Studies on Polytetrafluoroethylene Latices. Part 2. Coagulation by Hydrolysable Electrolytes

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The colloidal stability of polytetrafluoroethylene (PTFE) latices has been examined as a function of pH at different concentrations of aluminium nitrate. The basic behaviour observed can be subdivided into three pH domains, lower than pH 3.3, pH 3.3 to 5.2 and pH 5.2 to 7.5. In the lowest pH region, coagulation of the latex appeared to occur as a consequence of compression of the electrical double layer by a 3 : 1 electrolyte. In the pH region 3.3 to 5.2 cationic polynuclear aluminium ions were formed which adsorbed on the particles and neutralised the charge on the negative latex particles. Charge reversal and restabilization of the latices as cationic particles, however, was not observed. The appeared to be a consequence of the relatively high charge reversal concentration and the possible weak adsorption of polynuclear species on the PTFE surface. Coagulation in the pH region 5.2 to 7.5 appeared to be the consequence of several mechanisms operating together.

INTRODUCTION

The unique properties of polytetrafluoroethylene (PTFE) in surface chemistry, i. e. low surface energy[1] (18.5 mJ m^{-2}) and low Hamaker Constant[2] (4.4 $\times$ 10^{-20} J) make the properties of PTFE latices very important from the viewpoint of Colloid Science. Surprisingly, only very few investigations have been reported on PTFE latices[3,4,5] and their stability behaviour in the presence of electrolytes is virtually uninvestigated. In a previous communication[2] we have reported work on the characterisation of PTFE latices and on their stability behaviour in the presence of non-hydrolysable electrolytes. In this paper the work is extended to an examination of the effects of hydrolysed ions.

The effects of hydrolysed ion species on the properties of dispersions has been substantially clarified by the pioneer work of Matijević and his collaborators[6,7,8,9]. For example, they have shown in the case of aluminium salts that the hydrolysis of the Al^{3+} ion, which occurs as the pH of an aqueous solution of an aluminium salt is increased beyond ca. pH 3.3, has a direct effect on the critical coagulation concentration *(c.c.c.)* of a dispersion. Evidence has also been provided that the hydrolysed species can adsorb on to surfaces of various types much more readily than the unhydrolysed ions and that this adsorption frequently leads to the reversal of charge of the particles and to the formation

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of a stable dispersion with particles of opposite charge to the original material[6,7,8]. In particular, Matijević[9] has shown the usefulness of mapping out the coagulation domains for dispersions in the presence of hydrolysable electrolytes. Previous investigations of the properties of latices in the presence of hydrolysable electrolytes include the work of, Matijević and Force[10] on styrene butadiene latices, Wenning[11] on Buna latices and Kratohvil and Matijević[5] on Teflon latices in the presence and absence of the nonionic surface active agent, Triton X 100.

In this contribution, the stability domains for characterised, dialysed PTFE latices in the presence of aluminium nitrate have been determined over the pH range 2.5 to 7.4.

<center>EXPERIMENTAL</center>

Materials

All the water used was doubly distilled. The second distillation was carried out using an all-Pyrex apparatus.

Aluminium nitrate was obtained as B.D.H. Analar material and then recrystallised from 10^{-2} mol dm^{-3} nitric acid. Stock solutions of aluminium nitrate were prepared directly from recrystallised solid material and always replaced after a period of four days. More dilute electrolyte solutions, which were maintained at pH 3, were prepared from the stock immediately before their use in coagulation experiments.

The Polytetrafluoroethylene, PTFE, latex. — The methods used for the preparation, purification and characterisation of the latex have been described elsewhere[2]. The latex used, however, was not identical with that used for studying coagulation by simple electrolytes and hence the basic characteristics are given in Table I.

<center>TABLE I</center>

<center>*Characterisation of PTFE Latex*</center>

Modal long dimension	= 130 nm
Modal short dimension	= 75 nm
Aspect ratio	= 1.7
Specific surface area	= 22.7 $\pm$ 1.0 m^2 g^{-1}
Surface charge density	= 0.68 $\pm$ 0.05 μC cm^-
No. Av. Molecular Weight of Polymer	= 1.2 $\times$ 10^6
Density of particles	= 2.277 g cm^{-3}

Coagulation Experiments. — A concentrated PTFE latex (ca. 18.6% w/v) was used as the basic stock dispersion[2]. This material was diluted with dilute nitric acid in order to adjust the pH to 3 and to give a concentration (1.30% w/v) which was such that after addition of aluminium nitrate the resulting solids content was 0.65% w/v. The basic procedure used for the coagulation experiments was as described previously[2] except that 10 cm^3 of electrolyte was added to a test-tube containing 10 cm^3 of dilute latex. After the addition, the mixture was stirred with a glass-coated magnetic follower for a period of three minutes to ensure thorough mixing. The pH was adjusted to the required value durring the mixing period by addition of sodium hydroxide solution from an Agla micrometer syringe.

