

EFFECT OF ELECTROLYTE CONCENTRATION ON STABILITY
OF POLYMER LATEX

By

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The surface charge of Litex BL 112 polymer latex (Hüls AG) was characterized by means of potentiometric and conductometric titrations. It was found that there are two types of acidic groups: a small amount of strongly acidic groups and a larger amount of weakly acidic ones, with a surface charge density of $3.6 \mu\text{C}/\text{cm}^2$. The acidic dissociation constant was found to be 4.2. The ccc-s of CaCl_2 , AlCl_3 and LaCl_3 were determined, and were found to be 34, 15.8 and 2 mmol dm^{-3} , respectively.

Introduction

The behaviour of dispersions of pigments and/or polymer latexes in an aqueous medium is important for paint technology and research. The interactions between polymer latex particles can be attributed to electric double-layer repulsion and van

der Waals attraction, both based on electric interactions [1]; these two types of interaction can be described on the basis of the DLVO theory. The van der Waals attractive forces decrease quickly with the distance between two particles. As the particles approach each other, the repulsive coulombic forces increase. The higher the charge density on the particles, the stronger the resulting repulsion between them, and therefore the existence of charges on the surface plays a determining role in the stability of a polymer latex. This theory is accepted by most scientists, but it was originally developed for the interactions between infinite flat plates or two spheres of equal sizes.

Hogg, Healy and Fuerstenau [2] extended the DLVO theory to the interactions of dissimilar spherical particles, i.e. for the case of heterocoagulation. The major parameters of the theory are the double layer potential of each type of particle, the ionic strength of the medium, the particle size, and the relative concentrations.

In the work of Ottewill et al [3-5], we find the characterization of a number of monodisperse systems, the polystyrene latex particles produced by the emulsion polymerization of styrene using hydrogen peroxide as an initiator and a soap as an emulsifying agent. These systems appear to conform most clearly to an ideal model system. There have been many other investigations with respect to the characterization of polymer latexes [6-8]. Stone and Watillon [9] found that the type of emulsifier used in the emulsion polymerization influences the stability of the dispersion, and the sensitivity to electrolytes, i.e. the critical coagulation concentration (ccc). It also influences the viscosity, the surface conductivity and the electrophoretic mobility of the latex. Ottewill et al. [10, 11] observed that there is no relation between the stability ratio curves and the particle size, but the ccc

depends on the type and the density of the surface charge and the presence of stabilizing materials. Matijevic et al. [12-14] investigated the effects of aluminium nitrate on the stability of different types of polymer latexes. It was found that the stability depends on the pH of the medium. Under certain pH conditions, the electrolyte reacts with water to form hydrolysed species, which are strongly adsorbed onto the negatively charged particles.

Materials and Methods

The polymer latex dispersion was Litex BL 112, a product of Hüls AG, with a solid content of 50 %.

The latex dispersion was purified from the emulsifier and electrolyte by passing it through both cationic and anionic exchange resins. The cationic column was purified just before use by flowing 2 mol dm^{-3} hydrochloric acid through it, while 1 mol dm^{-3} sodium hydroxide was passed through the anionic one; the columns were then washed with distilled water till no acid or base reaction was observed. After this pretreatment of the columns, a 1 % polymer latex dispersion was passed through each column at a rate of $150 \text{ cm}^3/\text{minute}$.

The pH and conductivity titrations of the purified 1 % polymer latex dispersions were carried out with a Radelkis (Hungary) OP-204/1 pH-meter and an OK-102/1 conductometer, with $0.0525 \text{ mol dm}^{-3}$ potassium hydroxide. The contents of the titration vessel were stirred with a magnetic stirrer.

Coagulation rates were determined by measuring the rate of change of the turbidity of the polymer latex with a

Spekol 10 (GDR) spectrophotometer at 456 nm. The output was recorded on a Radelkis (Hungary) OH-814/1 recorder.

The average particle diameter was measured with a MOM. 3180 Ultracentrifuge (Hungary) the sedimentation coefficient being determined by a method given in [15].

All chemicals used were of AR grade. Aluminium chloride was a product of Reachim, USSR. Potassium hydroxide and calcium chloride were from Reanal, Hungary. Lanthanum chloride was a Merck product.

Results and Discussion

1. Surface characterization

1.1. Conductometric and potentiometric titrations

The conductometric and potentiometric titrations of the purified polymer latex were performed to determine its surface charge density and intrinsic dissociation constant.

The results of the titrations are shown in Fig. 1. It can be seen from the conductivity curve that there are two break-points. This means that the particles of polymer latex bear two types of acidic groups. This is more evident from the conductivity measurements than from the potentiometric ones, where the end-point of the titration can not be determined with high accuracy.

