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Adsorption of synthetic polyelectrolytes on colloidal spheres

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SUMMARY

The adsorption of synthetic polyelectrolytes on the surfaces of monodisperse polystyrene spheres and colloidal silica spheres is studied by electrophoretic mobility measurements. Electrolytes used are NaCl, $CaCl_2$, $LaCl_3$, Na_2SO_4, sodium poly(ethylenesulfonate) (NaPES), sodium poly(styrenesulfonate) (NaPSS), polybrene® (PB), poly-4-vinyl-N-ethylpyridinium bromide (C2PVP), poly-4-vinyl-N-benzylpyridinium chloride (BzPVP), and copolymer of 4-vinyl-N-benzylpyridinium chloride(95%) and 4-vinyl-N-n-hexadecylpyridinium bromide(5%)(C16BzPVP). Electrophoretic velocity (u) and the effective charge number(α) of a colloidal sphere increase in the presence of PB, C2PVP, BzPVP, and C16BzPVP, and turn to the positive from the negative values in their absence. Addition of NaPES and NaPSS further decreases u and α values. Adsorption of the polymers on the colloidal spheres are explained by the hydrophobic and/or dipole-dipole interactions in addition to the electrostatic forces. Weak adsorption of simple electrolytes on the colloidal spheres is deduced from the electrophoretic measurements.

INTRODUCTION

A study on the formation of ordered structure of monodisperse colloidal spheres in de-ionized suspension is helpful in the understanding of fundamental properties of solid crystals and also electrostatic interactions of macro-ions. It is now clear that essentially the important factor for the extraordinary properties is the electrostatic repulsion between spheres and the elongated Debye-screening length in the effective hard-sphere model(1-21). Polystyrene spheres are believed to be strongly hydrophobic in aqueous media. The hydrophobic interactions of linear-type macro-ions with other macro-ions or small molecules have been studied in detail(22-28). However, non-electrostatic interactions of colloidal spheres have not been clarified so much(29-33).

In previous papers(34,35), this author studied the influence of the addition of several neutral polymers, which have various hydrophobicities and/or polarities, upon the ordered structures of polystyrene spheres. It was clarified that the adsorption of the polymers on the colloidal surfaces was greatly influenced by the hydrophobic and/or dipole-dipole interactions. In this report, the adsorption phenomenon of linear-type macro-ions having different hydrophobicities is discussed as systematically as possible from the electrophoretic mobility measurements in order to analyse the contributions of the electrostatic and non-electrostatic interactions of colloidal spheres separately.

EXPERIMENTAL

Materials

D1B33 was a monodisperse polystyrene sphere purchased from Dow Chemical Co. G2210 was kindly donated by Japan Synthetic Rubber Co.(Tokyo). S080, G0202 and H1001 were monodisperse polystyrene spheres modified with carboxylic acid groups, products of Japan Synthetic Rubber Co. Colloidal silica spheres,CS02 were prepared according to the method of Stober et al(36-38). Diameters and other characteristics of the spheres are listed in table 1. The values for the number averaged diameters and their dispersions were measured using an electron microscope. The charge densities of strongly(sulfate ions) and weakly acidic ionic(carboxylic acid) groups were determined by the conductometric titration with a Wayne-Kerr autobalance precision bridge, model B331, mark II(Bognor Regis, Sussex). Previously, the charge density of D1B33 was determined for the strongly acidic groups only. However, in this work conductometric titration curves were reexamined and the concentrations of strongly acidic and weakly acidic groups were determined separately. These spheres were carefully purified several times using an ultrafiltration cell(model 202, membrane: Diaflo XM300, Amicon Co.). Then the samples were treated on a mixed bed of cation- and anion-exchange resins(Bio-Rad, AG501-X8(D), 20-50 mesh) for at least ten days. The resulting suspensions were believed to contain only the macro-ions(spheres) and their counter-ions(protons).

