The Effect of Emulsifiers and Oil Viscosity on Deposition of Nonionic Silicone Oils from Oil-in-Water Emulsions onto Keratin Fibers

M. D. BERTHIAUME AND J. JACHOWICZ[1]

Clairol Incorporated, 2 Blachley Road, Stamford, Connecticut 06922

Received April 13, 1990; accepted July 26, 1990

The effect of oil viscosity, as well as the type and concentration of emulsifiers, on the deposition of nonionic silicone oils from oil-in-water emulsions on both untreated and cationically modified human hair was investigated. The emulsifiers in the ionic emulsions consisted of a mixture of either sodium octadecyl sulfate (SODS) or cetyltrimethylammonium bromide (CTAB) in conjunction with the two nonionic, ethoxylated nonylphenol surfactants employed in neutral emulsion systems. At constant oil viscosity, the rates of deposition were found to decrease with increasing nonionic surfactant concentration. At constant surfactant concentration, increasing oil viscosity gave rise to increasing rates and extent of deposition. Incorporation of ionic surfactants into the emulsifier systems results in corresponding changes in the zeta potentials of oil droplets, and consequently leads to shifts in the rates of deposition on untreated (negatively charged) or cationically modified keratin surfaces. The deposition data are discussed in relation to oil droplet size, zeta potential, and viscosity.

INTRODUCTION

Modification of the surface properties of solid substrates such as fibers by deposition of silicone and other oils from aqueous emulsions is widely utilized in the textile and cosmetic industries (1–3). In cosmetics, silicone oils are used as lubricating or hydrophobic agents in a variety of hair and skin care formulations. The performance of these products is usually determined by the ability of the dispersed phase to interact and deposit on the keratinous surface, by the distribution and thickness of the deposited oil layer, and by the durability (resistance to detergents) of the treatment. Commercially available products are usually complex systems composed of a host of additional ingredients including surfactants (emulsifiers), polymers (thickeners), fragrances, and preservatives. In addition to this, oils of differing viscosities are frequently employed depending on the end-use of a specific product.

Previously, the deposition of cationic, anionic, and neutral silicone oils from oil-in-water emulsions, prepared primarily with nonionic surfactants, on unmodified and cationically modified human hair was explored (3). The deposition was shown to occur as a result of electrostatic as well as van der Waals forces which control the droplet–fiber interaction. Aminofunctional (cationic at neutral pH) silicone oils were shown to readily deposit on untreated (negatively charged) hair fibers, while neutral or anionic oils interact only with cationically modified surfaces. It was also suggested that the processes of spreading or coalescence of oil droplets might affect the rates and extents of oil deposition onto fiber surfaces.

This paper explores the contribution of other parameters including oil viscosity, emulsifier concentration, and the character of the emulsifier system (nonionic, cationic, and anionic) on the deposition process of emulsions based on neutral silicone oils. These factors were expected to influence the surface characteristics of emulsion droplets, their av-

---

[1] To whom correspondence should be addressed.

0021-9797/91 $3.00

erage size and size distribution, and their ability to spread on the fiber surface, and thus to affect the kinetics of deposition. Untreated hair, which is negatively charged above pH 4, and cationically modified fibers characterized by a positive zeta potential in the pH range from 3 to 10, were both used in this investigation (3).

EXPERIMENTAL

Materials

Samples of hair. All fiber samples were commercially blended virgin brown hair purchased from DeMeo Brothers, New York. The hair was precleaned with either 5% sodium dodecyl sulfate (Fluka Chem.) or Triton X-100 (Rohm and Haas) and thoroughly rinsed under running deionized water. Hair samples were then soaked in three 500 ml water baths for 15 min each to ensure complete removal of any residual surfactant. Cationically modified hair was prepared by adsorption of a 1% solution of poly(methacrylamidopropyltrimethyl ammonium chloride) (PMAPTAC, obtained from Alcolac, mol wt 2.5×10^5 as determined by GPC) for 17 h followed by the rinsing procedure described above. Hair swatches were dried *in vacuo* at 37°C.

Emulsions. All emulsions were prepared using methyl-endcapped poly(dimethyl siloxanes) obtained from Dow Corning (DC 200 Series fluids). There were six oils ranging in viscosity from 50 to 12500 centistoke. The general procedure for emulsion preparation was as follows: Silicone oil was combined with two nonionic surfactants nonoxynol-9 and nonoxynol-4 (Igepal CO Series 630 and 430, GAF Corp.) possessing HLB values of 13.0 and 8.8, respectively. The mixture was heated to 70–75°C, and water of the same temperature was slowly added while stirring on a homomixer, at a speed of approximately 5000 rpm with a tangential shear rate of 37,000 s^{-1} (assuming a gap setting of 1/10,000 in. and a turbine diameter of 1.72 in.). The initial water-in-oil emulsion formed, quickly inverted to an oil-in-water system. Stirring was continued for 20 min after addition of water, and then through cooldown on a propmixer. In all systems the oil concentration was 5% by weight. Total surfactant concentration was varied from 0.25 to 4.0% by weight. In experiments involving ionic surfactants, SODS and CTAB were dissolved in the water phase prior to addition to the oil.

Deposition

The silicone emulsion deposition experiments were conducted in 20-ml scintillation vials using 1.0 g of hair fibers and 10.0 ml of emulsion solutions at 0.25% oil concentration, prepared by diluting 5.5% stock solutions immediately prior to the deposition experiments. Such a dilution was selected in order to: (a) be able to perform kinetic deposition measurements, (b) approximate practical usage values, and (c) enable turbidimetric analysis as an analytical technique. The vials were tumbled continuously at a rate of 8 rpm at ambient temperatures for specified amounts of time. At completion of the adsorption process, 5-ml aliquots were removed and diluted for turbidity measurements. The amounts of silicone adsorbed were calculated from a calibration of solution turbidity versus concentrations. The transmittance was measured at 540 nm in a 1.0-cm path length cell by means of a Brinkman PC/600 dipping probe colorimeter with a Beckmann Tech 300 voltmeter attached for more accurate readings. The calibration was repeated twice over a period of 3 weeks, providing results which were reproducible within 1.5%. Stable readings could be made within 1 or 2 min. The overall error of deposition measurements is estimated to be about 10%.

Microelectrophoresis

The electrophoretic mobilities of the emulsion droplets were measured by a microelectrophoretic technique using a Pen Kem Lazer Zee Meter, Model 501 (3).

Particle Size Analysis

The size distributions of silicone oil droplets in emulsions were determined by using a laser diffraction instrument (Malvern particle sizer Model 2600) equipped with a 63-mm lens and a PS1 cell. The instrument was operated in the Easy Sizer mode. The results are presented as particle volume distributions (defined as the volume percent of particles as a function of their diameter), and also as particle size averages which are defined as

$$D(4,3) = \frac{\int_{D_1}^{D_2} D^4 n(D)dD}{\int_{D_1}^{D_2} D^3 n(D)dD} \quad [1]$$

$$D(3,2) = \frac{\int_{D_1}^{D_2} D^3 n(D)dD}{\int_{D_1}^{D_2} D^2 n(D)dD} \quad [2]$$

$$\text{Span} = \frac{D(90) - D(10)}{D(50)}, \quad [3]$$

where:

D_1, D_2 are the limits of integration of the diameter distribution function,

$n(D)$ is the diameter distribution function giving the number percentage of particles with diameter D,

$D(90)$, $D(50)$, and $D(10)$ are the diameters below which 90, 50, and 10% of the volume of the particles lies, respectively, and

Span and the ratio of $D(4,3)/D(3,2)$ characterize the width of the distribution

The measurements of size distributions were performed on very dilute emulsions prepared by adding 100–1000 μl aliquot of 0.25% emulsion solution (or a corresponding quantity of 5% emulsion) to 13.5 ml of deionized water in a measuring cell. The size distribution readings were taken as soon as the droplet became uniformly dispersed in the cell (approximately 1 min) and was found to be unchanged for about 10–15 min. Stirring of these dilute solutions for longer periods of time usually resulted in a significant change (broadening) in the droplet size distributions. Thus, it was assumed that the readings taken shortly after the dilution represent the size distribution of droplets in a concentrated emulsion dispersion.