All pH measurements were made using a combined electrode (type E.I.L. 1150) in conjuction with an Electronics Instruments Limited pH meter, model 7030. The pH was observed on a linear expanded scale covering three pH units with the first unit buffered to pH 4.0. In this way the pH was measured to $\pm$0.01 of a unit within the range 3 to 6. The pH of the latex was always measured 2 h after the addition of aluminium nitrate. The variation from the value that the dispersion was adjusted to initially was never more than 0.05 of a pH unit.

The onset of coagulation was determined from measurements of the optical density of the latex at various time intervals after the addition of electrolyte[2]. Samples of the dispersion were transferred from the tube to the optical cell by means of a

pipette with a wide-bore tip; the latter minimised mechanical stirring of the particles. A Unicam SP 600 spectrophotometer was used to determine the optical density of the dispersion at an incident wavelength of 546 nm. The critical coagulation concentrations (c.c.c.) were determined from plots of optical density against the logarithm of the molar concentration of aluminium nitrate two hours after its addition.

The coagulation process was also followed by monitoring the light scattered, at 60⁰ to the incident direction, using a Brice-Phoenix light scattering photometer (Universal 2000 series). An incident wavelength of 436 nm was used. For these experiments the concentration of PTFE used was 0.035% w/v in the supporting electrolyte.

Electrophoretic Mobility Measurements. — Electrophoretic mobility measurements of the PTFE particles were obtained using a mass transport apparatus[12]. The latex concentration in one half of the mass transport cell was measured before and after transport had occurred by means of pyknometry, the high density of the PTFE particles (2.277 g cm^{-3}) making this a very precise method of analysis. The latex concentration used for mobility determinations was the same as that used for the turbidimetric determination of *c.c.c.* values, namely, 0.65% w/v.

<div align="center">RESULTS</div>

Turbidimetric Examination of Coagulation

Figure 1. shows plots of the optical density of a PTFE dispersion for pH values less than 3.0 against the logarithm of the molar aluminium nitrate concentration two hours after the addition of electrolyte. An interesting feature of Fugire 1. is the change in slope of the optical density curves which
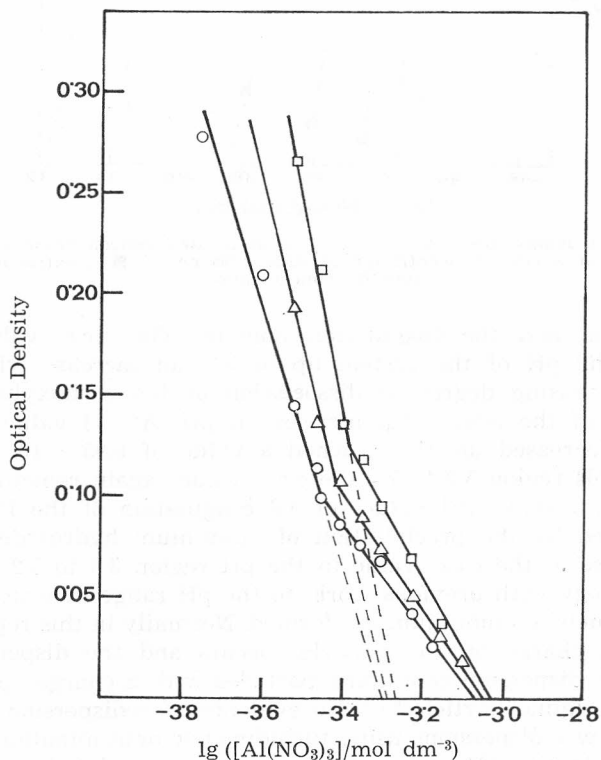

Figure 1. Optical density against log molar concentration of aluminium nitrate for experiments at different pH values at a latex concentration of 0.65 g/100 cm³, —O—, pH = 2.50; —△—, pH = = 2.65; —□—, pH = 3.00.

occurred in the aluminium nitrate concentration range 3×10^{-4} to 10^{-3} mol dm^{-3}. Small metastable aggregates were formed which were sensitive to the shearing stress caused by transferring the samples to the optical cell for measurement. This behaviour was not observed in measurements in the pH range 3.30 to 5.20.