Table 1. Properties of spheres used

sphere	diameter, nm	charge density, $\mu C/m^2$ strongly acidic	 weakly acidic
S080	252 ± 10	$2.2x10^4$	$6.9x10^4$
G2210	254 ± 10	$3.1x10^4$	$9.3x10^3$
G0202	264 ± 10	$1.3x10^4$	$4.3x10^5$
D1B33	269 ± 3	$1.5x10^4$	$1.9x10^4$
CS02	340 ± 30	$4.2x10^3$	---
H1001	1022 ± 5	---	$1.7x10^6$

Sodium poly(ethylene sulfonate)(NaPES) and sodium poly(styrene sulfonate)(NaPSS, molecular weight= 18000, polydispersity index; M_w/M_n= 1.14) were purchased from Polyscience Inc.(Warrington, PA) and Pressure Chemicals(Pittsburgh, PA), respectively. Aqueous solutions of NaPES and NaPSS were passed through columns of a mixed bed of cation- and anion-exchahge resins(Bio-Rad) repeatedly in acid forms. Sodium salts were obtained by neutralization of the acids with NaOH. Polybrene®(1,5-dimethyl-1.5-diazaundecamethylene polymethobromide) is an ionen-type cationic polymer purchased from the Aldrich Chemical Co.(Milwaukee, Wi).

The details on the preparation and purification of poly-4-vinyl-N-ethylpyridinium bromide(C2PVP), poly-4-vinyl-N-benzylpyridinium chloride (BzPVP), and copolymer of 4-vinyl-N-benzylpyridinium chloride(95%) and 4-vinyl-N-n-hexadecylpyridinium bromide(5%)(C16BzPVP) were described in previous papers(23,39). The degrees of quaternization were 0.96, 0.92, and 0.97, respectively. The degree of polymerization of poly-4-vinylpyridine (parent polymer) was 3800 by viscometry. NaCl, $CaCl_2$, $LaCl_3$, and Na_2SO_4 were used as guaranteed reagents. Water used for the purification and for solution preparations was deionized by using cation- and anion-exchange resins(Puric-R, type G10, Organo Co., Tokyo) and purified further by a Milli-Q reagent grade water system(Millipore Co., Bedford, Mass.).

Electrophoretic Mobility Measurements

Electrophoretic velocity was recorded on a Laser Zee meter(model 501, Pen Kem, Inc., Bedford Hills, NY). The chamber was made of quartz and Teflon. The anode and cathode were molybdenum and platinum, respectively. The mobilities were measured at room temperature(ca. 25°C). The pH values of the sample suspensions ranged between 5.1 and 6.3.

RESULTS AND DISCUSSION

According to Stokes(40,41), electrophoretic mobility, u',in an electric field is given by equation (1).

$$u' = QE/(3\pi\eta d), \qquad (1)$$

where Q is the effective charge of a spherical particle, d the diameter, E the electric field, and η the viscosity of the solvent. The electrophoretic velocity, u, obtained from the electrophoresis measurements is given by equation (2).

$$u = u'/E = Q/(3\pi\eta d). \qquad (2)$$

Since 299.8 V(abs)=1 esu, a field of 1 V/cm exerts a force of $1.602\text{x}10^{-12}$ $|\alpha|$ dyn on an ion of valency $|\alpha|$. Thus, the effective valency of a colloidal sphere, α is simply given by equation (3).

$$\alpha = 5.238\text{x}10^{10}ud. \qquad (3)$$

Here η was taken to be 0.008904 poise, and the units of u and d are $cm^2V^{-1}s^{-1}$ and cm, respectively. It must be mentioned here that the effects of the electrical double layers around spheres are neglected in the derivation of equations.

The values of u and α in the presence of various salts are shown in Figures 1 to 4 for G2210, D1B33, S080, and G0202 spheres, respectively. The salt concentrations are given by the basemol/L. Diameters(252-269 nm) and charge densities with strongly acidic groups(1.3-3.1 $\mu C/cm^2$) of the four samples are similar to one another, but charge densities for carboxylic acid groups are quite different and increase in the order G2210 < D1B33 < S080 < G0202. The values of u and α were negative in the absence of foreign electrolytes. When a small amount of the cationic polyelectrolytes such as PB, C2PVP, BzPVP, and C16BzPVP were added, the parameters began to increase and their signs turned to positive. This means that the cationic polymers were adsorbed on the surfaces of the polystyrene spheres, though the electrophoretic measurements give no indication of the amount adsorbed.