RESULTS

Droplet Volume Distributions and Emulsion Stability

The volume distribution of droplets in emulsions, prepared according to the method described in the experimental section, was found to be related to the viscosity of the oil. This was demonstrated by analyzing the emulsions prepared from 50, 200, 1000, and 12500 cs oils at 0.5% total surfactant concentration (nonoxynol-4/nonoxynol-9, 1:1 by weight). As shown in Fig. 1 which presents the volume distribution curves obtained immediately after 30 min homomixing, the average particle size increases, and the distribution becomes broader for emulsions prepared from higher viscosity oils. The system containing the 12500 cs oil displays even a bimodal distribution. Broad distributions in emulsion systems obtained from high viscosity oils might be related to the energy of homomixing being insufficient to disperse the viscous fluids into micrometer-sized droplets. In agreement with the size analysis data, it was observed that emulsions based on the high viscosity fluids are less stable than those prepared from the lower viscosity silicone oils, and undergo relatively fast flocculation or coagulation.

Emulsion stability was monitored by measuring the droplet size distributions with the Malvern particle sizer immediately after preparation, and after 2 days, 12 days, and 3 months storage under ambient conditions. All of the investigated emulsion systems (based on nonionic surfactants—1:1 by weight nonoxynol-4/nonoxynol-9), with the exception of those based on high viscosity oils (i.e., over 1000 cs), were found to be stable for 2 weeks, as indicated by relatively narrow distributions.

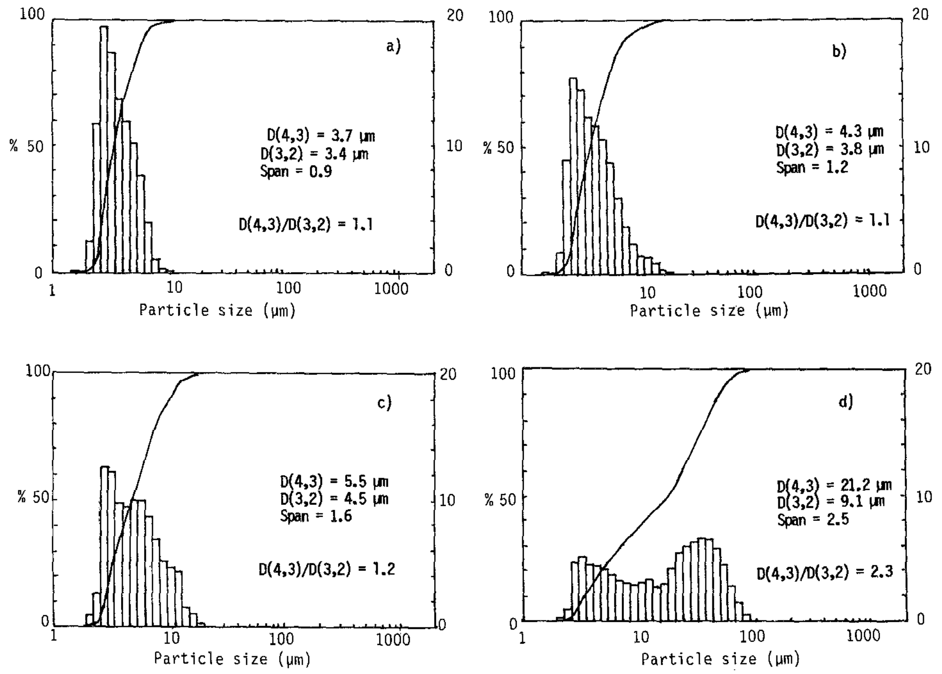

FIG. 1. The effect of oil viscosity on the volume distribution after homomixing for (a) 50 cs oil, (b) 200 cs oil, (c) 1000 cs oil, and (d) 12500 cs oil. All systems were prepared with 5% wt oil and 0.5% wt total surfactant concentration.

After 3 months storage, however, the distribution of particle sizes becomes broader, as a result of flocculation or coagulation. This effect appears to be dependent on the total amount of surfactant present, as the distributions of systems prepared at lower concentrations of surfactants (0.5% and less) undergo very little change with time, while the emulsions containing over 1.0% total surfactant display an increase in the average size of oil droplets and a broadening of the distribution. This effect is illustrated by the representative results shown in Figs. 2 and 3 for emulsions prepared with 50 cs oil at 0.5% and 2.0% total surfactant concentration. Although this result is difficult to interpret, it has also been observed, and discussed by other researchers (4). According to these authors, stability was found to depend both on the surfactant concentration and the length of the hydrocarbon chain. For the systems stabilized by long chain surfactants, electrokinetic potential was observed to decrease with surfactant concentration increase. This finding is confirmed by the data presented in Table I for the emulsion prepared from the 1000 cs oil.

Size Distribution of the Emulsion Droplets as a Function of Deposition Time

Emulsions prepared with the 50 cs oil at 0.25 and 1.0% total nonionic surfactant concentration (equal parts by weight nonoxynol-4/nonoxynol-9), and with the 1000 cs oil at 0.5% total surfactant concentration, were used in deposition experiments on cationically pretreated hair. The particle size distribution was measured immediately after dilution (from 5% oil concentration in the stock solutions to 0.25%) and after the exposure to hair for 5, 10, 20, and 40 min. The results, presented in Fig. 4 for the emulsion containing the 1000 cs oil, show that the droplet size decreased, and the distribution became narrower with increasing deposition time. Similar trends were

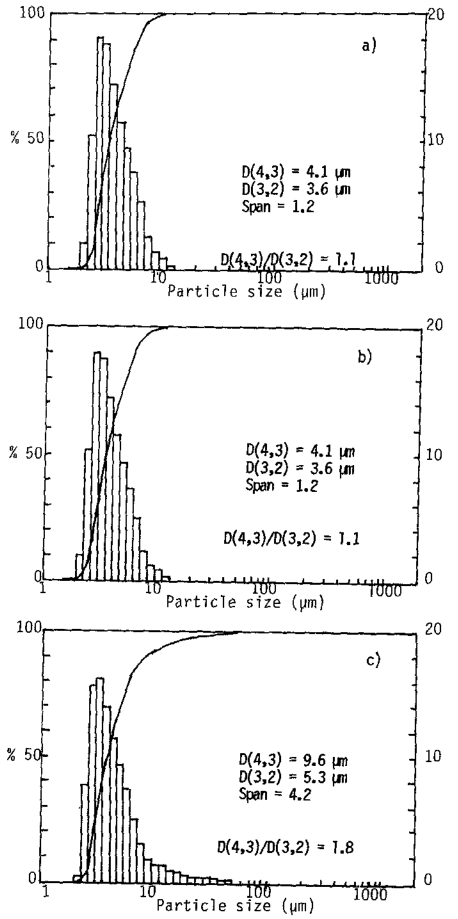

FIG. 2. Particle volume distributions in emulsions prepared with 50 cs oil as a function of storage time for (a) $t = 0$, (b) $t = 2$ days, and (c) $t = 3$ months. All systems contained 5% wt oil and 0.5% wt total surfactant concentration.

observed for the two other systems. It is, thus evident that the larger emulsion droplets deposit at a faster rate than do the smaller ones. Although the theory of deposition of monodisperse spherical particles onto cylinders, formulated by Spielman and Friedlander (5), predicts higher rates of delivery of smaller particles to the surface, these results suggest that the larger ones are more likely to become permanantly attached, possibly due to higher probability of collapse and spreading. Further analysis of this problem is presented later in the text of this paper.

