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Stoichiometric Salt-linkage Formation of Trimethylammonium Glycol Chitosan Iodide with a Carboxylic Type Ion Exchanger

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SUMMARY:

The adsorption of trimethylammonium glycol chitosan iodide (TGCI) on Dowex CCR-2 resin was investigated at different pH values and resin weights. The concentration of Na^+ or Ca^{2+} ions, released by the ion exchange reaction with TGCI, was measured by inductively coupled plasma spectroscopy. It was found that the amount of the released ions is comparable to that of the absorbed TGCI. This indicates that the salt-linkage formation of carboxylate ions of the exchanger with $^{\oplus}N(CH_3)_3$-groups in TGCI follows a stoichiometric relationship. This result is discussed in connection with the form of the polymer layer adsorbed on the solid surface.

Introduction

Study on the stoichiometry of salt-linkage formation of polyelectrolyte ions with ionizable groups of colloid particles gives an important information about the form of the polymer layer adsorbed on the colloid surface. Corry[1] reported that the salt-linkage between poly(L-lysine) and polystyrene latices in dilute aqueous solution follows a stoichiometric relationship. The previous study[2] from this laboratory also showed that the silanol groups on the surface of colloid silica form stoichiometrically the salt-linkages with trimethylammonium glycol chitosan iodide (TGCI) [6-*O*-(2-hydroxyethyl)-2-(trimethylamonio)-chitosan iodide]. However, other informations about the stoichiometric salt-linkage have not yet been obtained, although the adsorption of polyelectrolytes on hydrophobic colloids has been studied by many authors investigating the adsorption mechanism[3-10]. Thus, it seems desirable to undertake a more detailed investigation on the stoichiometry of the salt-linkage formation of polyions with ionizable groups on the solid surface.

In the present study, the adsorption of TGCI on a carboxylic type ion exchanger was carried out at different pH values and resin weights. Moreover, the amount of cation which is released from the ion exchanger caused by the binding of TGCI was measured by inductively coupled plasma (ICP) spectroscopy. The stoichiometry of the salt-linkage formation of carboxylate ions of the ion exchanger with $^{\oplus}N(CH_3)_3$-groups in TGCI was investigated by comparing the amount of the adsorbed TGCI with that of the released cation. The results obtained are discussed in connection with the form of the polymer layer adsorbed on the solid surface.

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Experimental Part

Materials: TGCI ($\bar{P}_n$ = ca. 400) was the same sample as used in the previous studies[2,11,12]. Dowex CCR-2 resin (a bead type carboxylic acid cation exchanger) was purified in the usual way. The hydrogen-form of the resin was prepared by leaching with 1 M HCl, washing with distilled water until chloride ion was no longer detectable, air-dried at room temperature for 2 days, and then dried at 60 °C for 1 day under vaccum. The hydrogen-form resin was completely converted to the sodium- and calcium-form with 0,1 M NaOH and 0,015 M $Ca(OH)_2$, respectively. The salt-form resins were washed satisfactorily with 0,1 M tetramethylammonium hydroxide (TMAH) solution in order to avoid the ion exchange reaction between resin and proton[*].

Potentiometric titration: The titrations with 0,1 M NaOH and 0,015 M $Ca(OH)_2$ were carried out on a dispersion (50 ml) containing 0,1 g of the hydrogen-form resin, according to the method of Kunin and Myers[13]. The pH of the dispersion was measured by using a Beckman digital pH meter (model 4500).

