Viscosimetric Determination of Latex Coagulation

*I. Jalšenjak, I. Štivić, and J. J. Petres**

Department of Pharmaceutical Technology, Faculty of Pharmacy and Biochemistry, University of Zagreb, and *Institute of Immunology, 41000 Zagreb, Croatia, Yugoslavia

The viscosity of latices was investigated in dependence upon the pH value of suspensions, their aging and the concentration of added electrolyte. The systems used were well-defined monodisperse polystyrene latices within the concentration range from 0.1 to 1%, and with a high negative charge on the latex particle surface. It was found that viscosity measurement in a dispersion at a certain concentration of the dispersed phase could be used for latex coagulation determination. On the basis of this finding an attempt was made to determine the critical coagulation concentration. The values obtained were concordant with those determined by turbidity measurements. In order to determine the exact pH region in which a decrease in the pH value leads to a sudden change of stability, viscosity measurements were performed in relation to the pH value of latex suspensions. The limiting pH value was independent of the time of measuring, latex concentration, and the ionic strength of the added electrolyte. In our opinion this value is characteristic of a given system and it points to the dependence of the destabilization of a dispersion on the pH value. Therefore, it can be called »critical pH value« by analogy to the term »critical coagulation concentration«.

INTRODUCTION

Monodisperse latices provide a convenient model system for investigating the rheological properties of suspensions of spherical particles. The rheological properties of synthetic latex systems have been studied in recent years to obtain information on the viscosity-concentration dependence of suspensions, the electroviscous effect, and the flow behavior of stable colloidal suspensions[1]. A review of the literature on the subject showed that little information is available about the viscosimetric determination of the coagulation of colloidal systems[2]. This is probably due to the fact that coagulation phenomena are very complex and the stability of colloidal sols, as well as the rate of coagulation are frequently determined by means of turbidity measurements.

The present work was undertaken to investigate the possibility of the use of viscosity measurements to detect the coagulation of latices.

EXPERIMENTAL

Polymer Latices

Monodisperse polystyrene latices used in this study were prepared by emulsion polymerization of styrene with potassium persulfate as initiator. Two procedures described earlier[3] were employed: the direct polymerization (LS 206-2) and the seeding polymerization method (LS 142-T). Also, a latex (LS 225) sample was specially

prepared by γ-ray initiated polymerization[4]. After preparation all latex samples were purified from coarse aggregates of particles by filtration through a filter paper. Then, in order to remove the emulsifier (Aerosol MA, American Cyanamid Co., Wayne, N. Y., U.S.A.) as well as other oxidation and decomposition products, the latices were extensively dialyzed against distilled water for 8 days. The Visking seamless cellulose tubing (Union Carbide Corp., Chicago, Ill., U.S.A.) was used and the dialysis procedure was essentially identical to the one described by Ottewill and co-workers[5]. The original concentrations of latex suspensions after dialysis were about 20% solid by weight. This was determined gravimetrically as earlier[4], with an accuracy of about ± 0.1%. Stock latex suspensions were prepared by diluting with double-distilled water the original concentrated suspension centrifuged at about $5 \times 10^3 \times G$ for 20 minutes to remove aggregates that might have been present[6].

Our paper published earlier, presents data about the measurement of electrophoretic mobility in relation to pH values, and the kind of functional groups on the surface of latex particles[4]. The latex particle surface of dialyzed samples LS 206-2 and LS 142-T is characterized by the presence of carboxyl, sulfate and sulfonate groups. During the deionization process the sulfonate groups were removed, because of the removal of the adsorbed emulsifier, while the carboxyl and sulfate groups remained. In the case of the dialyzed sample of LS 225 the sulfonate groups belong to the absorbed emulsifier, and the number of these groups is decreased after the deionization procedure. The presence of carboxyl groups on LS 225 is not probable.

Particle Size Determination

An Elmiskop I (Siemens) electron miscroscope was used and particle size measurements were made directly on electron micrographic plates. About 300—500 particles for each sample were measured using a calibrated low power microscope as described elsewhere[7]. The precision of these determinations was about ± 2 nm.