Effect of Emulsifier Concentration

The influence of emulsifier concentration on deposition of emulsions onto cationically modified hair was examined using a nonionic surfactant system nonoxynol-4/nonoxynol-9 (1:1 by weight) with 50, 200, and 1000 cs oils. The size distributions of droplets in all investigated systems were similar to the ones shown in Figs. 1a–c, and all experiments were performed on freshly prepared emulsions in order to avoid the effect of emulsion coagulation or flocculation on deposition.

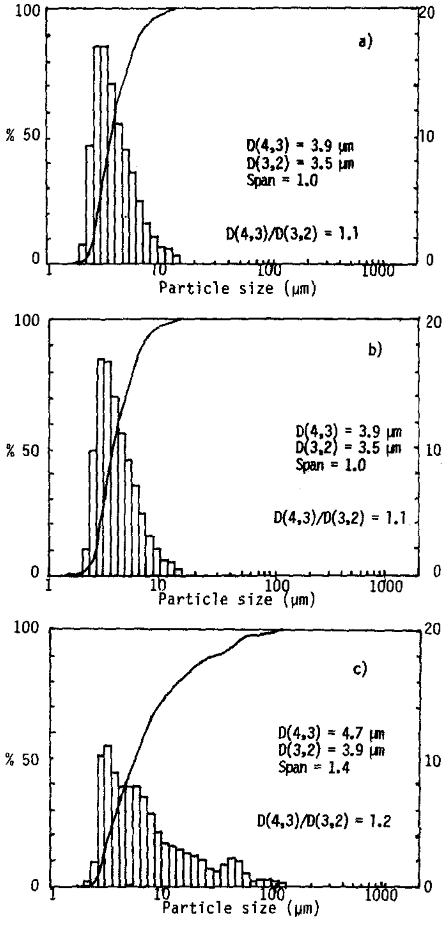

FIG. 3. Particle volume distributions in emulsions prepared with 50 cs oil as a function of storage time for (a) $t = 0$, (b) $t = 2$ days, and (c) $t = 3$ months. All systems contained 5% wt oil and 2.0% wt total surfactant concentration.

TABLE I

Zeta Potentials and Electrophoretic Mobilities as a Function of Surfactant Concentration for Emulsions Based on 50 and 1000 cs Oils

Surfactant concentration (wt %)	0.25		0.5		1.0		2.0		3.0		4.0	
	50 cs	1000 cs	50 cs	1000 cs	50 cs	1000 cs	50 cs	1000 cs	50 cs	1000 cs	50 cs	1000 cs
Zeta potential (mV)	−21.4	−26.9	−21.5	−27.3	−21.0	−25.7	−20.5	−22.1	−21.7	−22.1	−21.4	−22.1
Mobility (10^{-8} $m^2 s^{-1} V^{-1}$)	−1.52	−1.91	−1.52	−1.94	−1.49	−1.82	−1.45	−1.57	−1.54	−1.57	−1.54	−1.57

Note. Emulsion solutions prepared at 5% wt oil concentration and specified nonionic surfactant concentrations were diluted to 0.25% wt oil immediately prior to measurements.

Zeta potentials were measured for emulsions prepared from 50 and 1000 cs oils at pH 6.5. These values along with electrophoretic mobilities are presented in Table I. Although both the oil and the emulsifying system employed were nonionic, the emulsion droplets display a negative zeta potential ranging from −20.5 to −26.9 mV. Previous investigations of a similar neutral system (DC 347, (3)) showed an isoelectric point between pH 6 and 7, and suggested that the zeta potential variation with pH is caused by adsorption of H^+ and OH^- ions from solution. For emulsions prepared from 50 cs oil, there is virtually no variation of zeta potential as a function of surfactant concentration. On the other hand, the measurements involving emulsions prepared from the 1000 cs oil exhibited a decrease in the absolute value of zeta potential with an increase in the surfactant concentration. The observed decrease is small, however, it does exceed the limits of experimental error (±1.5 mV).

The kinetic curves of deposition on cationically modified fibers, for emulsions prepared at various emulsifier concentrations, are presented in Figs. 5 a–c. The measurements were obtained for emulsions prepared from 50, 200, and 1000 cs oils. The data for 50 and 1000 cs systems correspond to 0.25–4.0% emulsifier concentration range, while those for 200 cs emulsions were obtained over the range 1.0–4.0%. Generally, the shape of the kinetic curves suggests high initial rates of oil heterocoagulation followed by a leveling off in the rate of uptake. It can be seen that the deposition rates as well as the extent of deposition are higher for the systems containing lower amounts of surfactants. It should also be noted that experiments involving lower viscosity oils yield lower rates of deposition. Further discussion of this phenomenon is presented below.

Effect of Oil Viscosity

The effect of oil viscosity was examined using the emulsions prepared at 0.5 and 4% surfactant concentration (nonoxynol-4:nonoxynol-9 (1:1)). As was previously discussed, the

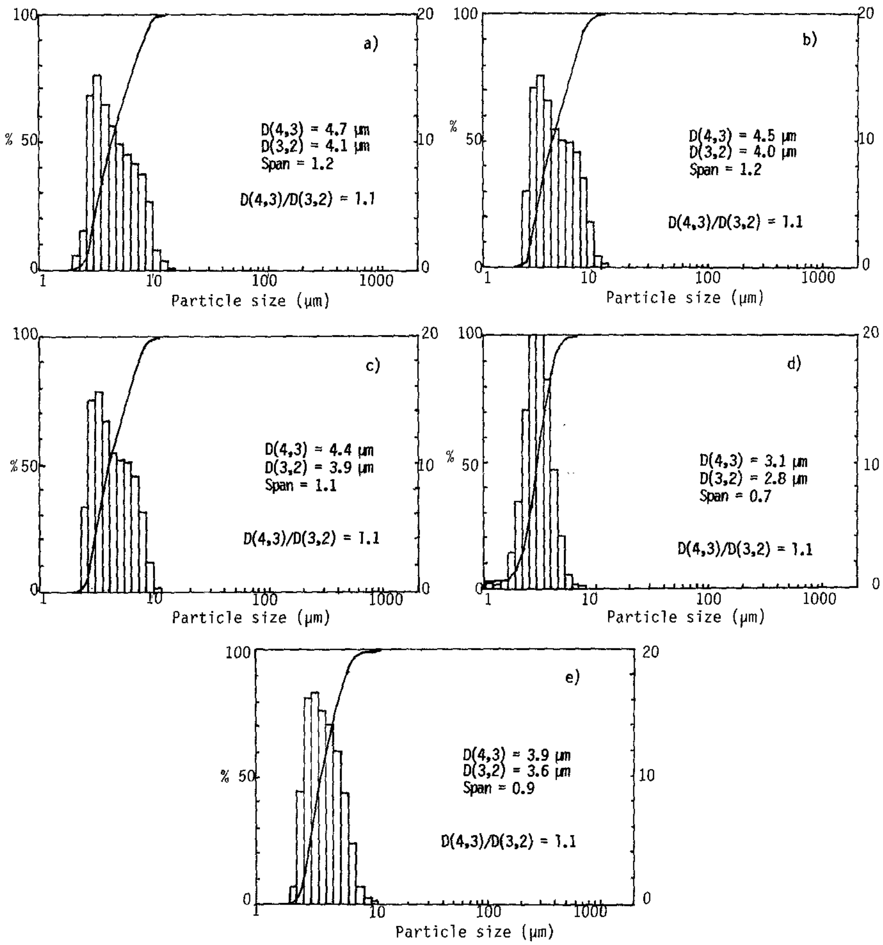

FIG. 4. The effect of deposition on the volume distribution of emulsion droplets in the supernatant for (a) $t = 0$, (b) $t = 5$ min, (c) $t = 10$ min, (d) $t = 20$ min, (e) $t = 40$ min. The emulsion was prepared with 1000 cs oil at 5% by weight, and 0.5% wt total surfactant concentration.

emulsions derived from high viscosity oils possess broader volume distributions than those obtained from less viscous fluids (Fig. 1). The zeta potentials and electrophoretic mobilities of the emulsions prepared from different viscosity oils are given in Table II. While the zeta potentials for the emulsions prepared from the four lowest viscosity oils are unchanged within the experimental limits, the systems based on high viscosity oils (5000 and 12500 cs) are characterized by slightly lower absolute values of zeta potential.

