Studies on the Adsorption of Detergents and on the Electrophoretic Mobility of Emulsion Particles in the Emulsion Polymerisation of Vinyl Acetate.

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Synopsis

The emulsion polymerisation of vinylacetate is carried out under the existence of anionic detergents (sodium dodecyl sulfate and sodium dioctyl sulfo succinate), non-ionic detergents (polyoxy ethylene dodecyl ether with various degrees of polymerisation) and cationic detergent (hexadecyl trimethyl ammonium bromide). The adsorption of detergents on and the electrophoretic mobility of the emulsion particles are measured. The degree of adsorption per gram of polymer is found to saturate at some constant value and the mobility is also recognized to become constant at above these concentrations of detergents. The amount of saturation is constant regardless of the concentration of detergents used or the size or the surface area of the polymer particles. These facts seem to be peculialities of a slightly water-soluble monomer such as vinylacetate. As is already reported, this is not the case with styrene.

1. Introduction

Harkins (1) has already reported in detail on the influences of detergents in the emulsion polymerisation of vinyl compounds. He discovered that the surface tension of the emulsion obtained in emulsion copolymerisation of styrene and isoprene with sodium oleate used as detergent increases as the polymerisation advances. Also, Corrin (2) studied on the disappearance of detergents in aqueous phase in the emulsion polymerisation of styrene. He pursued his study on this phenomenon by determining fluorescence by Rhodamine 6G, and others. Only in the case of anionic detergents such as potassium or sodium laurate, myristate or oleate, etc., they clarified the conversion of micellar soap into adsorbed soap. However, they have not touched upon the case of the non-ionic and cationic detergents, nor have they mentioned about the monomers, such as vinylacetate, which are more soluble in water than styrene,

isoprene, and others. It is the aim of this research to verify by a more direct method on a wider range of monomers and detergents.

On the other hand, Maron (3) made a research on the electrophoresis of the commercial grade *GR-S* latex. The effects of pH, ionic strength and temperature on the electrophoretic mobility were dealt in his reports. As the material used was of commercial origin, the type of detergents used in emulsion polymerisation was limited. The influences of detergents in charging emulsion particles can also be studied by the electrophoresis of emulsion. It is our aim to clarify the correlation of the adsorption of various detergents on and the electrophoretic mobility of the emulsion particles.

2. Experimental

i) Materials; Sodium dodecyl sulfate (SDS) and sodium dioctyl sulfosuccinate (SDSS) are purified by recrystallisation from ethanol and acetone solution of commercial grade "Emal No. 10" (KAO-Soap Co., Ltd., Japan) and "Aerosol OT" (Amer. Cyanamide Co., USA) respectively. Pure polyoxyethylenedodecylether is obtained by ether-extraction and hexadecyltrimethylammonium bromide is recrystallized from acetone solution of commercial products. Vinylacetate monomer is distilled under reduced pressure. Ammonium persulfate of C. P. grade is used as polymerisation catalyst.

ii) Emulsion polymerisation; 8 ml. vinylacetate is polymerized for 5 hours without agitation in 100 ml. aqueous solution containing 0.1 g of ammonium persulfate and a known amount of detergent. Polymerisation is performed almost complete in every case. No agitation was needed because the amount adsorbed did not vary whether there was agitation or not as shown in Table 1.

Table 1. The effects of agitation on the adsorption of SDS during emulsion polymerisation.

Amount of monomer in 100 ml. aqueous solution (ml.)	Temperature of polymerisation (°C)	Agitaiton	Amount of adsorption of detergent (g. SDS/100g. Polymer)
8	70	None	0.31
8	60	None	0.35
30	70	Agitating	0.36

iii) Determination of the amount of adsorption; The measurements of surface tension seem to be quite effective for such a detergent as SDS which has small critical micellar concentration. However, these methods can not be applied for nonionic or cationic detergents which have relatively large critical micellar concentration. In this report, the direct colloidal titration method is applied. After centrifuging the emulsion at 3,000 r.p.m. for one hour, the clear aqueous solution at the upper part is titrated. The standard 0.01 N-hexadecylpyridinium chloride solution for the titration of anionic detergent, the standard 0.01 N-SDS solution for the titration of cationic detergent and

bromphenol blue (0.01% aqeous solution) as indicator were used. Polyoxyethylene-dodecyl ether is determined gravimetrically, based on the Oliver method (4), by the complex formation with phosphormolibdic acid. Calibration curves in our experiments for weights of precipitation are presented in Fig. 1.