The driving forces for the adsorption are (1)electrostatic attractions between <u>anionic</u> spheres and <u>cationic</u> polymers, and (2)hydrophobic interactions between them. Both of spheres and polymers are highly multi-valent macro-ions, and the formation of the so-called polyelectrolyte complexation occurs. Thus, the electrostatic attractions are very significant. Furthermore, u and α values of the spheres of low charge densities of weakly acidic groups were observed clearly to increase in the order PB < C2PVP < BzPVP < C16BzPVP. The hydrophobicities of these cationic polymers have been discussed in detail with regard to the catalytic action of macro-ions on the various kinds of ionic reactions (23-25,39,42-44), and the hydrophobicities increased in the order PB < C2PVP < BzPVP < C16BzPVP. Thus, the hydrophobic interactions between the spheres and the cationic polymers also play an important role for the strong adsorption. It should be mentioned here that the importance of the hydrophobic interactions was shown for the adsorption of water-soluble neutral polymers on polystyrene spheres(34).

Note that the order in the magnitudes of the u and α values in the presence of cationic polymers became vague as the amount of carboxylic acid groups of the spheres increased. For G0202 spheres, for example, the increasing effects of the macro-ions upon u and α were very similar among C2PVP, BzPVP, and C16BzPVP. This implies that the carboxylic acid groups, which are highly hydrophilic, obstruct the hydrophobic attractions. In

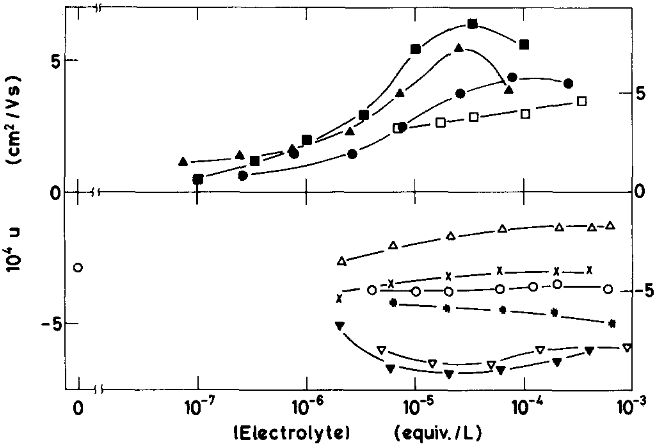

Figure 1. u and α of G2210 spheres in the presence of NaCl(O), CaCl$_2$(X), LaCl$_3$(Δ), PB(□), C2PVP(●), BzPVP(▲),C16BzPVP(■), NaPES(▽), NaPSS(▼), and Na$_2$SO$_4$(#).

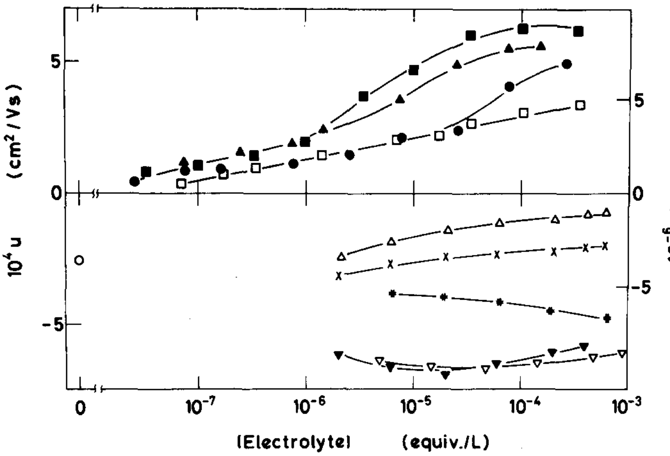

Figure 2. u and α of D1B33 spheres in the presence of CaCl$_2$(X), LaCl$_3$(Δ), PB(□), C2PVP(●), BzPVP(▲), C16BzPVP(■), NaPES(▽), NaPSS(▼), and Na$_2$SO$_4$(#).

other words, the hydrophobicity of polystyrene spheres decreases substantially as the carboxylic acid moeities increase.