Kinetic deposition experiments were performed on both untreated and cationically modified hair at 4% total surfactant concentration (Figs. 6a and b), and on cationically modified hair at 0.5% surfactant (Fig. 6c, data taken from Figs. 5a and c). In experiments involving unmodified hair, there appears to be an initial lag time in the deposition process, followed by a rise in the rate of oil deposition and then a leveling off in the curves over extended time periods as can be seen in Fig. 6a. Generally, the rates and extents of deposition on unmodified hair are low due to unfavorable electrostatic interactions. For PMAPTAC pretreated hair, the rate of deposition is initially high, tapering off with time. Similar

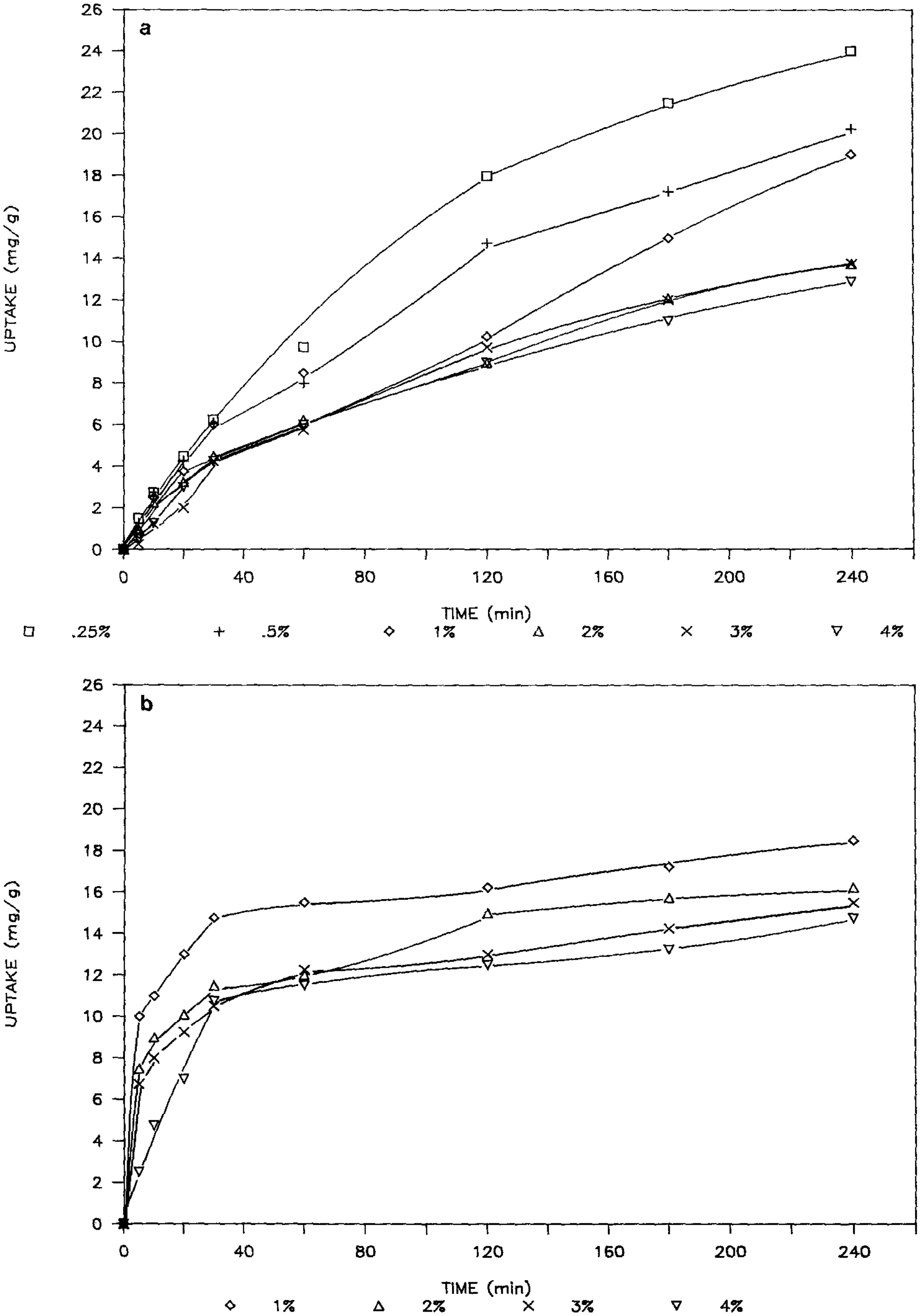

FIG. 5. The kinetic curves of silicone deposition on cationically modified hair for emulsions prepared at various surfactant concentrations for (a) 50 cs oil, (b) 200 cs oil, and (c) 1000 cs oil.

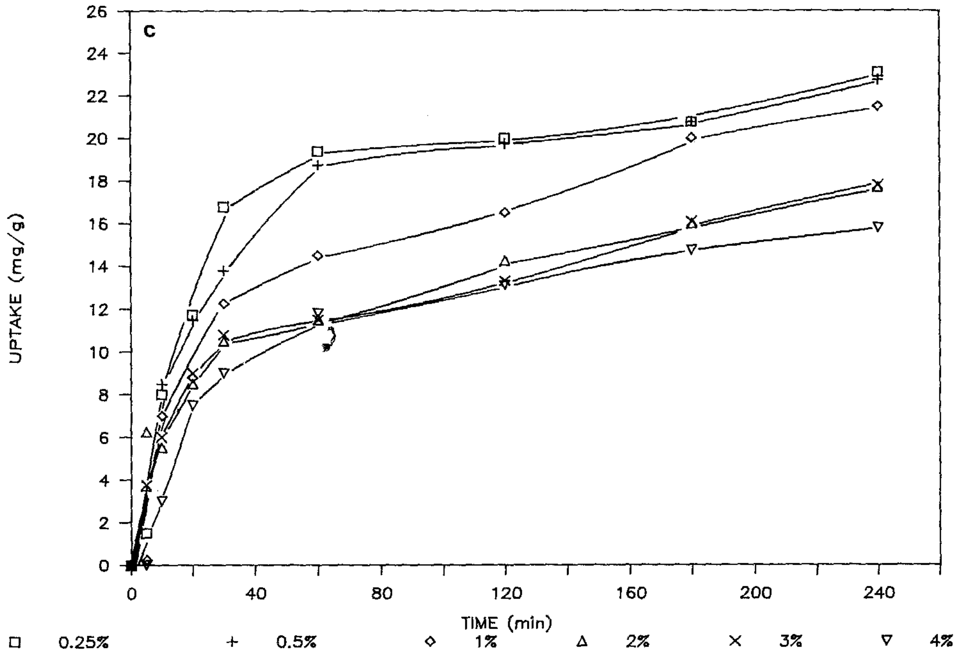

FIG. 5—*Continued*

shapes of the kinetic deposition curves were observed for the systems of varying surfactant concentration which were also studied using PMAPTAC pretreated hair. There is a distinct increase in the rate and extent of oil precipitation from the emulsions containing higher viscosity oils onto cationically modified fibers. Although not to the same extent, this increase was noted in the experiments on untreated hair as well.