Viscosity Measurements

A rheoviscometer according to Hoeppler (VEB Prüfgeräte-Werk, Medingen, DDR), a modification of the standard instrument with a falling ball, was used. Since this apparatus was employed for concentrations of suspensions lower than 1%, a glass cylinder for measuring the lowest viscosities (cylinder size 0.01) and a loading of 10 g cm^{-2} were used. All the measurements were made at (20.00 ± 0.05)°C. In order to ensure that all samples for viscosity measurements be subjected to the same »shear history«, the following sample preparation technique was employed: immediately before use each system was prepared volumetrically from a stock latex suspension diluted with thermostated water (20 °C); then they were allowed to stand for 10 minutes in a thermostat bath. In the tenth minute solutions of sodium chloride and sodium hydroxide or hydrochloric acid were added in order to obtain both the required ionic strength and the required pH value (for coagulation experiments only barium nitrate solution was added). Then the latex system was placed into the viscometer where it was kept at 20 °C for exactly 5 minutes to attain the temperature equilibrium before measurement. The pH value of each system under investigation was determined immediately after viscosity measurements by an electronic pH-meter.

The viscosity of some systems was also determined after deionizing latex samples, previously dialyzed, with a mixture of cation and anion exchange resins. The ion--exchange resins used were 20/50 mesh Dowex 50W-X4 and Dowex 1-X4 (Fluka AG., Buchs, Switzerland). The resins and latices were treated by the procedure proposed by Vanderhoff and co-workers[8]. The samples purified in this way amounted to about 5% and were iridescent. By shaking the flask this iridescence disappeared and appeared again after a short time. The preparation technique of both dialyzed and deionized systems for viscosity measurements was the same as mentioned above.

Electrophoretic Measurements

Electrophoretic mobilities of latex particles were measured by the moving boundary method. The experimental set-up and procedure were as before[4]. The zeta-potentials were calculated from the mobilities using the computations of Wiersema and co-workers[9].

RESULTS

Data on particle size distributions, electrophoretic mobilities u, and zeta-potentials ζ, of the investigated polystyrene latices are given in Table I. The particle size of each sample is characterized by arithmetic mean diameter $\overline{D}$, standard deviation of distributions $s\,(\overline{D})$ and polydispersity ratio P. All these

TABLE I

Particle Mean Diameters, Standard Deviations of Distributions, Polydispersity Ratios, Electrophoretic Mobilities and Zeta-Potentials for Differently Prepared Polystyrene Latices

Sample	Preparation method	$\dfrac{\overline{D}}{nm}$	$\dfrac{s(D)}{nm}$	P	$\dfrac{\mu^{a}}{\mu m\ s^{-1}\ V^{-1}\ cm}$	$\dfrac{\zeta^{a}}{mV}$
LS 206-2	Persulfate initiation. Direct polymerization.	177.2	4.7	1.006	—5.50	—77.5
LS 142-T	Persulfate initiation. Seeding polymerization.	727.0	6.1	1.065	—4.94	—64.2
LS 225	Irradiation initiation.	119.1[b]	3.2	1.006	—4.96	—69.4

[a] Determined at 25 °C; pH = 11.4; Ionic strength $\mu = 5.00 \times 10^{-2}$ mol/dm³
[b] Data from reference 4.

TABLE II

Specific Viscosity as a Function of Concentrations, pH Values, and Aging of Suspensions of Polystyrene Latex LS 206-2

$\dfrac{c_{LS}}{^0/_0}$	pH-value	1st day	$(n_{sp}/c)/(g^{-1}/dl)$ 2nd day	(14th day)
		Dialyzed latex		
0.1	1.75	0.73	0.84	2.44
	5.25	0.42	0.64	1.00
	8.80	0.25	0.55	1.16
0.5	1.75	0.28	0.70	0.78
	5.65	0.09	0.10	0.17
	10.63	0.11	0.26	0.76
1.0	1.75	0.09	0.17	0.34
	6.30	0.06	0.06	0.11
	8.80	0.14	0.22	1.00
		Dialyzed and deionized latex		
0.1	1.75	1.57	1.75	2.57
	5.53	0.70	1.10	1.00
	11.01	0.25	0.68	0.55
0.5	1.75	0.45	0.42	1.53
	5.50	0.31	0.39	0.76
	11.00	0.26	0.16	0.36
1.0	1.75	0.31		
	5.65	0.25	—	—

parameters are defined and computed as described elsewhere[10]. As seen from the values of P, all latex samples have a very narrow size distribution and can be regarded as monodisperse. The values of zeta-potentials show that all the investigated latices belong to the group of latices with a high negative charge on the particle surface.