The c.c.c. values obtained from the experiments over the pH range 2.5 to 7.4 are presented in Figure 2. These data define the boundary between the
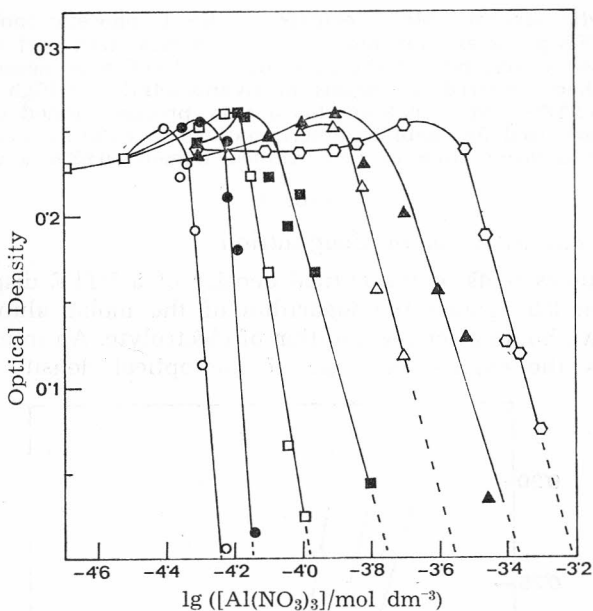

Figure 2. Lg [c.c.c.] against *pH*. —○—, c.c.c. data at a latex concentration of 0.65 g/100 cm³; —△—, c.c.c. value at a latex concentration of 0.033 g/100 cm³; —■—, extrapolated reversal of mobility concentration.

stable dispersion and the coagulation domain. The c.c.c. values increased slightly with the pH of the system up to 3.3, an increase which probably reflects the increasing degree of dissociation of the carboxylic acid groups on the surface of the latex with increase in pH. At pH values higher than 3.3, the c.c.c. decreased until it reached a value of 6.95×10^{-5} mol dm^{-3} at pH 5.2. In the pH region 5.2 to 7.3 the c.c.c. values again remained essentially constant although above pH values of 5.8 coagulation of the PTFE particles was accompanied by the precipitation of aluminium hydroxide.

The decrease of the c.c.c. value in the pH region 3.3 to 5.2 clearly corresponds, by analogy with previous work, to the pH range in which polynuclear hydrolysis products of aluminium are formed. Normally in this region, however, reversal of the charge on the particles occurs and the dispersion becomes restabilised as a dispersion containing particles with a charge opposite in sign to that of the original particles[6,7,9]. No evidence of redispersion was obtained with the 0.65⁰/₀ w/v dispersions using turbidimetric determinations; in all cases above the c.c.c. in this pH region the dispersions coagulated, leaving an optically transparent supernatant.

Light Scattering Measurements

In order to establish whether restabilisation could be effected at high aluminium nitrate concentrations, a much more dilute sol (0.035% w/v) was used to lower the surface area available for adsorption of complex species and this was examined by determination of the light scattered at an angle of 60° relative to the direction of the incident beam. The results obtained by this technique, using various aluminium nitrate concentrations at pH 5, are given in Figure 3. in the form of curves of intensity as a function of lapsed time after the addition of electrolyte. In the absence of added aluminium nitrate, the optical density after 18 h was identical with that at the start of the experiment. The high
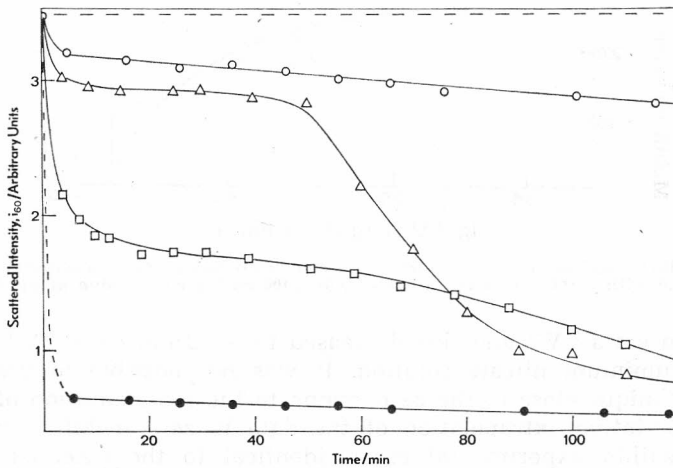