iv) Measurement of electrophoretic mobility; The apparatus employed for measuring electrophoretic mobility consisted merely of the electrophoretic U-type cell shown in Fig. 2.
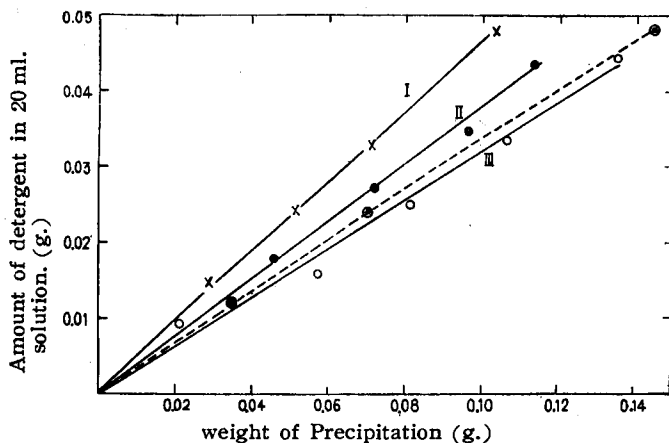

Fig. 1 Amount of detergent versus weight of preciptation formed at the addition of phosphormolybdic acid. Curve I is for $\bar{P}$(degree of polymerisation of polyoxyethylene) =6. Curve II is for P=22. Curve III is for $\bar{P}$=45. Dotted line represents Oliver's data.
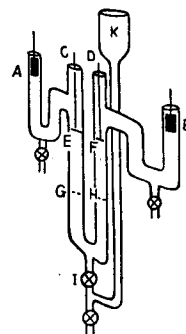

Fig. 2 Latex electrophoretic mobility cell. A and B are electrodes consisting of +Zn and —PbO. C and D are calibration electrodes of Pt-wires. G and H show boundaries.

Since emulsion is turbid, the movement of boundaries at G and H can be easily followed with a cathetometer placed in front of the cell. The distance between G and H in this tube is so constructed as to exactly one half of the distance between E and F. In experimenting, the aqueous solution of the same concentration of ammonium persulfate, glucose and detergent as the emulsion to be examined are filled in U-tube. Into the vessel K the emulsion containing 2% glucose is poured. Then cock I is gradually opened and the emulsion is filled into GHI. By electrodes A and B, approximately 200 volts is applied. Calibration electrodes C and D are used occasionally during the experiment for checking the magnitude and constancy of current flowing through the cell. In our experiment the movement of boundaries is very much uniform and the relations of distances of movement obtained by cathetometer-reading and time are strictly linear both for ascending and descending of boundaries at G and H respectively. For instance, the emulsion of polyvinylacetate obtained by polymerisation without any detergent [6.77% solid concentration, pH=3.0 and ionic strength $(\mu) = 0.012$] moves 2.74 cm per hour at 18°C. The actual distance between G and H

is 15 cm and 48 volts are applied. The correction factor for viscosity and dielectric constant from 18°C. to 20°C. is 1.05. Thus electrophoretic mobility u (in micron-cm per volt-sec.) is calculated by; $u=27400 \times 1.05 \times 15/48 \times 60 \times 60=2.38$. Movement toward the anode is shown by minus sign and that toward the cathode is represented by plus sign. The values of U increase from -2.38 (when $\mu=0.012$) to -2.50 (when $\mu=0.36$) and from -2.38 (when pH=3.0) to -2.55 (when pH=10.6); but they decrease from -2.38 (when solid conc. $=6.77\%$) to -2.19 (when solid concentration $=13.2\%$). These changes are small compared with those of the case of GR-latex. The next experiment is made at pH=3.0 and solid conc.$=5.0\%$.