In our initial experiments the viscosity of latex suspensions was determined as a function of the time elapsed following the preparation of the sample for measurement. The characteristic curves obtained for suspensions of latex LS 206-2 at different pH values are shown in Figure 1. Generally, it was found that viscosity increased rapidly with time and assumed an almost constant value after about 45 minutes. A similar behavior in the change of viscosity with time was observed with all other polystyrene latices. Figure 1 also shows that viscosity decreases with an increase in the pH values of latex suspensions.

In order to study the influence of the concentration of latex particles and the aging of their suspensions on viscosity properties, the systems of concentrations ranging from 0.1 to 1% were prepared and measured at several time intervals after preparation. During aging the systems were kept at room temperature at a place isolated from great temperature oscillations. The typical numerical data obtained in the case of latex LS 206-2 are summarized in
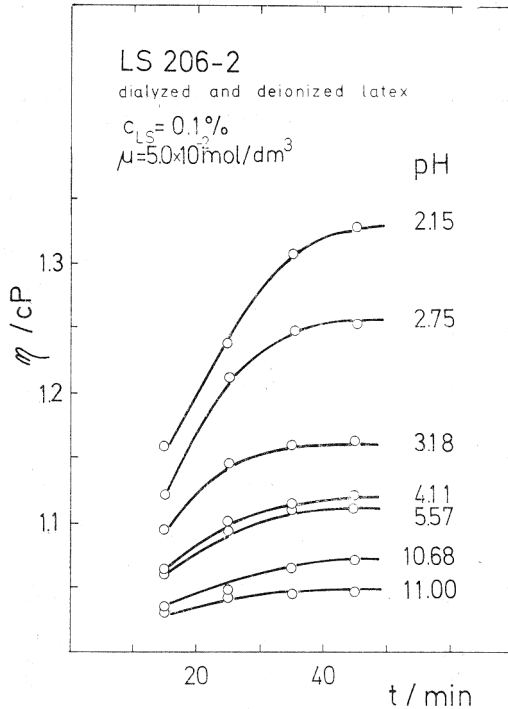

Figure 1. Time dependence of viscosity at different pH values of polystyrene latex LS 206-2 suspensions; the dialyzed and deionized sample measured at concentrations $c_{LS} = 0.1\%$ and ionic strength $\mu = 5.00 \times 10^{-2}$ mol dm^{-3}
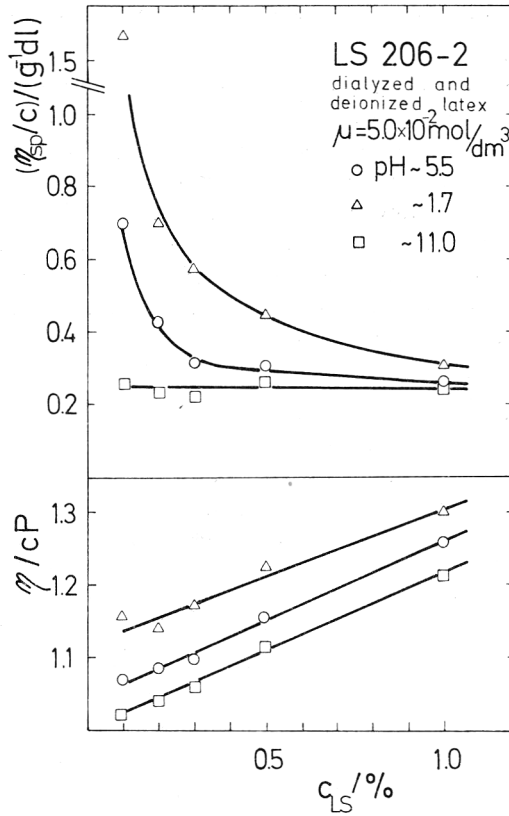
Figure 2. Concentration dependence of viscosity and reduced viscosity η_{sp}/c at different pH values of polystyrene latex LS 206-2 suspensions; the dialyzed and deionized sample measured at ionic strength $\mu = 5.00 \times 10^{-2}$ mol dm^{-3} and 20 °C.