Adsorption experiment: The amount of TGCI adsorbed on the hydrogen-form resin was determined in the pH range of 5 – 11. The sample resin (0,5 g) was dispersed in 50 ml of distilled water, and the pH of dispersion was adjusted with 0,01 – 1 M NaOH or $Ca(OH)_2$. After the pH was equilibrated, the TGCI solution (0,0866 mol · l^{-1}), adjusted to the pH of the sample dispersion, was added from a microburet with a precision of 0,005 ml and then stirred until the adsorption equilibrium was established. On the other hand, the adsorption of TGCI on the salt-form resin was also carried out for 50 ml of the dispersion (pH 10) containing TGCI (0,866 mmol) and the resin (0,5 – 2 g). The pH of the sample was then adjusted with 1 M TMAH solution. All of the adsorption experiments were performed at 25 ± 0,1 °C in a nitrogen atmosphere to avoid the contamination with carbon dioxide gas. The concentration of the residual TGCI in the supernatant was determined by means of colloid titration. The titration technique was described in detail in the previous papers[2,14,15].

Measurement of the concentration of cations released from the salt-form resin caused by adsorption of TGCI: The adsorption of TGCI on the salt-form resin was carried out in the same manner as described above. The concentration of Na^+ or Ca^{2+} ions in the supernatant liquid before and after the adsorption was measured to compare the amount of the released cation with that of the adsorbed TGCI. The measurement was performed by ICP spectroscopy using a Jarrell-Ash Plasma AtomComp Direct Reading Spectrometer (model 975).

Results and Discussion

In order to clarify the difference in the adsorption behavior for polycations and small cations, the adsorbed amount (A_s in eq/g) of small cations was at first investigated as function of pH by means of potentiometric titrations of the hydrogen-form resin with NaOH and $Ca(OH)_2$ titrants (Fig. 1). From the curves of A_s vs. pH for NaOH and $Ca(OH)_2$, it is evident that the adsorption of Ca^{2+} ion is saturated at lower and narrower pH range than that of Na^+ ion. This seems to be related to the

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[*] The adsorption experiment of the metal cation from NaOH or $Ca(OH)_2$ solution (pH 10) in the presence and absence of TMAH ion (0,1 mol/l) onto the hydrogen-form resin showed that no pronounced difference is observed in the adsorptive amounts obtained in the presence and absence of TMAH. Thus, it is clear that the metal cation bound to the resin is not exchanged with TMAH ion in the bulk phase.

difference in affinities of both metal ions towards the carboxyl groups of the ion exchanger[16]. On the other hand, the base adsorptive capacity*) for the resin used here was 11 meq/g for Na^+ ion and 12 meq/g for Ca^{2+} ion, as estimated from the A_s value at the plateau region of the curves in Fig. 1.

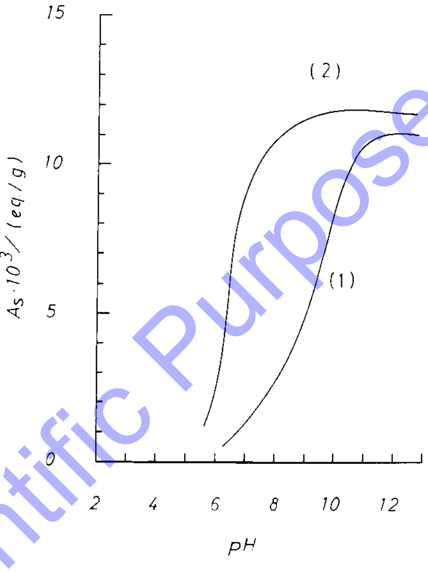

Fig. 1. Relationship between the adsorbed amount (A_s) of small cations and pH obtained by potentiometric titration for the hydrogen-form of Dowex CCR-2 resin; cation: Na^+ (1) and Ca^{2+} (2)

The dependence of the adsorbed amount (A_p in unit mol/g) of TGCI ions on pH was measured for comparison with the results for small cations (Fig. 2). The change in A_p with pH was found to be similar to the curves depicted in Fig. 1, except that there is a remarkable difference in A_p values caused by the pH-adjusters because of the difference in the affinities between Na^+ and Ca^{2+} ions. From the fact that the A_p value increases with increasing pH, it can be deduced that the binding of TGCI ion to Dowex CCR-2 resin is due to the salt-linkage formation of $^{\oplus}N(CH_3)_3$-groups in TGCI with carboxylate ions of the exchanger. The other important feature of Fig. 2 is that the A_p value at the plateau region is much less than the base adsorptive capacity. This result is explicable as follows: the salt-linkage formation between TGCI ion and Dowex CCR-2 resin does not take place in the pores of the exchanger because of a steric hindrance effect of the polymer chain. Analogous results have been observed in the adsorption of polymeric substances on ion exchangers[19] and other porous particles[2, 12]. Thus, it is considered that TGCI ions form salt-linkages with only carboxylate ions on the surface of Dowex CCR-2 resin and also that the number of the