3. Experimental Results

i) Surface tension of polyvinylacetate emulsion : The measurements of surface tension (γ) in the process of emulsion polymerisation are done up to date only on the case of polymerisation or copolymerisation of styrene. On account of low affinity between styrene and water, the emulsion obtained without detergent can not stable and so the values of surface tension based on the polymer particles themselves can not be obtained accurately. In the case of vinylacetate monomer, however, a wider range of experiments covering zero concentration of detergent is possible. The relationship between the yield of polymerisation and the surface tension γ of emulsion of polyvinylacetate measured by Du Nouy ring tensiometer is shown in Fig. 3.
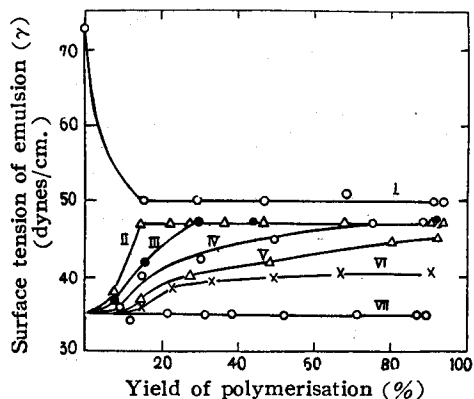

Fig. 3 Relationship between the yields of polymer and the surface tension of emulsion obtained in SDS solution. Curve I represents the case without detergent, Curve II SDS 0.02% aq., Curve III 0.05%, Curve IV 0.07% Curve V 0.08%, Curve VI 0.1%, and Curve VII 1.0% respectively.

γ-values of the emulsion polymerized without detergent as shown in Curve I of Fig. 3 decreases approximately 23 dynes per cm at the initial stage of polymerisation and they become constant after about 10% yield of polymer. It is conceivable that this decrease of γ for about 23 dynes per cm. is caused by the surface action of small polymer particles. With existence of detergent the γ-values become constant after the completion of adsorption and the γ-values are increase by about 12 dynes per cm. The lowering of γ caused by the unabsorbed detergent in the aqueous solution is not estimated as 73–47=26 dynes per cm., but only as 50–47=3 dynes per cm. The yields of polymerisation at which the γ-values become constant are increases as the concent-

ration of detergent increases. For instance the amount of adsorption can be calculated as $0.02/8 \times 0.93 \times 0.15 = 0.018$ g detergent per g polymer, because the γ-value are constant when the emulsion polymerized in 0.02% aqueous detergent solution is about 15% yield of polymer (where 0.93 means the density of vinylacetate). These values are 0.022 (at 0.05%), 0.013 (at 0.07%) and 0.012 (at 0.08%), and their average value 0.016. These values appear to be inaccurate when compared with the results obtained by direct measure. The above-mentioned calculation includes the value equivalent to approximately 3 dynes per cm., hence the true adsorption should be less than these values. Especially in the case of non-ionic or cationic detergents accurate quantitative values can not be obtained by this γ-method.

ii) Anionic detergent; By the method of colloidal titration the unadsorbed amount of detergent in aqueous solution is directly measured. The absorbed amount of anionic detergents after the completion of polymerisation is presented in Table 2.

Table 2. The adsorption of anionic detergents during polymerisation.

Concentration of detergent before emulsion polymerisation starts, (g per 100 ml. solution) A	Unadsorbed amount of detergent titrated directly (g per 100 ml. solution) B	Adsorbed amount of detergent calculated from C=A −B (g per 100 ml. solution)	Yield of polymeri- sation (%) D	Adsorbed amount of detergent calculated by values of column C and D.	
				(g detergent per g polymer)	(mol detergent per mol vinyl- acetate Unit)
(1) Sodium dodecyl sulfate					
0.0101	0.0000	0.0101	94.3	—	—
0.0303	0.0072	0.0231	95.9	0.0033	0.0010
0.0475	0.0201	0.0274	96.7	0.0038	0.0011
0.1070	0.0830	0.0240	96.0	0.0034	0.0010
				Av. 0.0035	0.0010
(2) Sodium dioctyl sulfosuccinate					
0.0200	0.0000	0.0200	96.6	—	—
0.0422	0.0000	0.0422	96.8	—	—
0.0865	0.0133	0.0732	96.8	0.0094	0.0018
0.1620	0.0895	0.0725	96.2	0.0094	0.0018
0.2031	0.1292	0.0739	96.8	0.0095	0.0018
				Av. 0.0094	0.0018

