Electrophoretic Properties in Aqueous Detergent Systems

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Abstract

Electrophoretic mobilities and zeta potentials were developed for triolein, Nujol, and glass particles in aqueous detergent solutions. Zeta potentials in deionized water were: −79, −69, and −62 mv, respectively, for triolein, Nujol, and glass. Electrolyte builders and anionic surfactants markedly increase triolein and Nujol particle mobilities and negative zeta potentials; this effect probably contributes to their detersive action. Nonionic surfactants lower mobility of triolein and glass, and thus show slight cationic character. Significant inflection points are found for nonionic detergents near cmc. A cationic detergent produced high positive charge and zeta potentials with triolein and glass. Data for surfactant-builder combinations show mobilities are primarily determined by the electrolyte. It was concluded that electrokinetic effects are important for dispersion and emulsification, but are not necessary and sufficient conditions for removing oily soil from glass.

Introduction

Electrokinetic forces have been considered important by many workers in the detergent field (1). Some limited correlations were evident between zeta potential and the detergent properties of suspending action, critical micelle concentration (cmc) and soil removal. However, the need for more definitive data was stressed.

When fine hydrophobic particles such as carbon, graphite, and oil are suspended in aqueous solutions, adsorption of ions takes place, imparting a surface charge to the particle. These charges are referred to, in a relative sense, as being fixed to the surface of the particle. Attracted to this charged surface will be ions of opposite sign, which are held more loosely than the adsorbed ions, some of which move about within the sphere of influence of the charged surface due to irregular Brownian motion.

This condition of a fixed surface charge surrounded by more loosely held counter ions is referred to as an electrical double layer. With emulsions stabilized by the addition of surfactants like soap, the adsorption of the soap anion gives rise to the fixed negative portion of the double layer with the attracted sodium gegenion representing the mobile part of the electrical double layer.

The significance of electrical forces, double layers, and zeta potential in detergent systems was given in a comprehensive review by Harris (1). Zeta potential was defined as the difference in charge between the immovable liquid layer attached to the surface of a solid phase and the movable part of the diffuse layer in the body of the liquid.

When dispersions or emulsions having electrical double layers are placed in an electrical field, the particles can be observed to migrate toward one of the electrodes. If the fixed portion of the double layer is negative at the slipping plane, migration to the positive anode is observed. Surface charge and zeta potentials of colloidal particles are not easily measurable, but are reflected in the experimentally derivable electrophoretic mobilities:

$$V = \frac{D\zeta E}{\pi\eta} \times f \qquad \text{Equation 1 (2,3)}$$

where V = particle velocity
ζ = zeta potential at the shear plane of the diffuse double layer
D = dielectric constant of solvent phase
E = field strength
η = viscosity of solvent phase
f = the Henry factor, dependent on N a, where a = particle radius and N is the reciprocal thickness of the double layer

$$N = \frac{1}{\sqrt{\frac{8\pi e^2 \Sigma n z^2}{D k T}}}$$

It follows that the surface charge density, σ, is given by

$$\sigma = \frac{D\zeta}{\pi N} \times f$$

and σN, the electric moment per cm² of surface is

$$\sigma N = \frac{D\zeta}{\pi} \times f$$

In this study, electrophoretic mobility and zeta potential data were developed for Nujol, triolein, and glass particles in detergent solutions. Various surfactant types, electrolyte builders, and surfactant builder combinations were examined. Results are discussed in relation to ability of the agents to remove fatty and oily soils from the glass substrate. The particle size measured was constant at 3.2 μ diam. The factor f was found to be essentially constant at 0.25 for all ionic solute concentrations tested. For water and solutions of nonionic surfactants, the f value was 0.18. Considering the relative constancy of f, mobility, zeta potential, and the electric moment (a measure of charge) roughly are directly proportional. Values reported in the work are mobilities and zeta potentials. No attempt was made to calculate the other quantities as such calculations would not alter the conclusions drawn.

Experimental

Materials

Water—deionized to 1 million ohms resistance.