Figure 3. Scattered intensity, i_{60}/arbitrary units, against time at different aluminium nitrate concentrations after adjusting to pH 5. Latex concentration = 0.033 g/100 cm³. Aluminium nitrate concentrations in mol dm⁻³: —○—, 5×10^{-5}; —△—, 6×10^{-5}; —□—, 10^{-4}; —●—, 5×10^{-4}. Results in absence of aluminium nitrate - - -.

intensities were a characteristic of the stable dispersions and the decrease in intensity indicated the settling of aggregates in the presence of aluminium nitrate with consequently clearer supernatants. Thus the dispersion in 5×10^{-5} mol dm⁻³ showed only very slow coagulation, the initial decrease being a consequence of dilution. At 6×10^{-5} mol dm⁻³ a small initial decrease occurred and was followed after a 50 minute delay by a more rapid decrease, presumably as a consequence of the settling of aggregates formed by a slow coagulation process. An alternative explanation is that a finite time interval was required at this aluminium concentration to form aluminium hydroxide particles and that once formed, these heterocoagulated with the PTFE particles.

A comparison of the light scattering measurements with turbidity measurements two hours after the addition of electrolyte at pH 5.0 showed that the c.c.c. by light scattering at pH 5.0 was 6.3×10^{-5} mol dm⁻³ compared with 7.1×10^{-5} mol dm⁻³ from turbidity measurements. Thus changing the sol concentration by a factory of approximately twenty did not substantially change the c.c.c.

Similar results were obtained from experiments carried out at pH 4 and pH 6. No evidence for restabilisation of the PTFE latex was obtained in any of the light scattering experiments.

Electrophoretic Measurements

The electrophoretic mobility of PTFE particles at a concentration of 0.65⁰/₀ w/v was determined as a function of aluminium nitrate concentration in solutions which prior to each measurement were adjusted to pH 5.0. The results are presented in Figure 4. In the absence of electrolyte the particle mobility
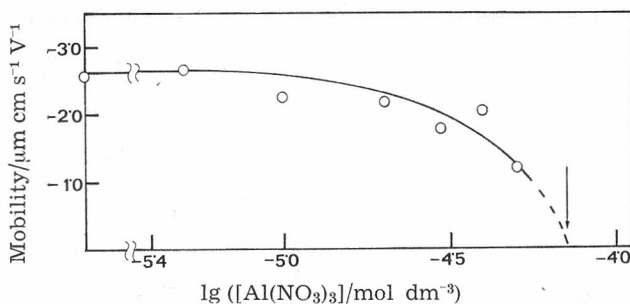

Figure 4. Mobility against lg aluminium nitrate concentration for measurements made at pH 5.0 with a latex concentration of 0.65 g/100 cm³. ↓ c.c.c. value at pH 5.0.

was —2.6 μm cm s^{-1} V^{-1} and this decreased to —1.2 μm cm s^{-1} V^{-1} in 5×10^{-5} mol dm^{-3} aluminium nitrate solution. It was not possible to use the mass transport technique close to the c.c.c. owing to the sedimentation of the particles but a tentative extrapolation of the data to zero mobility gave a concentration, within experimental error, identical to the c.c.c. i. e. 7.1×10^{-5} mol dm^{-3}. The change in mobility over a small concentration range, close to the c.c.c., provides clear evidence for the adsorption of cationic species to the particles.

DISCUSSION

The curve of log (c.c.c.) against pH given in Figure 2. can be subdivided into three pH domains, less than 3.3, 3.3 to 5.2 and greater than 5.2.

Coagulation at pH Values less than 3.3

In this region the c.c.c. increases slowly with increase in pH and reaches the maximum value of 6.31×10^{-4} mol dm^{-3} aluminium nitrate at pH 3.3. At these low pH values it can be anticipated from solution studies and stability constants[13] that aluminium exists in solution as Al^{3+} and that consequently coagulation occurs as a consequence of compression of the electrical double layer with increasing concentration of a 3 : 1 electrolyte. By analogy with previous studies coagulation would be expected to occur at a finite value of zeta-potential[6]. The small increase in the c.c.c. with pH is probably to be expected as a consequence of the increasing degree of dissociation of the acid groups on the latex surface[4].