At the concentration of 0.01% (SDS) and 0.02 or 0.04%(SDSS) respectively, no detergent remains in aqueous phase and the total amount of detergens used is adsorbed on the polymer particles. Only a part, a constant amount, of detergent used is adsorbed at the concentrations above 0.03% (SDS) and 0.08% (SDSS) respectively. The amount of detergent adsorbed per g polymer (or per mol polymer) is constant regardless of the concentration of detergent used. These constant adsorptions attain to 0.35 g SDS.

and 0.94 g SDSS per 100 g polymer respectively. The authers (5) have previously studied the relation between size of emulsion particles and turbidity of emulsion, and found that they were in a simple relation under the normal condition of emulsion polymerisation. As was previously reported (6) and also is shown later in this report, it is conceivable that the size of emulsion particles decreases with the increase of concentration of detergent. The surface area of particles, therefore, increases as the concentration of anionic detergent increases. The fact that the adsorption is constant in this case, however, shows that the detergent penetrates into the surface to a certain depth.

To confirm this fact, the adsorption is investigated by the addition of detergent into the emulsion after the completion of polymerisation. The particles are relatively large in the emulsion obtained in the polymerization without detergent. It was obtained by adding 5 ml. of aqueous solution of SDS (conc. 0.331%) to 20 ml. of emulsion (solid conc. approximately 8%) and, after an

Fig. 4. Adsorption of detergent in the case of addition after the completion of polymerisation.

interval at constant temperature, titrating the unadsorbed amount of detergent in aqueous phase. The results are shown in Fig. 4.

As shown in Fig. 4, the adsorption is constant for those which have elasped 2 hrs or more at 60°C. and the value of 0.39 g per 100 g polymer shown in the figure is almost the same as that shown in Table 2. But the turbidity of the emulsion used in case of Table 2 is about one fifth of that in Fig. 4. Thus the adsorption seems irrelevant to the surface area of particles. The fact that the adsorption during emulsion polymerisation is equal to that of addition after complete polymerisation is very important and will be studied
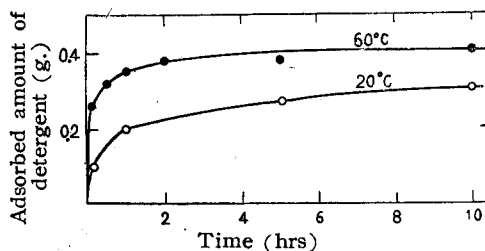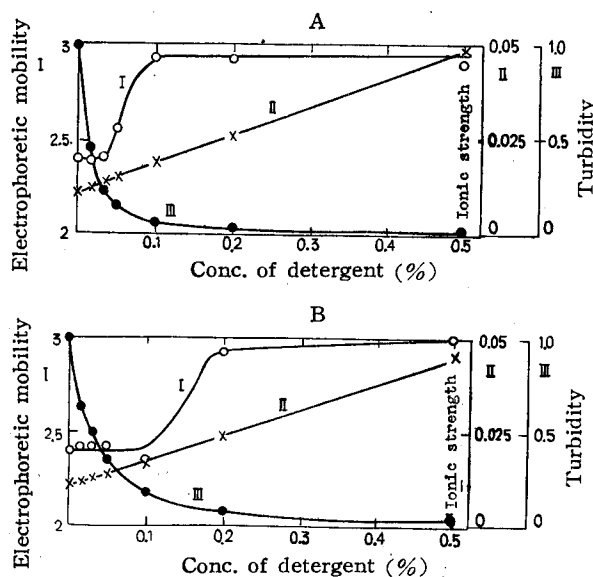

Fig. 5 Electrophoretic mobility of anionic emulsion.
A, SDS;   B, SDSS.

in future.