The values of the equivalency points can be determined by extrapolation of the linear parts of the conductometric curve. The first point was found at 8.6 mmol/g solid, which is equivalent to the strong acidic groups on the surface of the polymer latex particles. The second one, at 124 mmol/g

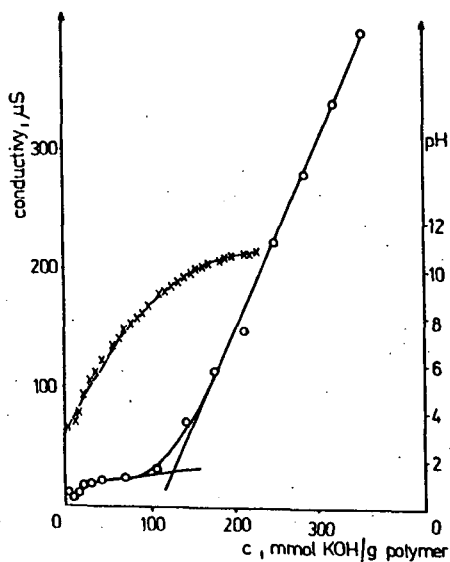


Figure 1: Conductometric and potentiometric titration of a polymer latex with KOH
 (x) potentiometric curve
 (o) conductometric curve

solid, corresponds to the total amount of all acidic groups on the surface of the polymer spheres.

The average size of the polymer spheres was calculated from the sedimentation coefficient of the particles of the latex. The average diameter was found to be 85 nm.

From the amount of acidic groups, the density of 1.054 g/cm^3 for the polymer particles, the average particle diameter of 85 nm, and the supposition that the particles are spherical in form, the surface charge density was calculated to be $0.15 \text{ } \mu\text{C/cm}^2$ for the strong acidic sites and $3.6 \text{ } \mu\text{C/cm}^2$ for the total amount of acidic surface sites.

1.2. *Intrinsic dissociation constant*

The dissociation of acidic surface groups in a polymer latex may be characterized by determination of the intrinsic acidity constant, pK_{int} , as follows.

The degree of dissociation, α , is the ratio between the amount of partially dissociated charges on the surface of polymer particles and their total amount. It can be calculated from the conductivity curve data. The apparent acidity constant is calculated from the titration data via the following equation [16]:

$$pK_a = pH_{solution} - \log \frac{\alpha}{1-\alpha}$$

$pH_{solution} - \log(\alpha/(1-\alpha))$ is plotted as a function of α , and extrapolation of the straight part of the curve to $\alpha = 0$ (Fig. 2) gives the intrinsic acidity constant, pK_{int} . This was determined to be 4.1. This value relates to the dissociation of weakly acidic groups on the surface. In this case, the determination of the intrinsic dissociation constant of the strongly acidic groups is not possible by this method, because their amount (8.6 mmol g^{-1}) is much smaller than that ($115.4 \text{ mmol g}^{-1}$) of weakly acidic groups. Therefore some of the titration data relating to the first dissociation step can not be evaluated.

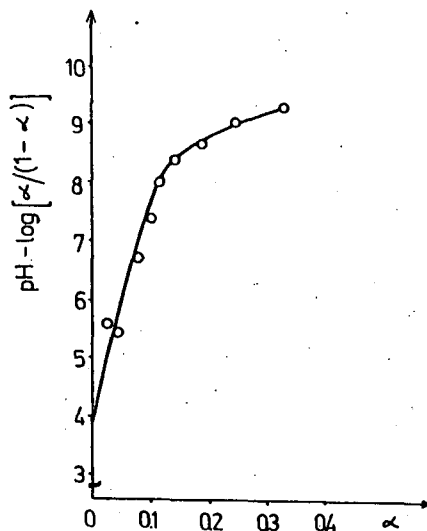


Figure 2: Relation between $\text{pH} - \log(\alpha/(1-\alpha))$ and α

2. Stability of polymer latex dispersion

Measurements of the coagulation kinetics of the polymer latex dispersion were carried out to obtain information about its stability.

The number of particles N_t present in the dispersion at time t after the addition of electrolyte is given by the Smoluchowski equation [17]:

$$N_t = N_0 / (1 + kN_0 t)$$

where N_0 is the number of particles in the initial dispersion, and k is the rate constant of coagulation, which can be put equal to k_0/W , where W is the stability ratio and k_0

is the rate constant of rapid coagulation. The values of k_0 and k can be determined experimentally in the rapid and the slow region of coagulation, respectively.

Measurements of the coagulation kinetics were carried out within 1 minute after electrolyte addition, by determination of the turbidity of the diluted dispersion. The slope of the turbidity vs time function could be taken as proportional to the initial rate of coagulation.