Table II and graphically presented in Figure 2, which shows the dependence of both viscosity η, and reduced viscosity η_{sp}/c on the concentration of latex suspensions at three different pH values. The reduced viscosity is defined in the usual way as η_{sp}/c, where η_{sp} is the specific viscosity (i. e. $(\eta - \eta_0)/\eta_0$, η denoting the viscosity of the suspension and η_0 that of the pure dispersing medium) and c the concentration of the suspension expressed in grams per 100 ml. As shown in Table II, an increase in reduced viscosity in the course of the aging of suspensions is obvious. It shoud be noted, however, that the viscosity values after 7 days, and those after 14 days, in particular, were measured with greater errors than those after one day. The reason is an intensive coagulation appearing during the aging of suspensions for several days at lower pH values and preventing exact readings of measured values, because the ball of the rheoviscometer reacts by sudden »jumps« when coming into contact with the coagulum. The points in Figure 2 are means of two readings performed 15 minutes after the preparation of the samples. The viscosity values obtained are characteristic of three pH regions: at pH 1.7 the functional groups on the particle surface are not ionized, the middle pH value

corresponds to partial ionization, and at pH 10 all the surface groups are ionized[4].

We tried to investigate, using the same experimental set-up, the influence of an inorganic electrolyte on the stability of latex suspensions. For this purpose low concentration latex suspensions (1.37×10^{-4} g cm^{-3}) were prepared with various concentrations of barium nitrate, and in the preliminary experiments viscosity changes were followed in relation to the period of time that elapsed after the preparation of the samples. It has been found that viscosity remains practically constant within a time interval of 15 to 30 minutes; the deviations observed being neither systematic nor greater than the experimental error. In view of this experience, all subsequent viscosity measurements were made 15 minutes after the preparation of each coagulation system.

For the evaluation of the critical coagulation concentration c_{coag}, i. e., the concentration of the electrolyte that at a given time coagulates a colloidal sol[11], the viscosity or reduced viscosity of suspensions were plotted against the logarithm molar concentrations of the added barium nitrate. Figure 3 gives an example of such plots obtained for sample LS 225. One can see that the viscosity of suspensions slightly decreases with the increasing concentration of barium nitrate up to a certain limiting value, above which a sudden, rapid increase in viscosity is observed. Thus, the intersection of the two straight lines corresponding to the slow and the rapid change in viscosity, respectively, gives the concentration of the added electrolyte, which may be taken as the critical coagulation concentration. The critical coagulation concentrations of barium nitrate determined from both η vs. log $c_{Ba(NO_3)_2}$ and η_{sp}/c vs. log $c_{Ba(NO_3)_2}$ for differently treated polystyrene latex suspensions are given in
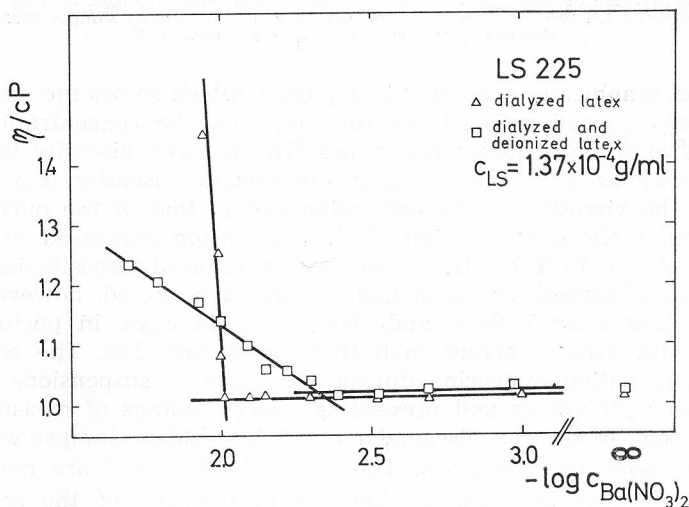

Figure 3. Determination of critical barium nitrate coagulation concentrations for dialyzed and both dialyzed and deionized latex sample LS 225; pH 5.80.

Table III. Taking into consideration the magnitude of the experimental error, one can conclude from Table III that in most cases the c_{coag} values were the same, irrespective of the way of their evaluation.

TABLE III

Critical Coagulation Concentrations of Barium Nitrate Calculated from Both η *vs.* log c $_{Ba(NO_3)_2}$ *and* η_{sp}/c *vs.* log c $_{Ba(NO_3)_2}$ *for Differently Treated Polystyrene Latex Suspensions*

Sample	$\dfrac{c_{LS} \times 10^4}{g/ml}$	Deionized	$\eta/\log c$ — log c_{coag}	$\eta_{sp}/c/\log c$ — log c_{coag}	$\dfrac{c_{coag} \times 10^3}{mol/dm^3}$
LS 206-2	1.37	+	2.0 ± 0.10	2.02 ± 0.01	9.8
	1.37	—	2.01 ± 0.01	2.02 ± 0.01	9.8
LS 225	1.37	+	2.33 ± 0.02	2.34 ± 0.05	4.8
	1.37	—	2.01 ± 0.01	2.02 ± 0.01	9.8
LS 142-T	1.37	+	2[a]	2[a]	10[a]
	1.37	—	2.02 ± 0.01	2.04 ± 0.01	9.7
LS 225	2.74	+	2.31 ± 0.02	2.32 ± 0.01	4.7

[a] Determined after 24 hours.