The PTFE latex used in the present work had a surface charge density of 0.68 μC cm^{-2} whereas in previous experiments[2] the latex used had a surface

charge density of 0.38 μC cm^{-2}. Determination of the *c.c.c.* for the latter material using aluminium nitrate[2] gave a value of 1.5×10^{-4} mol dm^{-3}. Thus increasing the surface charge density by a factor of 1.79 increased the *c.c.c.* by a factor of 4.21 suggesting that the *c.c.c.* is very sensitive to surface charge density at these low values.

In a number of previous studies it was found by Matijević that a plot of log *(c.c.c.)* against counter-ion valency was linear[5,9]. A plot of this form (Figure 5.) from our previous data[2] shows that this does not appear to be the case for
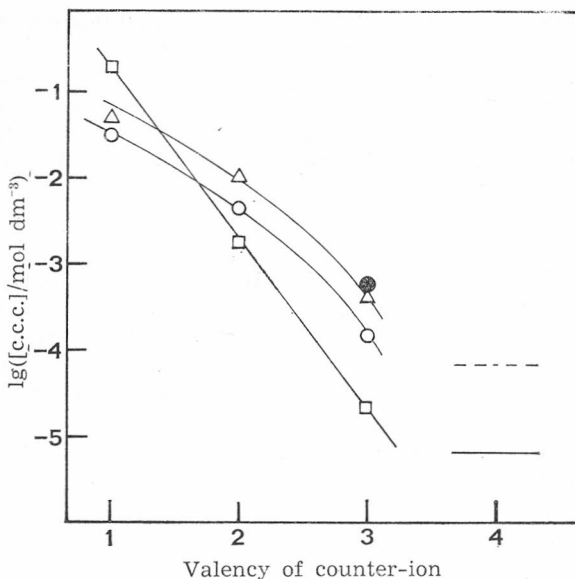

Figure 5. Lg [c.c.c.] against valency of counter-ion.
—□—, data for silver iodide sols[9];
—△—, data for Teflon dispersions[5];
—○—, data for PTFE dispersions[2] — surface charge density = 0.38 μC cm^{-2};
● , value for a PTFE dispersion (present work) — surface charge density = 0.68 μC cm^{-2};
———, c.c.c. for hydrolysed aluminium ions at pH 5.2 using silver iodide sols[7];
- - - -, c.c.c. for hydrolysed aluminium ions at pH 5.2 using PTFE dispersions (present work).

PTFE latices. However, it can also be seen from Figure 5. that our data are essentially parallel to those obtained by Kratohvil and Matijević[5] using a PTFE dispersion in the absence of surface active agent. Moreover, if the value obtained with the present latex, using aluminium nitrate, is included in the plot, it falls close to their value obtained with a 3 : 1 electrolyte, lanthanum nitrate, suggesting that the two latices were of comparable surface charge density.

pH Region 3.3 to 5.2

In this pH range the *c.c.c.* values decrease regularly with increase in pH. It is well known that in this region the Al^{3+} ion undergoes hydrolysis to form polynuclear hydrolysis species[6,7,8,9]. The available evidence indicates that these species have a higher charge than $+3$ and also have a high adsorption affinity for surfaces. Thus, in addition to compressing the double layer more effectively

than a 3 : 1 electrolyte, they can also adsorb and reduce the surface charge. As the pH increases so the concentration of hydrolysed species also increases and consequently the *c.c.c.* decreases.

The exact structure of the polynuclear species is still a subject of active investigation. However, our data are not inconsistent with the $Al_8(OH)_{20}{}^{4+}$ ion proposed by Matijević et al[6,7,9], although the slope of the curve, d log (*c.c.c.*)/dpH, of —0.51 is somewhat lower than that obtained with some other dispersions[9].

An examination of the electrophoretic mobility of the particles as a function of aluminium nitrate concentration at pH 5, Figure 4, showed that the mobility decreased rapidly as the *c.c.c.* was approached and a tentative extrapolation of the curve indicated that the point of zero mobility could coincide with the *c.c.c.* It is clear, therefore, that at pH 5 coagulation occurred as a consequence of the neutralisation of the negative charge on the particles by the adsorption of cationic polynuclear species. Experimental difficulties prevented the determination of the mobility of the particles beyond the *c.c.c.* where in view of the steep gradient, d(mobility)/d(log[Al(NO₃)₃]), it appeared that charge reversal could occur.