The change in turbidity is

$$\frac{d\tau}{dt} = v \cdot \text{constant}$$

where v is the rate of coagulation and the constant depends on the optical parameters of the measurements. If the initial concentrations are the same,

$$W_{\text{expt}} = \frac{v_{\text{fast}}}{v_{\text{slow}}}$$

Thus,

$$W_{\text{expt}} = \frac{v_{\text{fast}} \cdot \text{constant}}{v_{\text{slow}} \cdot \text{constant}} = \frac{d\tau/dt_{\text{fast}}}{d\tau/dt_{\text{slow}}}$$

The variation in turbidity of the dispersion for different amounts of aluminium chloride is presented as an example in Fig. 3. It can be seen that the slope of the curves increases up to a certain value with increasing amount of electrolyte.

The stability of the polymer latex is characterized by plotting $\log W_{\text{expt}}$ against \log molar concentration of the electrolyte. The ccc can be calculated by extrapolating the $\log W_{\text{expt}}$ values to $\log W_{\text{expt}} = 0$. The intercept on the $\log c$ axis gives the ccc.

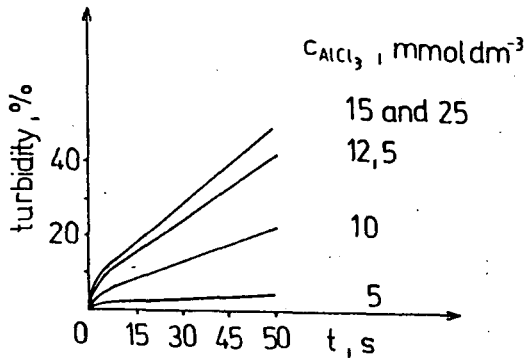


Figure 3: Effect of AlCl_3 amounts on turbidity of polymer latex as a function of time

2.1. Effect of electrolyte concentration

The effects of the electrolyte concentration on the stability of the polymer latex dispersion were studied by using calcium chloride as a divalent electrolyte and aluminum chloride and lanthanum chloride as trivalent electrolytes. The variation of $\log W_{\text{expt}}$ with $\log c$ is shown in Fig. 4.

From the Figure, the values of ccc are 34, 15.8 and 2 mmol dm^{-3} for CaCl_2 , AlCl_3 and LaCl_3 , respectively. The ccc of LaCl_3 is in good agreement with that obtained by others [12, 18], but it differs from that of AlCl_3 . This may be due to the interaction of AlCl_3 with water. Matijevic et al. [12-14] found that the Al^{3+} ion exists in different hydrolysis forms at $\text{pH} < 3.3$. As the pH increases, reaction occurs with water to form a sequence of hydrolysed species.

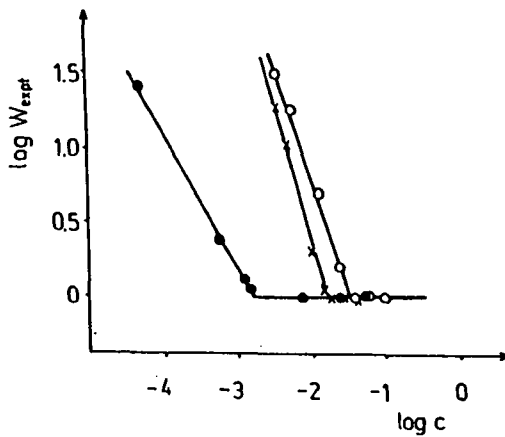


Figure 4: Stability of polymer latex dispersion as a function of electrolyte concentration in mol dm⁻³.

- (o) calcium chloride
- (x) aluminum chloride
- (●) lanthanum chloride

The pH of the dispersion was measured after electrolyte addition. It was found that the AlCl₃ electrolyte decreases the pH of the dispersion to a large extent, while LaCl₃ and CaCl₂ have smaller effects on it. The ratio of the ccc values for CaCl₂ and AlCl₃ was 2.1, whereas that for CaCl₂ and LaCl₃ was 17, in approximate agreement with the theoretical value of 11.4 to be expected from the valency rule.

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ЭФФЕКТ КОНЦЕНТРАЦИИ ЭЛЕКТРОЛИТА НА СТАБИЛЬНОСТЬ ПОЛИМЕРНОГО ЛАТЕКСА

А. А. Абд Эл Хахим, Э. Томбац и Ф. Санто

С применением потенциометрической и кондуктометрической титрования characterized поверхностный заряд полимерного латекса (фирмы Hüls AG) Litex VL 112. Было показано наличие кислотных групп двух типов: небольшое количество сильнокислотных и большее слабокислотных групп, образующих поверхностную плотность заряда 3.6 мк/см^2 . Постоянная кислотной диссоциации была найдена равной 4.2. Определены критические концентрации коагуляции для CaCl_2 , AlCl_3 и LaCl_3 , которые составляли 34, 15.8 и 2 ммоль/дм³ соответственно.