrium adsorption vs. pH

The dependence of equilibrium adsorption on pH for TGCl and PEO was investigated to obtain information about the adsorption mechanism for nonionic and cationic polymers. The results are shown in *Figure 4*. In the curve of TGCl, the equilibrium adsorption obtained by colloid titration is included to confirm the result by the TOC method. From the curves of PEO at different molecular weights, it can be noted that there is a remarkable difference in the values of equilibrium adsorption. This also suggests involvement of the steric hindrance effect mentioned previously.

From the comparison of TGCl and PEO in *Figure 4*, it is found that the equilibrium adsorption of TGCl is of order of a few per cent of the adsorption of PEO. The same result is obtained by the comparison of the isotherms for TGCl and PEO (see *Figure 3*). The difference between both polymers is considerably larger, even if the change in equilibrium adsorption caused by the molecular weights of TGCl and PEO is taken into account. As a reasonable interpretation of these results, the difference in the forms of polymer layer adsorbed on the silica gel surface could be considered. In the case of nonionic polymer, it has been frequently pointed out that the polymer chain is adsorbed in the form of a loop layer on the hydrophobic colloid[20]. Alternatively, the authors reported that the $^+N(CH_3)_3$ ions in TGCl form the salt-linkages with the charged silanol groups on the nonporous colloidal silica, and the salt-linkage formation follows stoichiometric relationship at different pH[9]. These results could suggest that the TGCl ion is adsorbed in the form of a flat layer on the colloidal silica. Thus, the TGCl and PEO on the silica gel surface could take the forms of flat and loop layers, respectively.

A remarkable feature of *Figure 4* is that the equilibrium adsorption curve for TGCl shows a rapid increase in the pH range 9–11, whereas that for PEO decreases in this pH range. As was described above, the adsorption of TGCl on colloidal silica is due to the salt-linkage between the charged silanol groups and the $^+N(CH_3)_3$ groups. In the case of silica gel, the rapid increase of equilibrium adsorption in the basic range where the silanol groups are highly ionized is also suggestive of the salt-linkage formation with the TGCl ion. To clarify the ionization property of the silanol groups of silica gel, the density (D) of the ionized (and/or cation-exchanged) silanol groups was obtained as a function of pH (*Figure 5*). From the comparison of *Figures 4* and *5*, it is found that the

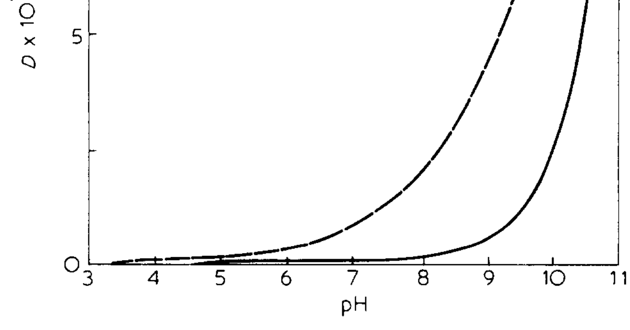

Figure 5 Density of ionized (and/or cation-exchanged) silanol groups of silica gel as a function of pH at ionic strengths of 0 (full line) and 0.5 (broken line)

equilibrium adsorption of TGCI is proportional to the *D* value, although the agreement between the equilibrium adsorption expressed in the unit moles of TGCI and the *D* value is not observed. Therefore, the adsorption mechanism is explained as follows: the TGCI ion is adsorbed on silica gel by the salt-linkage of the $^+N(CH_3)_3$ groups with the charged silanol groups on the surface, but the stoichiometric relationship of the salt-linkage formation, which is observed for the colloidal fails in the case of silica gel. This could be because the salt-linkage between TGCI ion and the silanol groups in the pores of the silica gel is made impossible by the steric hindrance effect of the polymer chain.

Compared with the case of cationic polyelectrolyte, the mechanism for the adsorption of nonionic polymer onto a silica particle is relatively complex. The adsorptions of poly(acrylamide) (PAAm)[10], poly(vinyl alcohol) (PVA)[13] and PEO[11,12] have been interpreted in terms of: hydrogen bonding of silanol groups with PAAm[10]; hydrophobic interaction of siloxane (Si–O–Si) groups with methine groups and/or the residual acetate groups in PVA[21]; hydrophobic interaction and hydrogen bonding of siloxane and silanol groups with PVA[13]; hydrogen bonding and hydrophobic interaction of silanol and siloxane groups with PEO[11,12]. As is summarized above, no general explanation for the adsorption mechanism has been accepted. However, the results obtained here indicate that, contrary to cationic polymer, the amount of adsorbed PEO decreases with the ionization of the silanol groups. Therefore, the hydrogen bonding mechanism could play, at least in a qualitative way, an important role in the adsorption of nonionic polymers on silica particles.

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