The *c.c.c.* values for an 0.035 w/v dispersion at pH 5 was found to be 6.3×10^{-5} mol dm⁻³ compared with 7.1×10^{-5} mol dm⁻³ for an 0.65⁰/₀ w/v dispersion. Hence, changing the particle number concentration by a factor of about twenty had only a small effect on the *c.c.c.* This suggests that polynuclear aluminium ions may have a lower affinity for PTFE particles than for high energy surfaces such as silver iodide. The adsorption of polynuclear ions at pH 5 would also occur in the presence of a substantial equilibrium concentration of polynuclear ions in solution, thus making the system rather insensitive to changes in surface area.

pH Region Greater than 5.2

Above pH 5.2 the *c.c.c.* values levelled off and then increased slightly with increase in pH up to the limit of the investigation, pH 7.35. At ca. pH 5.2 the system approaches closely to the »equilibrium« solubility boundary of aluminium hydroxide in the absence of particles. Thus, two possibilities occur. Firstly, owing to the adsorption of polynuclear species on the PTFE surface, the nucleation of aluminium hydroxide occurs on the particles and these become coated and then coagulation occurs by a charge neutralisation and bridging mechanism; under these conditions, nucleation and aluminium hydroxide particle formation in the solution phase might be delayed until a higher pH. Secondly, aluminium hydroxide particles could be nucleated in the bulk phase and then heterocoagulate with the PTFE particles.

It was anticipated that in this region charge reversal would occur and that the particles would form a stable dispersion of positively charged particles. Although this was observed by Kratohvil and Matijević[5], no restabilisation could be detected in the present work, and it is noticeable that the mobilities observed by them, although positive, were small indicating that charge reversal had only just been achieved. In the present work, however, the particles did not acquire a high enough positive potential to achieve restabilisation.

The reason for the difficulty of restabilizing PTFE particles, compared to other materials such as silver iodide[6], would seem to lie in the fact that the *c.c.c.* values for PTFE occur at substantially higher electrolyte concentrations.

For example, for PTFE, the *c.c.c.* at pH 5.2 was 6.95×10^{-5} mol dm^{-3} compared with 7.2×10^{-6} mol dm^{-3} for silver iodide sols[6], approximately an order of magnitude higher. Therefore in the case of PTFE the concentration of charge reversal in a polyvalent electrolyte occurs at a relatively high ionic strength and consequently a high positive charge would be required to stabilise the particles under these conditions owing to the extent of double layer compression. The much higher concentrations at which coagulation occurs with PTFE latices, both with 3:1 electrolytes and with hydrolysed species, are emphasized in the plot given in Figure 5. where results are given for silver iodide[6,9]. Another major difference between the two materials is the low Hamaker Constant for PTFE, 4.4×10^{-20} J (cf. 2×10^{-19} J for silver iodide), a value very close to that of water, 3.82×10^{-20} J. The attractive interactions of PTFE will be discussed in more detail elsewhere[12].

Despite the relatively inert nature of much of the surface of a PTFE particle, the evidence presented indicates hydrolysed species can be adsorbed to neutralise the negative charge on the particles and hence cause coagulation. The most probable site for adsorption would appear to be the acidic groups on the latex surface. In general, PTFE dispersions behave as hydrophobic sols.

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SAŽETAK

Studije politetrafluoroetilenskih lateksa. Dio 2. Koagulacija elektrolitima koji se mogu hidrolizirati

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Koloidna stabilnost politetrafluoroetilenskih (PTFE) lateksa ispitivana je kao funkcija pH kod različitih koncentracija aluminijeva nitrata. Opažena temeljna svojstva omogućuju podjelu u tri područja pH: pH < 3.2, 3.2 < pH < 5.2, i 5.2 < pH < 7.5. U području ispod pH 3.2 izgleda da je koagulacija posljedica kompresije električ-

nog dvostrukog sloja 3 : 1-elektrolitom. U području 3.2 < pH < 5.2 stvaraju se poli-
nuklearni aluminijevi kationi koji se adsorbiraju na čestice i neutraliziraju naboj
negativnih čestica lateksa. Promjena naboja i restabilizacija lateksa kao kationskih
čestica nije opažena. To je možda posljedica razmjerno visoke koncentracije potrebne
za promjenu naboja kao i moguće slabe adsorpcije polinuklearnih specija na površini
PTFE. Koagulacijski efekti u području 5.2 < pH < 7.5 izgleda da su posljedica više
mehanizama koji djeluju istovremeno.

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