The electrophoretic mobility of anionic emulsion of polyvinylacetate is measured and the effects of concentration of detergent are presented in Fig. 5A (the case of SDS) and in Fig. 5B (the case of SDSS), and the data of relative turbidity τ (with the value of emulsion obtained without detergent as unity,) and the ionic strength μ of emulsion are also shown.

As shown in Fig. 5, the constant mobilities are obtained above 0.1% (SDS) and 0.2% (SDSS) of concentration of detergent. The zeta-potentials of particles could not be considered directly from the mobility measurements because both the ionic strength and the size of particles changed vigorously. The effects of pH and μ on the mobility of the non-emulsified and also polyvinylalcohol-stabilized emulsion are shown in Table 3.

Table 3. The effects of pH and μ on the electrophoretic mobility of
polyvinylacetate emulsion [pH is adjusted by addition of
HCl or NaOH].

Kind of emulsion	pH	μ	$-u$
None-emulsified	3.0	0.012	2.38
"	3.0	0.036	2.50
"	5.2	0.012	2.41
"	7.2	0.012	2.49
"	10.6	0.012	2.55
Stabilized with polyvinylalcohol (0.5%)	3.0	0.012	0.39
"	3.0	0.036	0.44
"	3.0	0.10	0.32
"	3.0	0.20	0.27
"	6.6	0.012	0.44
"	10.6	0.012	0.49

With the increase of pH, the mobility U increase slightly and the maximum values for μ variations are noticeable. The influence of the size of particle on mobility is considered to be vigorous as had already been reported in the case of oil droplets by Mooney (7) and by Kemp (8). The mobility of emulsion swollen, by various amounts of dibutylphthalate is measured and is presented in Fig. 6.
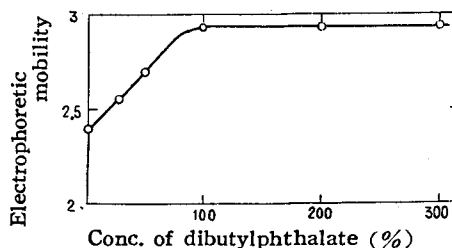

Fig. 6 Relationship between mobility and the amount of dibutylphthalate added in emulsion.

In the figure, it appears that the size of particles above 100% dibutylphthalate becomes constant and the mobilities are also constant. In order to compare mobilities

at constant size of particles, a detergent of a known concentration is added to non-emulsified emulsion after the completion of polymerisation and the electrophoretic mesurements are taken. Some results are shown in Fig. 7 A (SDS) and 7 B(SDSS). The constancy of mobilities is observed above the concentration of approximately 0.05% (SDS) and approx. 0.1% (SDSS). These values of concentration are much closer to the results of adsorption experiments than the values shown in Fig. 5A or 5B.
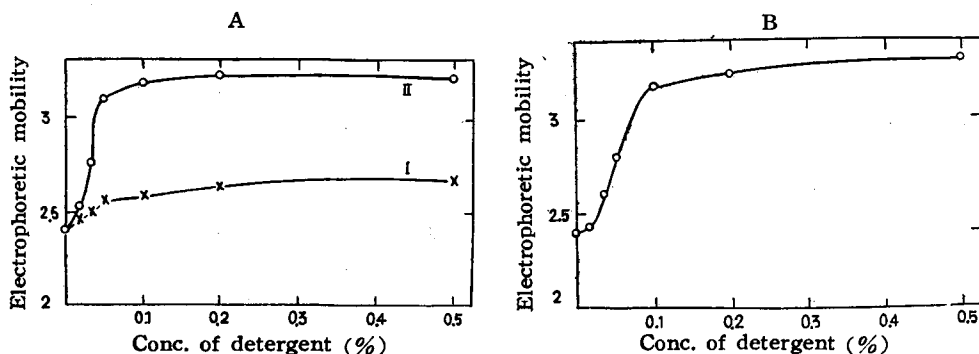

Fig. 7. Electrophoretic mobility in the case of addition after the completion of polymerisation.
A, SDS; I: 20°C II: 60°C. B, SDSS.