Effect of Ionic Surfactants

Experiments designed to investigate the influence of ionic surfactants on the deposition process employed emulsions prepared using the 1000 cs oil. The ionic character of the emulsions was altered by replacing 20% of the total 0.5% emulsifier concentration with either CTAB or SODS. The volume distributions of the anionic and cationic systems immediately after preparation, and after 3 months storage at ambient conditions, are presented in Figs. 7a–d. As was expected, the initial distribution is similar to that obtained for the 1000 cs oil emulsified by a nonionic surfactant system; however, it should be noted that upon aging there is a marked decrease in the average droplet size.

Table III compares zeta potentials and electrophoretic mobilities of the emulsions prepared using ionic and nonionic surfactant systems. The zeta potential of the system emul-

TABLE II

Zeta Potentials and Electrophoretic Mobilities as a Function of Oil Viscosity for Emulsions Prepared at 5% wt Oil and 4% wt Total Nonionic Surfactant Concentration

Oil viscosity (cs)	50	100	200	1,000	5,000	12,500
Zeta potential (mV)	−19.7	−18.7	−19.0	−17.5	−13.0	−13.8
Mobility (10^{-8} m^2 s^{-1} V^{-1})	−1.40	−1.33	−1.35	−1.24	−0.924	−0.976

Note. Emulsion solutions were diluted to 0.25% wt oil immediately prior to measurements.

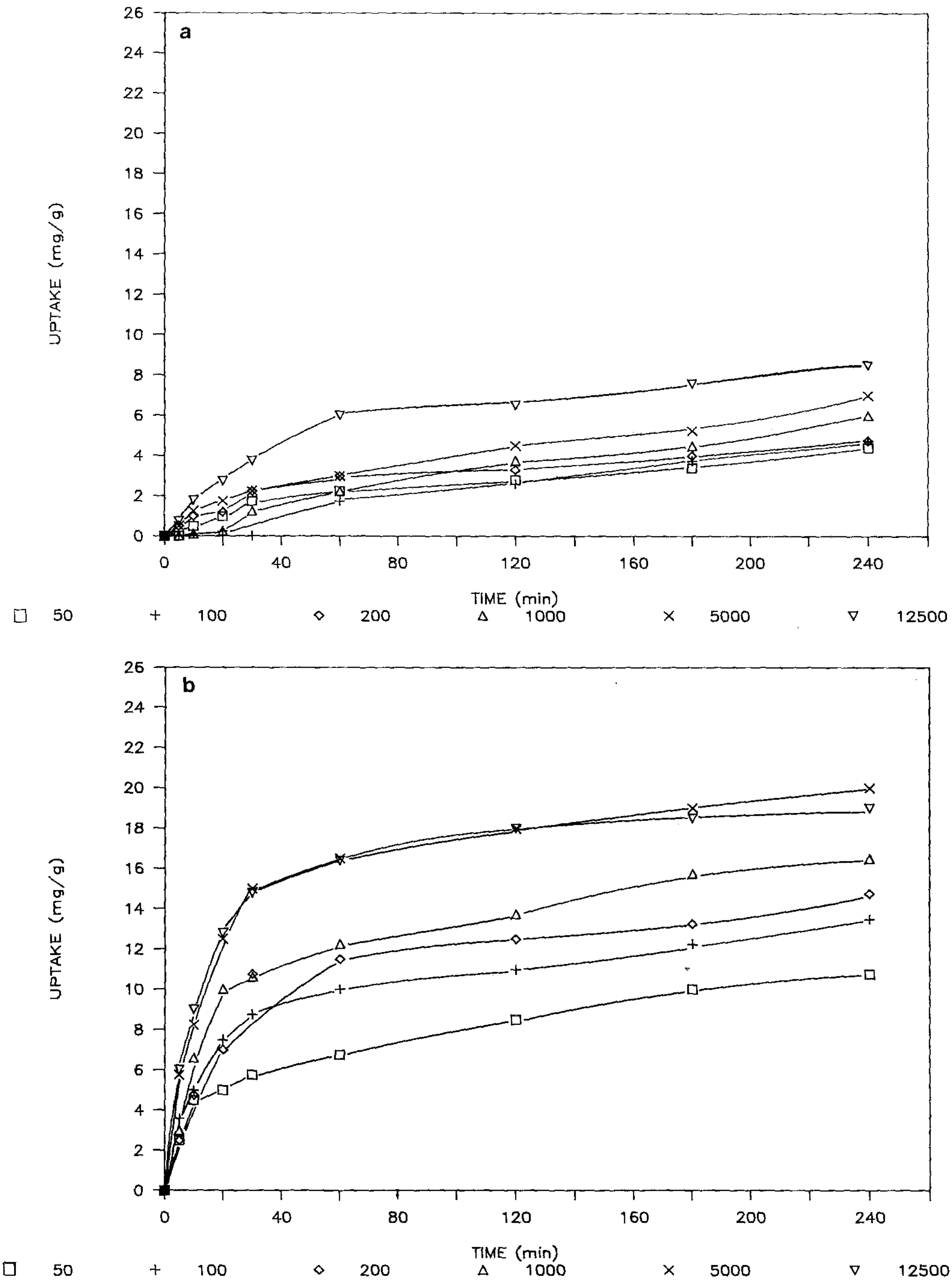

FIG. 6. The kinetic curves of silicone deposition for emulsions prepared with oils of various viscosities. Deposition on (a) untreated hair, emulsions prepared at 4% wt total surfactant concentration, (b) cationically modified hair, emulsions prepared at 4% wt total surfactant concentration, and (c) cationically modified hair, emulsions prepared at 0.5% wt total surfactant concentration.