When di-valent and tri-valent simple electrolytes(CaCl$_2$ and LaCl$_3$) of 10^{-6} to 10^{-3} M were added, u and α increased slightly, although their signs remained negative. This shows that these simple electrolytes are adsorbed weakly on the spheres. Addition of sodium chloride was insensitive to these electrophoretic parameters.

When the anionic polymers such as NaPES and NaPSS were added to the G2210 suspension, u and α decreased, and the decreasing effects were more

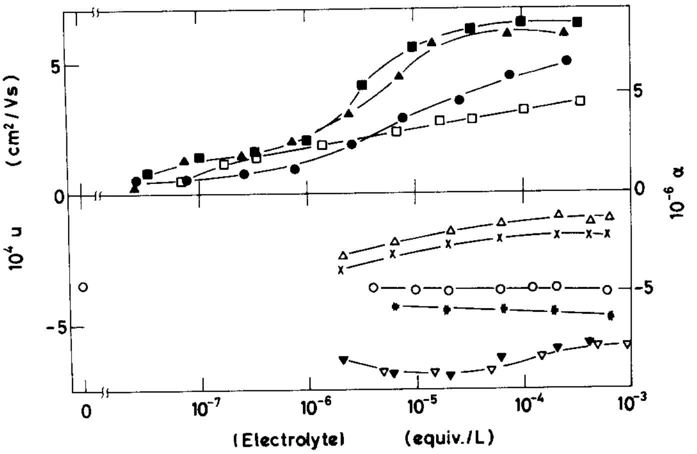

Figure 3. u and α of S080 spheres in the presence of NaCl(O), CaCl$_2$(X), LaCl$_3$(Δ), PB(□), C2PVP(●), BzPVP(▲),C16BzPVP(■), NaPES(▽), NaPSS(▼), and Na$_2$SO$_4$(#).

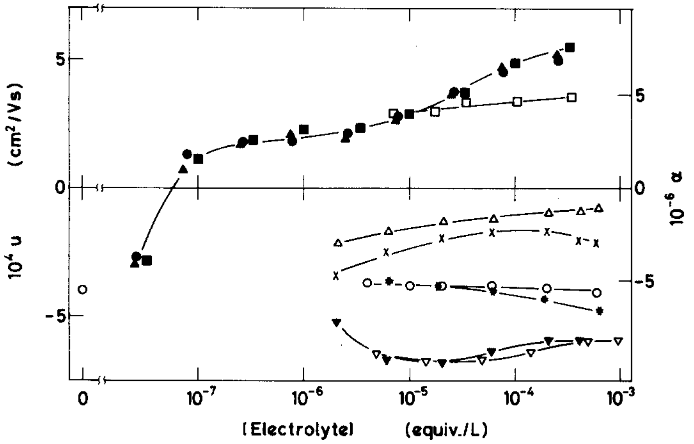

Figure 4. u and α of G0202 spheres in the presence of NaCl(O), CaCl$_2$(X), LaCl$_3$(Δ), PB(□), C2PVP(●), BzPVP(▲),C16BzPVP(■), NaPES(▽), NaPSS(▼), and Na$_2$SO$_4$(#).

significant for NaPSS as is shown in Figure 1. It has been clarified that the hydrophobicity of NaPSS is much stronger than that of NaPES(23,28,40, 42). Thus, the hydrophobic attractions between NaPSS and G2210 spheres are very important for the adsorption, and even stronger than the repulsive forces between the anionic spheres and anionic macro-ions. The magnitude of the decreasing effects did not differ between NaPES and NaPSS for the spheres having a large amount of carboxylic acid groups. This again indicates how weak are the hydrophobic interactions between the macro-ions and the spheres modified with carboxylic acid groups. Here it should be noted that the adsorption of NaPES and NaPSS molecules certainly occurred