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*) This quantity does not represent the total capacity of the resin, but rather an equilibrium adsorption (see refs. [17] and [18]).

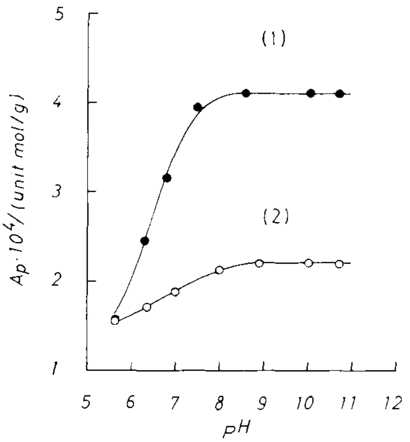

Fig. 2. Relationship between the adsorbed amount (A_p) of TGCI and pH for the hydrogen-form of Dowex CCR-2 resin; pH-adjuster: NaOH (1) and $Ca(OH)_2$ (2)

salt-linked sites varies with the amount of the carboxylate ions, which is influenced by the pH, and the species of small cations acted as the counterion.

To investigate further the salt-linkage formation between TGCI and Dowex CCR-2 resin, the adsorption isotherms were obtained for the salt-form resins in the region where A_p is independent of pH. The pH of the adsorption system was adjusted with TMAH, since an exchange between the metal cation bound to the resin and TMAH ion in bulk phase does not take place (see Exptl. Part). The results obtained are shown in Fig. 3. The equilibrium adsorption for the salt-form is in fair agreement with the A_p value for the hydrogen-form at the plateau region of the curves in Fig. 2. This means that the small cations bound to the resin are exchanged with the $^{\oplus}N(CH_3)_3$-groups in TGCI:

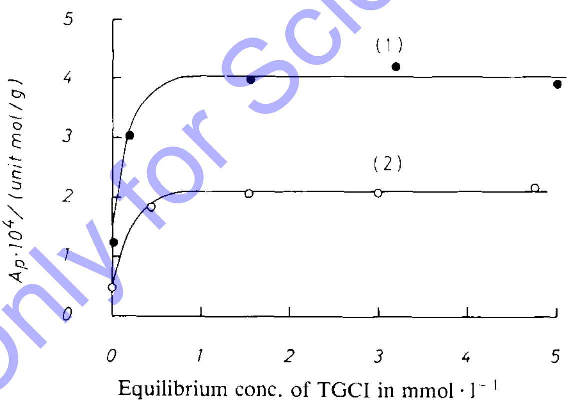

Fig. 3. Adsorption isotherms of TGCI for the salt-forms of Dowex CCR-2 resin; resin: sodium-form (1) and calcium-form (2). The pH of adsorption system was adjusted to 10 ± 0,1 with TMAH. The adsorbed amount is expressed on the basis of the resin weight in the hydrogen-form

$$R{-}COO^{\ominus}\,Mt^{\oplus} + {}^{\oplus}N(CH_3)_3{-}TGCI \rightarrow R{-}COO^{\ominus}\,{}^{\oplus}N(CH_3)_3{-}TGCI + Mt^{\oplus}$$

where $Mt^{\oplus}$ and R represent metal cation and ion exchanger, respectively. Therefore, it was anticipated that a more detailed information about the stoichiometry of the salt-linkage between the Dowex CCR-2 resin and TGCI ion could be obtained by comparing the amount of the adsorbed TGCI with that of the released cation.