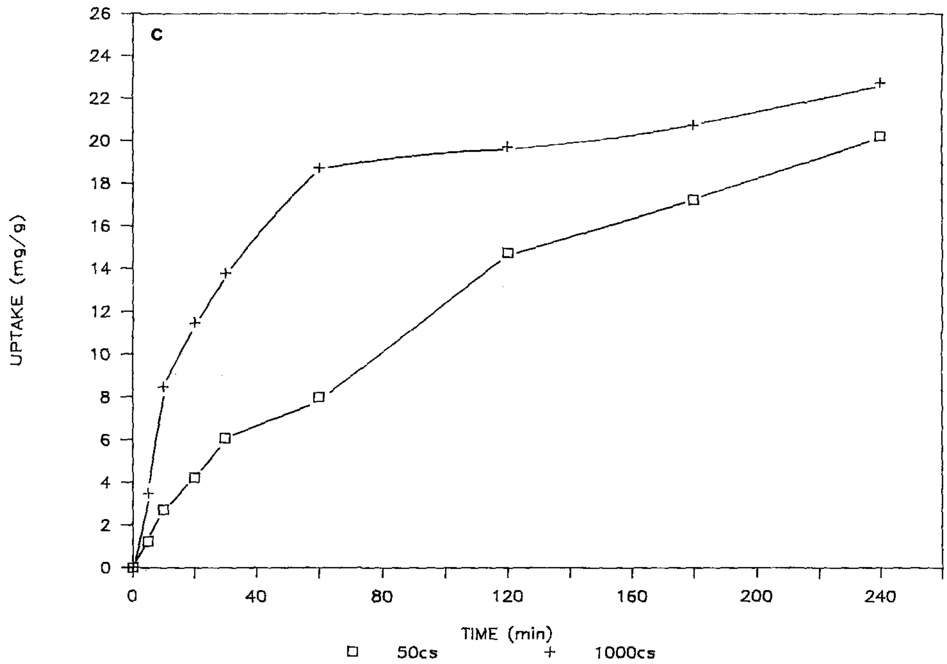

FIG. 6—*Continued*

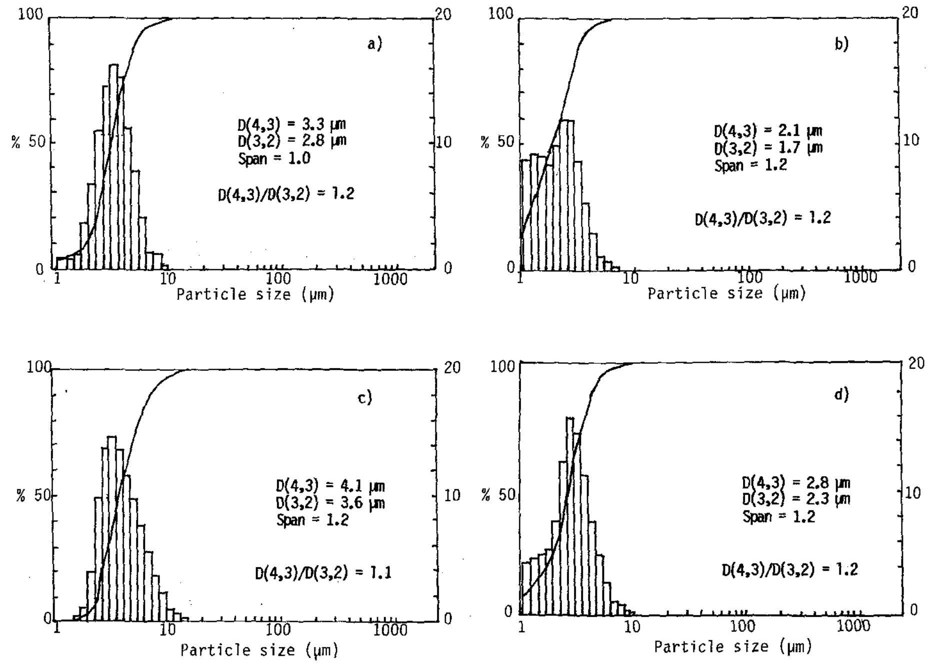

FIG. 7. Particle volume distributions in emulsions prepared with 5% wt 1000 cs oil, at 0.5% total surfactant concentration for (a, b) anionic emulsifying system, (c, d) cationic emulsifying system immediately after homomixing, and after 3 months storage at ambient conditions.

TABLE III

Zeta Potentials and Electrophoretic Mobilities for Emulsions Prepared with Anionic, Nonionic, and Cationic Emulsifier Systems

Surfactant type	Anionic	Nonionic	Cationic
Zeta potential (mV)	−39.4	−26.8	+7.5
Mobility (10^{-8} m^2 s^{-1} V^{-1})	−2.79	−1.90	+0.53

Note. Emulsion solutions were prepared at 5% wt oil and 0.5% total surfactant concentration, and were diluted to 0.25% wt oil immediately prior to measurements.

sified by SODS/nonoxynol-4/nonoxynol-9 was more negative than that prepared with the nonoxynols only. The zeta potential of the CTAB-containing system was found to be positive. These data demonstrate that the ionic surfactants are capable of altering the electrostatic characteristics of the oil droplets. The changes in the electrostatic nature of emulsions prepared with ionic and nonionic surfactant systems are reflected in the deposition process. The kinetic curves of oil uptake on untreated and PMAPTAC modified hair are shown in Figs. 8a and b. Qualitatively, the variations in rates and extents of deposition follow the changes of zeta potential of both hair and oil droplet surfaces. The emulsion containing cationic surfactant readily precipitates on the untreated hair surface which possesses a negative zeta potential at pH 7. On cationically modified hair, oil uptake of this system was much less. The nonionic and anionic emulsions, on the other hand, both deposited at higher rates and to a greater extent on cationically modified surfaces which is consistent with their electronegative nature. It should be noted, however, that the anionic emulsion, characterized by a more negative zeta potential than the neutral and cationic systems, precipitates at a relatively low rate on PMAPTAC pretreated hair.

DISCUSSION

In order to analyze the rates and extents of coagulation of oils from oil-in-water emulsions on solid substrates the following factors have to be taken under consideration:

electrostatic characteristics of both the substrate and oil droplets provided by the zeta potentials measurements;

the physical characteristics of the dispersed phase in the emulsions, including droplet size and size distribution as well as oil viscosity; and

composition of the aqueous phase.

As pointed out previously (3), the coagulation of silicone emulsions on keratin fibers appears to be primarily determined by electrostatic interactions, at least in the early stages of the process. The ionic nature of the fiber surface can be modified by the adsorption of cationic polymers which reverse the negative zeta potential of untreated hair to positive. In the neutral pH range, hair samples used in this investigation were characterized by a zeta potential of about −12 mV which, after the adsorption of PMAPTAC, was changed to +20 mV (for the measurements performed at pH 6 and 10^{-4} M KCl). The emulsions comprised of neutral oils and nonionic emulsifiers possess a zeta potential in the range from −13.8 to −27.3 mV depending on the surfactant concentration and oil viscosity (Tables I and II). In agreement with predictions provided by theoretically calculated stability ratios (3), these systems minimally deposit onto untreated hair fibers at a very low rate (Fig. 6a). On the other hand, the neutral emulsions readily precipitate on cationically modified hair surfaces.

The electrostatic characteristics of the emulsion droplets can be changed by incorporation of ionogenic groups into the oil structure or by introduction of ionic surfactants into the emulsifying system. Previously, it has been shown that oils with incorporated amino or carboxyl groups, and emulsified with nonionic surfactant systems, possess positive or negative zeta potentials at neutral pH, respectively (3). Consequently, aminofunctional emulsions exhibited strong interactions with untreated hair, while the carboxyfunctional