From the experimental results obtained here, it has become clear that the adsorption of anionic detergent on polymer particles attains to some saturation point regardless of the size of particles and also the electrophoretic mobility becomes constant at this saturation point.

iii) Non-ionic detergents : In the emulsion polymerisation of vinylacetate, the adsorption of polyoxyethylene dodecylether is measured gravimetrically by the titration of phosphormolybdic acid. The experimental results are shown in Table 4.

As shown in Table 4, the constant adsorption is also obtained as in the case of anionic detergents (Table 2.). Emulsion of polyvinylacetate obtained with the non-ionic detergent is found to stabilized at 0.2% to 0.5% concentration of detergent as previously reported by the authers (9). The results of adsorption coincides with the data reported then. The emulsion becomes stable as the degree of polymerisation of polyethyleneoxide increases, but the adsorption is almost constant independent of the degree of polymerisation.

The electrophoretic results are shown in Fig. 8.

In the case of polymerisation degree $P=6$, the emulsion is partly precipitated in the polymerisation process, the mobility is therefore, obtained from the stable emulsion on the upper layer. The electrophoretic mobility decreases with the increase of degree of polymerisation. Constancy of mobilities is attained at 0.3 to 0.5% concentration of detergent. These results are considered to coincide qualititatively with the adsorption

Table 4. The amount of adsorption of non-ionic detergents.

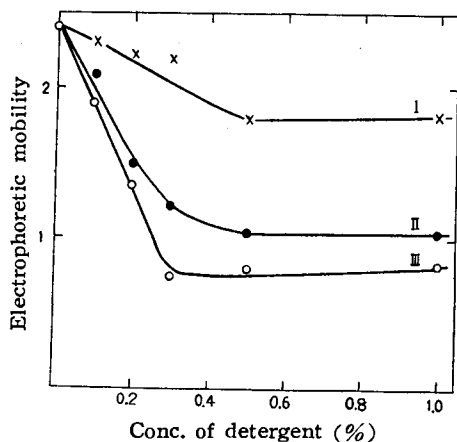| Average degrees of polymerisation of polyoxyethylene as the raw material of the ether used.	Concentration of detergent in emulsion polymerisation (g per 100 ml. solution) A	Unabsorbed amount of detergent titrated directly (g per 100 ml. solution) B	Adsorbed amount of detergent calculated (g per 100 ml. solution) A = B − C	Yield of polym. (%) D	Adsorbed amount of detergent calculated by values in column C and D	
					(g per g polymer	(mol per mol vinyl-acetate unit)
6	0.152	0.000	0.152	94.5	—	—
"	0.287	0.002	0.285	93.1	—	—
"	0.486	0.100	0.386	92.7	0.052	0.011
"	0.721	0.331	0.390	91.7	0.053	0.011
"	1.103	0.706	0.397	90.2	0.055	0.012
22	0.250	0.000	0.250	94.0	—	—
"	0.312	0.000	0.312	92.2	—	—
"	0.470	0.095	0.375	92.1	0.051	0.0050
"	0.964	0.594	0.370	91.2	0.051	0.0050
45	0.080	0.000	0.080	92.2	—	—
"	0.194	0.000	0.194	—	—	—
"	0.597	0.196	0.401	92.8	0.054	0.0030
"	0.896	0.507	0.389	91.9	0.053	0.0029
"	1.333	0.718	0.415	90.2	0.057	0.0031
				Av.	0.053	

Fig. 8 Relation between the electrophoretic mobility and the concentration of polyoxyethylene dodecylether. Curve I is represented for $P=6$, Curve II for $P=22$, and Curve III for $P=45$.