The measurements repeated after 24 hours showed that the intersections of the straight lines for samples LS 206-2 and LS 225 were no longer so sharp as before, while for dialyzed and deinized sample LS 142-T it was possible to determine a reliable c_{coag} value only after that time. In the case of sample LS 225 some measurements were performed using suspension concentrations twice as high as those used earlier. The c_{coag} value obtained was practically equal to that obtained with lower concentration.

In order to determine the exact pH region in which decrease in pH leads to latex destabilization and coagulation, we performed systematic viscosity measurements in relation to the pH value of latex suspensions under different conditions (variation of concentration and ionic strength). A schematic graph of both viscosity and reduced viscosity values obtained after 15, 25, 35, and 45 minutes for sample LS 206-2 is shown in Figure 4. It is obvious that the position of the limiting pH value, determined by the intersection of two straight lines, is independent of the time of measuring. For this reason all other latex suspensions were measured only after 15 minutes, and pH values, at which a sudden, substantial increase in viscosity occurs, were determined in the same way as the above mentioned critical coagulation values. The critical pH values obtained for all the latices investigated under different experimental conditions are summarized in Table IV.
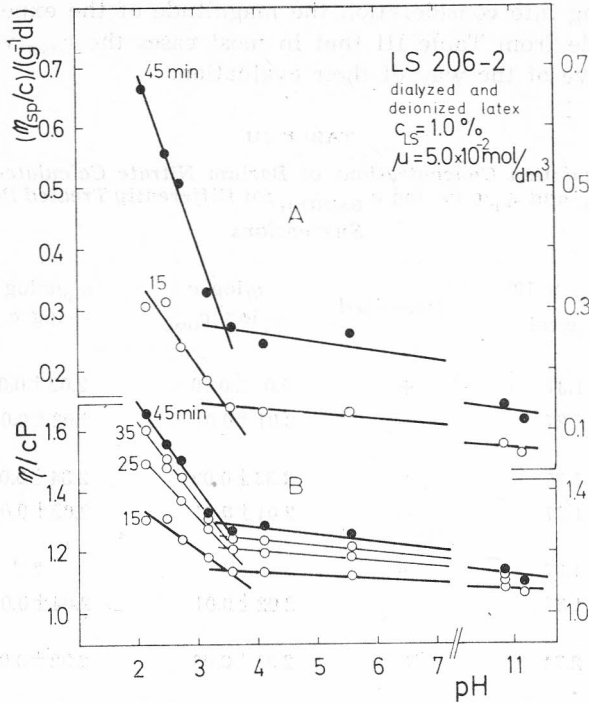
Figure 4. Determination of critical pH values for both the dialyzed and deionized latex sample LS 206-2 at different times of measuring (15, 25, 35 and 45 minutes); A reduced viscosity vs. pH; B viscosity vs. pH.

TABLE IV

Critical pH Values as a Function of Ionic Strength and Deionization Procedures for Different Polystyrene Latices

Sample	$\dfrac{\mu \times 10^2}{mol/dm^3}$	$\dfrac{c_{LS}}{\%}$	Deionized	c_{pH}
LS 206-2	5.0	0.1	+	3.5
	5.0	0.1	—	2.7—2.8
	5.0	0.3	+	3.3—3.5
	2.5	0.1	+	3.5
	0.5	0.1	+	3.5
LS 225	5.0	0.1	+	2.5
	5.0	0.1	—	2.3
LS 142-T	5.0	0.1	+	3.1
	5.0	0.1	—	2.8