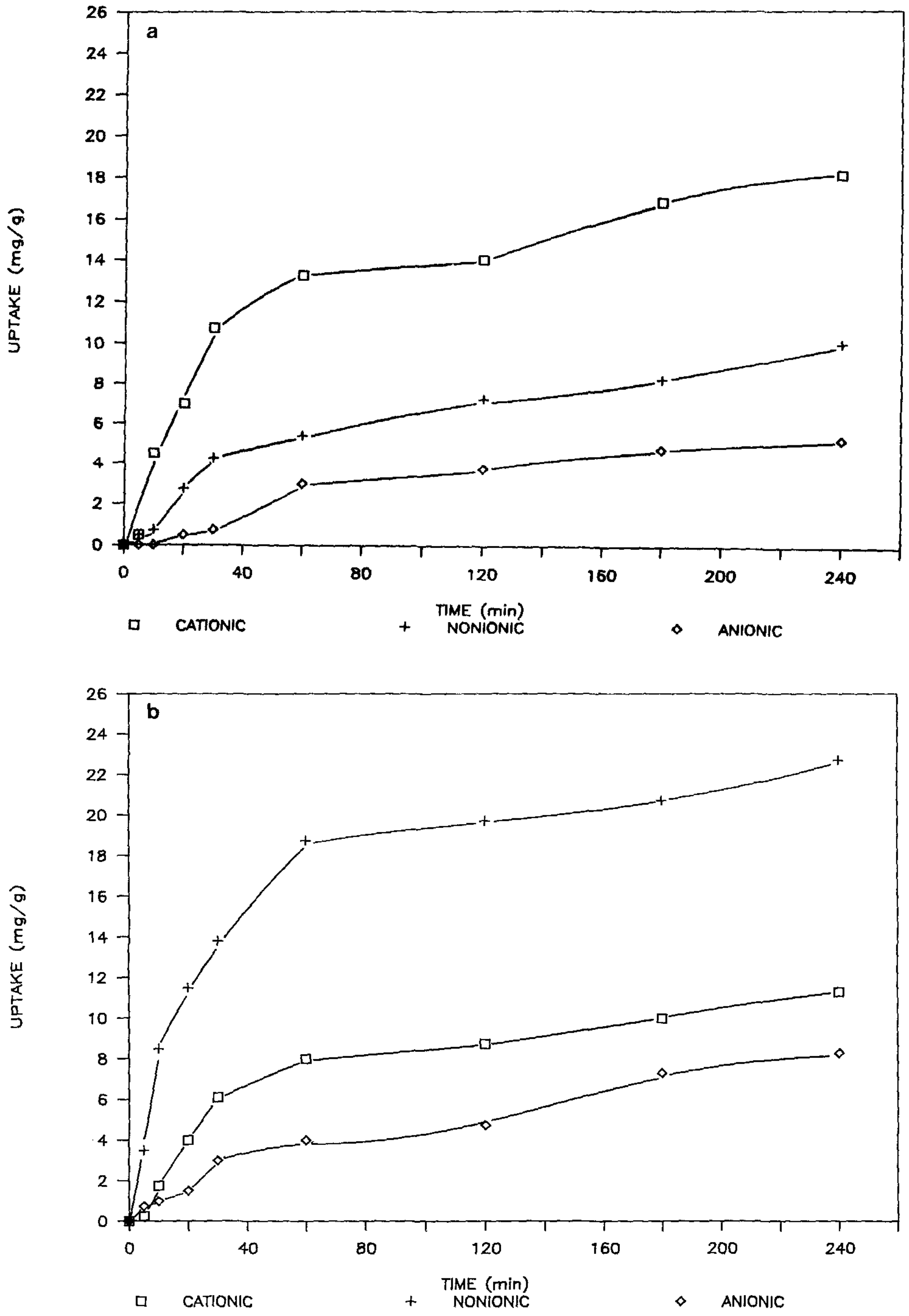

FIG. 8. The kinetic curves of silicone deposition for emulsions prepared with anionic, nonionic, and cationic emulsifying systems on (a) untreated and (b) cationically modified hair.

systems readily deposited onto cationically modified fibers. The data presented in this report demonstrate that ionic surfactants can also affect the zeta potentials of emulsions prepared with neutral oils, and produce corresponding changes in rates and extents of heterocoagulation (Table III and Fig. 8). Another factor to consider in these systems is the possibility of excess surfactant in the continuous phase of the emulsion, not bound at the oil–water interface. This free detergent may hinder the deposition process by itself adsorbing to the available sites on the fiber surface, thus creating electrostatically unfavorable deposition conditions. This might explain the relatively low adsorption rates for the emulsions prepared with anionic detergent on cationically pretreated hair.

The average droplet size and distribution can affect the process of deposition by altering the interaction potential and the diffusion coefficients, i.e., the rate of delivery of particles to the surface. The effect of the average droplet size on the interaction potential, calculated according to the HHF theory, is illustrated in Fig. 9. The calculations were performed by the summation of the electrostatic potential energy and the van der Waals energy for the case of a sphere–plate interaction. For oppositely charged surfaces, such as cationically modified hair and nonionic or anionic emulsion systems, there is no energy barrier for deposition. The increase in droplet size considerably increases the attractive potential, although, under these conditions, the deposition might be diffusion controlled. The theoretical prediction of increased attractive interactions for larger droplets is consistent with the observed in-

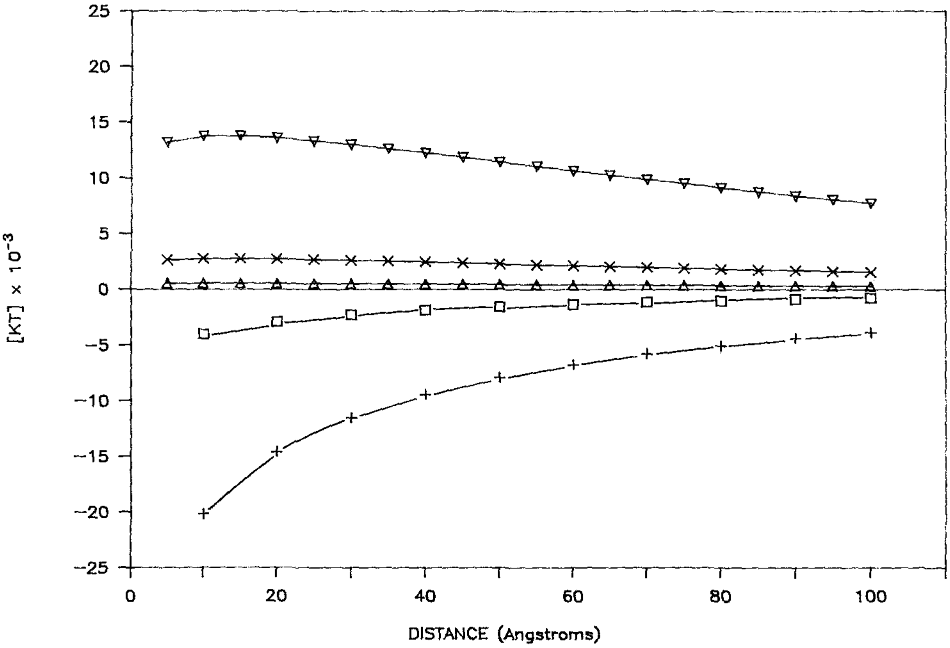

FIG. 9. Total interaction energy between emulsion droplets and untreated or cationically modified hair as a function of distance from the fiber surface. The calculations were performed according to the equations presented in Ref. (3). The following parameters were employed: Hamaker constant $A = 4.5 \times 10^{-16}$ (erg), zeta potential of untreated hair = −12 mV, zeta potential of cationically modified hair = +20 mV, zeta potential of emulsion droplet = −20 mV, ionic strength = 10^{-3} M. Interaction between cationically modified hair and emulsion droplets were calculated for droplet sizes of $d = 2 \times 10^{-4}$ cm (□), and $d = 10^{-3}$ cm (+). Interaction between untreated hair and emulsion droplets were calculated for droplet sizes of 2×10^{-4} cm (△), 10^{-3} cm (×), and 5×10^{-3} cm (▽).

crease in deposition rates of emulsions obtained from higher viscosity oils, characterized by larger particles, as seen in Figs. 6b and 6c. For substrate and droplets possessing a zeta potential of the same sign, e.g., untreated hair and nonionic and anionic emulsions (Figs. 6a and 8a), the height of the potential barrier for deposition rises with an increase in the average droplet diameter. It was also pointed out by Verwey and Overbeek (10) that a combination of repulsive electrostatic potential with attractive van der Waals forces would always produce a secondary potential minimum at large separations (not shown in Fig. 9). The depth of this minimum increases with increasing particle size. The larger particles might, thus, be prevented from depositing into the primary minimum, but are likely to be collected in the secondary minimum. This type of deposition is reversible since a layer of water separates the fiber surface from the particles thus prohibiting collapse, and subsequent spreading, of the oil droplets. Since, on untreated hair, the deposition rates and extents were found to be higher for emulsions comprising larger particles, secondary minimum deposition might be a possible explanation of this effect. This argument is, however, weakened by the fact that the silicone–keratin system is characterized by a relatively low value of the Hamaker constant which could produce only a shallow secondary minimum.