data. The size of particles, pH and also ionic strength are conceivable to be almost constant in the experiments range in which non-ionic detergents are used. The zeta-potentials can be calculated by the following Helmholtz-equation,

$$\xi = 4\,\pi\eta u/D\,,$$

where u means the mobility, η the viscosity of aqueous phase and D the dielectric constant of water. Zeta-potential for the non-emulsified emulsion is calculated to -44, and the constant values for emulsions obtained with the non-ionic detergents of $P=6$, 22 and 45 attain to -34, -20 and -14 millivolts respectively. It is recognized that the zeta-potential decreases with the increases of the adsorption of non-ionic detergent and also with the increase of the stability of emulsion. Thus in the case of polyvinylacetate, it is possible to produce stabilized emulsion which is almost neutral in electric charge.

iv) Cationic detergent: The adsorption of hexadecyl trimethylammoniumbromide on the polyvinylacetate particles is measured by the titration of aqueous phase using the standard anionic detergent (SDS) and the results are shown in Table 5.

Table 5. Adsorption of hexadecyl trimethylammonium-bromide during emulsion polymerisation.

Concentration of detergent before emulsion polymerisation starts. (g per100 ml. solution) A	Unadsorbed amount of defergent titrated directly (g per 100 ml. solution) B	Adsorbed amount of detergent calculated (g per 100 ml. solution) C = A − B	Yield of polym. (%) D	Adsorbed amount of detergent calculated by values in column C and D	
				(g per g polymer)	(mol per mol vinyl acetate unit)
0.149	0.000	0.149	87.1	—	—
0.217	0.000	0.217	—	—	—
0.383	0.000	0.383	85.5	—	—
0.588	0.011	0.577	91.2	0.079	0.026
1.032	0.432	0.600	90.3	0.083	0.027
1.281	0.701	0.580	89.0	0.082	0.027

As previously reported by present authers (10), the stable cationic emulsion of polyvinylacetate has been obtained at above 0.75% concentration of detergent. The saturated adsorption occurs also in this same range of concentration. Below 0.5% concentration of detergent, the electrophoresis can not be performed because of the precipitation of emulsion. The electrophoretic results above 0.7% concentration of detergent are presented in Table 6.

Table 6. Relationship between concentration of cationic detergent and electrophoretic mobility.

Concentration of hexadecyl trimethyl-ammoniumbromide before the emulsion polymerisation starts. (g per 100 ml. solution)	Mobility (micron-cm per volt-sec.)
Below 0.5	Ppt.
0.7	+1.83
1.0	+1.83
2.0	+1.64

It may be due to the effect of particle-size that the mobility decreases again as the concentration increases from 1.0% to 2.0%. It is recognized that the mobility becomes constant when the adsorption reaches the point of saturation in the case of cationic detergent also.

v) Change of mobility accompaning polymerisation; In the styrene emulsion polymerisation (11) and also in the case of vinylacetate (12), the enlargement of the particle-size during emulsion polymerization has been confirmed by the electronmicroscopic investigations. The change of surface tension during polymerisation has already been shown in Fig. 3. The change of mobility has not yet been measured by anybody including Maron (3). Some results obtained under a condition (to 200 ml solution containing 3g SDS and 1 g ammonium persulfate is added 100 g of vinyl-

Fig. 9 The yield of polymerisation versus the electrophoretic mobility.

acetetate monomer and polymerized at 70°C with slight agitation) is shown in Fig. 9.

Below 20% yield of polymerization, the boundaries between emulsion and aqueous phase was difficult to determine, but the curve obtained in this figure can be extrapolated to zero-point. The increase of mobility during polymerization can not be explained as caused solely by the increase of electric charge on particles, because the mobility increasese as the size of particles is enlarged in the polymerisation process.
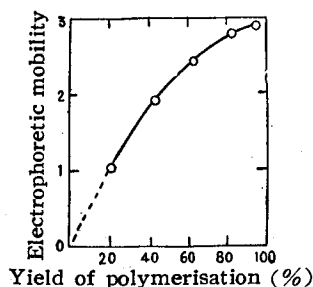
Acknowledgements

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