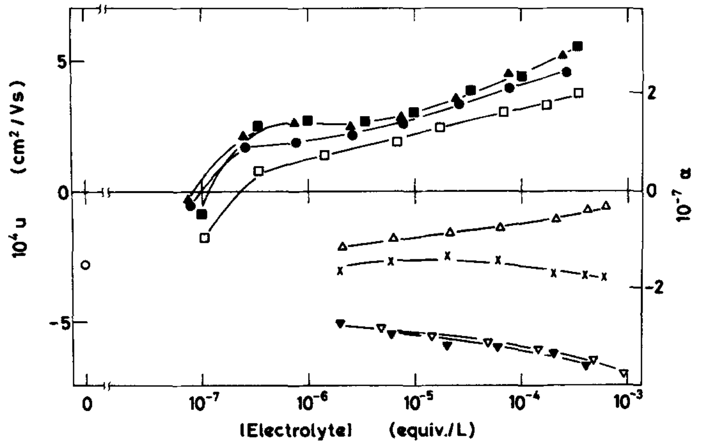

Figure 5. u and α of H1001 spheres in the presence of CaCl$_2$(X), LaCl$_3$(Δ), PB(□), C2PVP(●), BzPVP(▲), C16BzPVP(■), NaPES(▽), and NaPSS(▼).

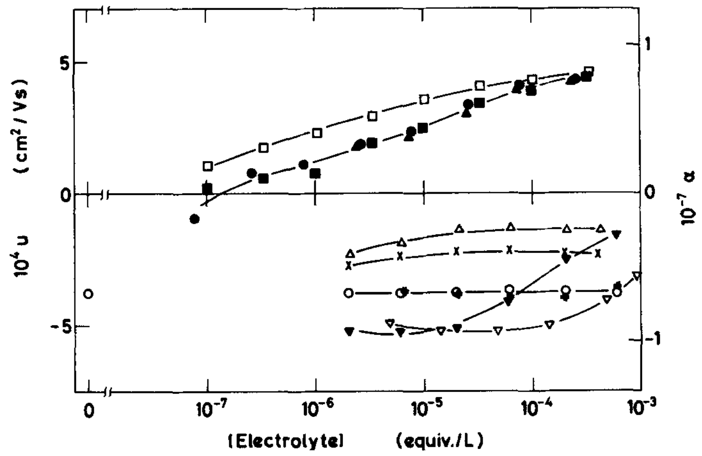

Figure 6. u and α of CS02 colloidal silica spheres in the presence of NaCl(O), CaCl$_2$(X), LaCl$_3$(Δ), PB(□), C2PVP(●), BzPVP(▲), C16BzPVP(■), NaPES(▽), NaPSS(▼), and Na$_2$SO$_4$(#).

even for the hydrophilic spheres, which suggests that some other driving forces exist. The dipole-dipole interactions are most plausible to be effective between the spheres and the polymers.

The u and α values of very large polystyrene spheres modified with carboxylic acid groups(H1001) are shown in Figure 5 in the presence of simple- and poly-electrolytes. The profiles of the curves are quite similar to those shown in Figures 1 to 4, which implies that the adsorption takes place by the electrostatic and hydrophobic interactions. Note that most of weakly acidic groups are undissociated in suspensions.

Figure 6 shows the plots of u and α against the concentration of colloidal silica spheres. The salt effect was different from that of polystyrene spheres; strongly hydrophobic polymers (both cationic and anionic) adsorbed weakly on the surfaces of the colloidal silica. This supports the notion that the hydrophobicity of the colloidal silica spheres is very weak. Instead of the hydrophobic interactions the dipole-dipole forces may play an important role for the adsorption in addition to the electrostatic interactions. The silanol groups of silica spheres are highly hydrophilic. The experimental fact that the adsorption increased in the orders C16BzPVP < BzPVP < C2PVP, and NaPSS < NaPES, which were just opposite to the observations for polystyrene spheres described above, may imply that the adsorption of the bulky macro-ions by stereo-chemical effects is not easy.