According to the theory of deposition of monodisperse spherical particles onto cylinders, at a given flow velocity, the rate of deposition (I) onto a unit length of a cylinder, in the absence of an energy barrier, i.e., under electrostatically favorable conditions, is controlled by the diffusion coefficient as shown in Eq. [4] (5)

$$I = 4.591(D^2 a A_c u)^{1/3} c(0) \qquad [4]$$

$$D = \frac{kT}{6\pi\eta a} \qquad [5]$$

and A_c is a flow parameter for an isolated cylinder defined by

$$A_c = 0.5[2 - \ln(2Ru/\nu)]^{-1} \qquad [6]$$

where $c(0)$ is the particle number concentration, u is the flow velocity far from the cylinder, D is the diffusion coefficient, a is the droplet diameter, ν is the kinematic viscosity, and η is the viscosity.

Equation [4] predicts that the rate of deposition is inversely proportional to the cube root of the particle diameter. For example, the theoretical rate of deposition of 4 and 20-μm droplets on the hair surface was calculated to be 0.659 and 0.384 mg/(g(fiber)min), respectively (6). Experimentally, however, the initial rates of deposition on cationically modified hair were higher for larger droplets, corresponding to emulsions obtained from high viscosity oils, and were found to vary from 0.44 to 1.1 mg/(g(fiber)min) for 50 and 12500 cs emulsions, respectively (Fig. 6b). Similarly, for untreated hair, the initial rates of deposition were also faster for higher viscosity oils, and varied from 0.05 to 0.14 mg/(g(fiber)min) for 50 and 12500 cs emulsions, respectively (Fig. 6a). Based on these results, it is obvious that in spite of good numerical agreement between the calculated and observed rates of deposition, there are other operational factors which influence the process of deposition.

It has been previously suggested that the phenomenon of spreading and coalescence of oil droplets may play an important role in the process of deposition (3). This is because the interaction of droplets remaining in solution is probably different with the untreated fiber surface than with the surface covered by a layer of oil. Although the increasing surface coverage with oil creates a repulsive potential for further deposition, the experimental data indicate that the process of oil precipitation continues and in some cases, is even enhanced by a layer of oil. For example, the deposition curves of negatively charged emulsion droplets on untreated hair show an induction period which is followed by a gradual increase in the rate of precipitation (Fig. 8a). The shape of the kinetic curves suggests that the heterocoagulation takes place on the oil-modified fraction of the surface. Both the size and the viscosity of deposited oil droplets influence the rate of spreading and consequently the extent of surface coverage. Quantitatively, the spreading of liquids on solid surfaces was recently discussed by Dodge (7), and is given by the equation which demonstrates the dependence of spreading rate on the droplet volume and viscosity

$$d = K[(\sigma V_0^2/\mu)t + (d_i/K)^7]^{1/7}, \quad [7]$$

where d is the diameter of the contact area, σ is liquid surface tension, V_0 is the initial volume, μ is liquid viscosity, K is a nondimensional parameter, and t is time.

From the data given in the paper, it can be calculated that for a silicone oil droplet of 60 cs viscosity the surface coverage would increase approximately 6 times in 10 min, but to achieve the same increase in coverage by a 6000 cs oil would require 1000 min. This demonstrates that the rate of spreading of the oils employed in this work (50–12500 cs) occurs within the same time scale as the deposition experiments (0–1440 min). However, it should be noted that the rate of increase in surface coverage is proportional to the term

$$K(\sigma V_0^2/\mu)^{1/7}, \quad [8]$$

which implies a very strong dependence on the initial volume. Since the emulsions prepared from 12500 cs oil had an average particle size of about 21 μm as opposed to 4μm in emulsions based on 50 cs oil, the rate of surface modification by the high viscosity oil should be approximately 4 times as fast as that by the low viscosity oil. This could be a contributing factor in the observed high rates and uptakes of emulsions prepared from higher viscosity oils.

Finally, the composition of the continuous phase, especially as related to surfactant concentration, has to be taken under consideration. The surfactant can absorb at both the fiber–water and oil–water interfaces and thus modify the interaction between undeposited droplets and oil coated, as well as virgin, fiber surfaces. In the case of ionic surfactants the change in interaction may be primarily due to electrostatic repulsion. This might explain the deposition patterns observed in the experiments involving CTAB and SODS as emulsifying agents, and amounts deposited lower than expected based on the comparison of zeta potentials of hair and emulsions. A similar trend was observed in a codeposition experiment involving an aminofunctional silicone emulsion combined with a cationic polymer. It was found that the adsorption of polymer considerably reduced deposition of silicone from this system (8). For nonionic surfactants, it was shown that an increase in surfactant concentration did not significantly alter either the particle size or the zeta potential of the emulsions (Table I). It is also not expected to affect the value of the zeta potential of the fiber surface. Therefore, the observed reduction in rates and amounts deposited for the systems containing a higher concentration of surfactant (Fig. 5) can probably be ascribed to steric hinderance effects caused by the surfactant adsorption on the fiber. A similar explanation was also proposed in interpreting the results of deposition experiments involving polymer latices on a variety of synthetic or natural fibers in the presence of surfactants and nonionic polymers (9, 10).

CONCLUSIONS

It has been shown that many factors contribute to the process of deposition of silicone emulsions based on nonionic silicone oils. The ionic nature of the emulsifying system is the most important because it can influence the sign and value of the zeta potential of oil droplets. Since van der Waals forces play a relatively unimportant role in the deposition process (very low value of the Hamaker constant for the silicone–keratin interface (3)), the electrostatic potential determines the interaction between the oil droplets and the fiber surface. The concentration of nonionic emulsifier can also influence the rates and extents of deposition probably resulting from steric hindrance effects. The influence of oil viscosity and the droplet size were difficult to separate because emulsions based on the more viscous oils were characterized by larger average droplet size and broader size distributions. The theoretically evaluated delivery rates of particles to the surface, based on hydrodynamic considerations including diffusion coefficients, are relatively insensitive to the droplet size. Therefore, the observed higher rates and extents of deposition for systems containing larger droplets (and simultaneously more viscous oils) could result from an increased attractive interaction and the ability to cover a larger fiber surface area by deposition and spreading.

REFERENCES

1. Carroll, B. J., *Text. Res. J.* **58,** 495 (1988).
2. Disapio, A., and Fridd, P., *Int. J. Cosmet. Sci.* **10(2),** 75 (1988).
3. Jachowicz, J., and Berthiaume, M. D., *J. Colloid Interface Sci.* **133(1),** 118 (1989).
4. Carroll, B. J., *in* "Surface and Colloid Science" (E. Matijevic Ed.), Vol. 9, Chap. 1, p. 29. Wiley-Interscience, New York, 1976, and references cited therein.
5. Spielman, L. A., and Friedlander, S. K., *J. Colloid Interface Sci.* **46(1),** 22 (1974).
6. The following parameters were used in the calculations of deposition rates: $R = 3.5 \times 10^{-3}$ cm, $u = 0.5$ cm/s, $\nu = 0.8930 \times 10^{-2}$ cm^2/s, $\eta = 0.8904 \times 10^{-2}$ g/(cm s), $c(0) = 0.0025$ g/cm^3, and specific surface area of hair = 900 cm^2/g.
7. Dodge, F. T. *J. Colloid Interface Sci.* **121(1),** 154 (1988).
8. Unpublished results.
9. Kawasaki, K., Tamai, H., and Suzawa, T., *Text Res. J.* **56,** 598 (1986).
10. Kitchener, J. A., *J. Soc. Cosmet. Chem.* **24,** 709 (1973).