The analytical results of the released cations at different resin weights are listed in Tab. 1, together with the amount of the adsorbed TGCI. It was found that the amount of Na^+ ion released is comparable to that of the adsorbed TGCI within the experimental error of ICP spectroscopy. In the case of Ca^{2+} ion, furthermore, the agreement between the amounts of the released ion and adsorbed TGCI can be accepted if we consider that 1 mol of Ca^{2+} ions is exchanged with 2 mol of $^{\oplus}N(CH_3)_3$-groups in TGCI. The difference in the amounts of the released ion (or the adsorbed TGCI) for both resins in sodium and calcium forms can be explained again in part due to the difference in the affinities of Na^+ and Ca^{2+} ions to Dowex CCR-2 resin. From these results it follows that metal cations, which are bound to the carboxyl groups on the exchanger, are released in a stoichiometric exchange reaction with TGCI ions. In conclusion, this result suggests that the salt-linkage formation of $^{\oplus}N(CH_3)_3$-groups in TGCI with carboxylate ions of Dowex CCR-2 resin follows a stoichiometric relationship.

Tab. 1. Comparison of the amount of adsorbed TGCI with that of cation released from the salt-forms of Dowex CCR-2 resin caused by the adsorption of the polyion[a]

Resin	Resin weight[b] in g	Amount of adsorbed TGCI in mmol	Analytical result[c] in mg · l⁻¹			Amount of released cation[d] in mmol		
Na form	0,515	0,333	146	(2,81)	Na^+	0,311	(—)	Na^+
	1,062	0,415	179	(6,39)		0,375	(—)	
	1,486	0,528	238	(4,23)		0,508	(—)	
	2,013	0,796	374	(5,12)		0,802	(—)	
Ca form	0,446	0,115	41,7	(<0,05)	Ca^{2+}	0,052	(0,104)	Ca^{2+}
	0,835	0,186	79,4	(<0,05)		0,099	(0,198)	
	1,172	0,236	113	(<0,05)		0,141	(0,282)	
	1,578	0,341	136	(<0,05)		0,170	(0,340)	

[a] pH 10 ± 0,1 (adjusted with TMAH), 25 °C.

[b] The weight of the sodium- and calcium-form resins was converted to that of the hydrogen-form.

[c] The results in parentheses were obtained by a blank test which was carried out for the salt-form resin in the absence of TGCI ion.

[d] The results in parentheses were calculated by assuming that one mole of Ca^{2+} ion is released by the binding of 2 moles of $^{\oplus}N(CH_3)_3$-groups in TGCI.

Most of the previous studies[5,9,10] of the adsorption of polyelectrolytes on solid surfaces with ionizable groups have shown no strong evidence that the polyion is stoichiometrically bound to the ionizable groups. For example, Froehling and Bantjes[9] have recently studied the adsorption of a synthetic heparinoid polyelectrolyte, $—[CH_2—C(CH_3)(NHSO_3Na)—CH(COONa)—CH_2]_n—$, on beads of poly(vinyl chloride) having tridodecylmethylammonium chloride as the surface groups, and reported that the amount of Cl^- ion released by the binding of the polyion is of the order of a few per cent of that (in unit mol) of the adsorbed polyion. Thus, they pointed out that the polyion is adsorbed in the loop form on the surface of the beads. In contrast to this result, the stoichiometric salt-linkage formation between TGCI and Dowex CCR-2 resin obviously indicates the adsorption in a flat form. It is thought that the stoichiometry of the salt-linkage of a polyion with ionizable groups on a solid surface may be affected by many factors: hydrophobic or hydrophilic character of the solid surface, distribution and density of ionizable groups on the solid surface and also in the polymer chain, and flexibility of polymer chain, etc. Although it should be preferable to investigate the stoichiometry by considering these factors, the present results reported above apparently seem to include a useful information about the flat adsorption of a polyion on a solid surface.

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