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REFERENCES

1. Luck,W.,Klier,M.,Wesslau,H.,Ber.Bunsenges.Phys.Chem.67,75,84(1963).
2. Stone-Masui,J.,Watillon,A.,J.Colloid Interface Sci.28,187(1968).
3. Hiltner,P.A.,Krieger,I.M.,J.Phys.Chem.73,2386(1969).
4. Kose,A.,Ozaki,M.,Takano,K.,Kobayashi,Y.,Hachisu,S.,J. Colloid Interface Sci.44,330(1973).
5. Brown,J.C.,Pusey,P.N.,Goodwin,J.W.,Ottewill,R.H.,J.Phys.A 8,664(1975).
6. Crandall,R.S.,Williams,R.,Science 198,293(1977).
7. Schaefer,D.W.,J.Chem.Phys.66,3980(1977).
8. Mitaku,S.,Otsuki,T.,Okano,K.,Jpn J.Appl.Phys.17,305,627(1978).
9. Clark,N.A.,Ackerson,B.J.,Phys.Rev.Lett.44,1005(1980).
10. Lindsay,H.M.,Chaikin,P.M.,J.Chem.Phys.76,3774(1982).
11. Hansen,J.P.,Haytor,J.B.,Mol.Phys.46,651(1982).
12. Gruner,F.,Lehman,W.,J.Phys.A.15,2847(1982).
13. Hess,W.,Klein,R.,Adv.Phys.32,173(1983).
14. Schmitz,K.S.,Macromolecules 16,1550(1983).
15. Pieranski,P.,Contemp.Phys.24,25(1983).
16. Hartl,W.,Versmold,H.,J.Chem.Phys.81,2507(1984).
17. Joanicot,H.M.,Jorand,M.,Pieranski,P.,Rothen,F.,J.Phys.45,1413(1984).
18. Ottewill,R.H.,Ber.Bunsenges.Phys.Chem.89,517(1985).
19. Lindsay,H.M.,Dozier,W.D.,Chaikin,P.M.,Klein,R.,Hess,W.,J.Phys.A 19, 2583(1986).
20. Okubo,T.,J.Chem.Phys.86,2394,5182(1987).
21. Okubo,T.,J.Chem.Phys.87,3022,5528,6733(1987).
22. Okubo,T.,Ise,N.,J.Phys.Chem.73,1488(1969).
23. Okubo,T.,Ise,N.,J.Am.Chem.Soc.95,2293,4031(1973).
24. Okubo,T.,Ise,N.,J.Biol.Chem.249,3563(1974).
25. Kitano,H.,Tanaka,M.,Okubo,T.,J.Chem.Soc.,Perkin 2 1074(1976).
26. Mita,K.,Okubo,T.,Ise,N.,J.Chem.Soc.,Faraday Trans.1 72,504(1976).
27. Maruno,T.,Okubo,T.,Ise,N.,Ber.Bunsenges.Phys.Chem.85,667(1981).
28. Turro,N.J.,Okubo,T.,J.Phys.Chem.86,1535(1982).
29. Stromberg,R.R.,Tutas,D.J.,Possaglia,E.,J.Phys.Chem.69,3955(1965).
30. Ottewill,R.H.,Walker,T.,Kolloid Z.Z.Polymere 227,108(1968).
31. Killmann,E.,Eckart,R.,Makromol.Chem.144,65(1971).
32. Fleer,G.J.,Koopal,L.K.,Lyklema,J.,Kolloid Z.Z.Polymere 250,689(1972).
33. Varoqui,R.,Dejardin,P.,J.Chem.Phys.66,4395(1977).
34. Okubo,T.,J.Chem.Soc.,Faraday Trans.1 83,2497(1987).
35. Okubo,T.,Colloid Polymer Sci.265,597(1987).
36. Stober,W.,Fink,A.,Bohn,E.,J.Colloid Interface Sci.26,62(1968).
37. van Helden,A.K.,Vrij,A.,J.Colloid Interface Sci.78,312(1980).

38. Shimohira,T.,Ishijima,H.,J.Chem.Soc.Jpn 1503(1981).
39. Ishiwatari,T.,Okubo,T.,Ise,N.,J.Polymer Sci.18,1807(1980).
40. Robinson,R.A.,Stokes,R.H., "Electrolyte Solutions", 2nd Ed., Butterworths, London(1959).
41. Okubo,T.,Ber.Bunsenges.Phys.Chem.,91,1064(1987).
42. Okubo,T.,Ise,N.,J.Phys.Chem.38,3120(1973).
43. Kitano,H.,Okubo,T.,J.Chem.Soc.,Perkin 2 432,(1977).
44. Maruno,T.,Okubo,T.,Ise,N.,Ber.Bunsenges.Phys.Chem.85,667(1981).

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