DISCUSSION

Our measurements of the viscosity of latex suspensions at about pH 10 and within the concentration range from 0.1 to 1% gave the expected results, i. e., an increase in viscosity parallel to the increase in concentration (Figure 2). In the region of high pH values (pH ~ 10) polystyrene latex particles are maximally negatively charged because of the complete ionization of the functional groups present[4], and therefore in this region viscosity might be expected to be higher than that of suspensions at lower pH values. However, as can be seen in Figure 2, this was not observed in our experiments, and measurements of suspensions at pH values 5.5 and 1.7, especially when expressed in terms of reduced viscosity, showed an interesting effect: an increase in η_{sp}/c with a decrease in latex concentration. In our opinion, the increase in viscosity, far above the values expected according to the Einstein equation, at lower pH should be attributed to the coagulation of latex particles. This is in accord with our earlier findings that deionized samples at low pH values spontaneously coagulate[4]. The coagulation process probably occurs because the process of deionization reduces the particle surface charge, which in turn decreases the stability of suspensions. The increase in viscosity in the course of the aging of suspensions (Table II) might also be explained as a result of coagulation processes which are particularly intensive at low pH, so intensive that a coagulum may be clearly observed after several days.

A comparison of critical barium nitrate coagulation concentrations as determined in this study (Table III) with those obtained by measuring turbidity is presented in Table V. Despite the differences among the experimental procedures employed, all the values obtained are fairly concordant. The greatest difference between the critical coagulation values for the deionized and dialyzed sample was obtained in the case of LS 225. The explanation may lie in the fact that this latex, synthesized by γ-rays initiated polymerization, shows a lower particle surface charge after deionization than any of the other investigated latices. This indicates that the process of deionization reduces the particle surface charge density to a value near the critical one required for the stabilization of latex particles and that, therefore, a smaller barium ions concentration is sufficient for the coagulation of latex particles.

TABLE V

Critical Coagulation Concentration of Barium Nitrate Determined by Viscosity and/or Turbidity Measurements for Different Polystyrene Latices

Sample	$\dfrac{D}{nm}$	Deionized	Method of determination	$\dfrac{c_{coag} \times 10^3}{mol/dm^3}$
LS 225	119.1	+	viscosity	4.8
		−	"	9.8
		+	turbidity	8.7[a]
		−	"	7.9[a]
LS 206-2	177.2	+	viscosity	10.0
		−	"	9.8
LS 205	232.6	+	turbidity	10.3[a]
		−	"	12.6[a]
LS 97—10	396.5	−	"	9.5[a]

[a] Taken from I. Jalšenjak, M. Sci. Thesis, University of Zagreb, 1973; to be published.

The measurements carried out pointed to the dependence of the destabilization of the dispersions on the pH value. The data in Figure 4 and Table IV show a sudden increase in viscosity at a certain pH, which should be attributed to coagulation. It can be also noted that the point at which viscosity increases does not depend, under our experimental condition, on the concentration of the latex suspension, ionic strength of the electrolyte added and time of measuring, but only on the treatment of the suspensions, i. e., on the dialyzation and deionization procedure. It is therefore proposed that the pH value at which destabilization of the suspensions occurs should be termed »critical pH value«, c_{pH}. Thus, it denotes the value at which the force which attracts latex particles is sufficiently strong to make the system coagulate. In the region of pH $>c_{pH}$ the number of ionized functional groups increases, whereby the suspension becomes stabilized. By latex deionization a certain amount of electric charge is removed and the c_{pH} shifts towards higher values (2.8 for the dialyzed LS 206-2 in contrast to the deionized sample, which becomes destabilized at pH 3.5).

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SAŽETAK

Viskozimetrijsko određivanje koagulacije lateksa

I. Jalšenjak, I. Štivić i J. J. Petres

Ispitivana je viskoznost polimernih lateksa u zavisnosti o pH-vrijednosti suspenzija, starenju suspenzija, odnosno dodatku elektrolita. Upotrijebljeni sustavi bili su monodisperzni polistirenski lateksi (koncentracija dispergirane faze: $0.1—1^0/0$) s visokim negativnim nabojem na površini čestica. Nađeno je da se mjerenjem viskoznosti, pri određenoj koncentraciji dispergirane faze, može ustanoviti koagulacija lateksa. Zbog toga smo pokušali viskozimetrijski odrediti kritičnu koagulacijsku koncentraciju. Dobivene su vrijednosti bile identične vrijednostima određenim turbidimetrijski. Odredili smo i točno pH-područje u kojemu promjena pH dovodi do promjene stabilnosti sustava. Prema našem mišljenju dobivena »kritična pH-vrijednost« karakteristična je za uzeti sustav, a pokazuje i u kojem području dolazi do destabilizacije i koagulacije.

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