Dispersed Phases
- Nujol
- Triolein—technical, Matheson, Coleman & Bell, stored under refrigeration.

Powdered Glass: Harshaw microscope slides, ball-milled with borundum balls to obtain particles in the 3.2 μ range, then washed with acetone and water, and dried before use. Particles irregular, specific surface: 1.0 m²/g.

Electrolytes and Detergents
- Sodium hydroxide, reagent grade.
- Sodium tripolyphosphate (STP), Monosanto, Form I
- Sodium dodecylbenzenesulfonate (NaDDBS), Monsanto Santomerse No. 3 Paste solids, cmc = 0.12% concn at 25C.

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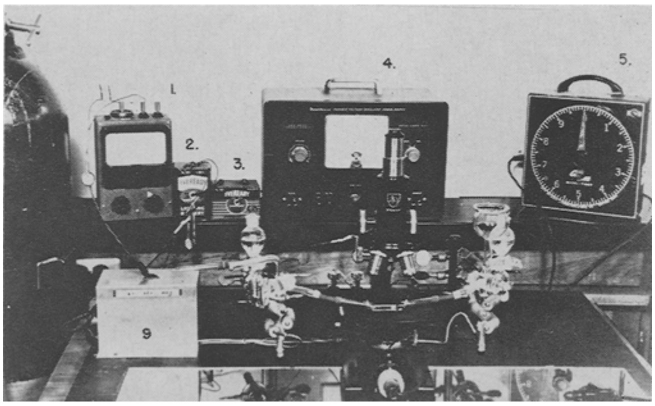


FIG. 1. Electrophoresis assembly.

1. Electrometer
2. 6 volt, electrometer calibration
3. 25 volts potential source
4. 0–500 volt source (variable)
5. Timer
6. Cataphoresis cell
7. Microscope
8. Hand switch—timer
9. Multiple contact switch

Sodium oleate, Fisher, purified, cmc = 0.029% concn
Tridecanol (TDA)—10 EO, cmc = 0.009% concn
Decanol (DA)—10 EO, cmc = 0.16% concn
Decanol (DA)—15 EO, cmc = 0.28% concn
Cetyltrimethylammonium bromide (CTAB), Eastman Organic Chemicals, cmc = 0.033% concn

Apparatus

Kady Mill
Eberbach Mechanical Shaker
Bowser Constant Temp Cabinet at 25 ± 0.5C
Electrophoretic Mobility Apparatus (A. H. Thomas Co.) as described in Figure 1.

Procedures

Stock Emulsions and Dispersion Preparation

Nujol and Triolein. 800 ml deionized water (preheated to ca. 95C) was milled in the Kady Mill 2 min, then 2 ml oil was added and mixing continued 10 min. The resulting emulsions stood overnight and were then siphoned down to 100 ml. The siphoned emulsions were used as stocks in preparing test dispersions.

Powdered Glass. 2 g glass powder was mixed with 800 ml deionized water in a quart bottle, using the mechanical shaker at high speed for ca. 2 hr to achieve dispersion.

Test Dispersions. 50 ml portions of shaken dispersion stock were placed in 250 ml vol flasks. Aliquots of concd detergent of salt solutions were added in amounts to yield the desired concn on diluting to volume. The resulting test dispersions were stored overnight at 25C and shaken again before measurement.

Electrophoretic Mobilities. In general, measurement of the electrophoretic mobility of a suspended phase was conducted as follows: a flat rectangular cell was filled with the dispersion containing the suspended matter under study and a potential was applied to the solution using a voltage source. The potential was applied through liquid/liquid junctions to avoid polarization. A microscope, containing a calibrated scale in the eyepiece, was adjusted to observe the particles at the proper depth in the cell corresponding to the stationary liquid level. The particles were timed, using a stopwatch, as they were observed to move in reference to the scale in the eyepiece. Several determinations were made and the average speed in μ/sec was calculated.

TABLE I

	Mobility μ/sec/v/cm	Zeta Potential (mv)
Triolein	4.1 ± 0.2 [a]	−79 ± 4
Nujol	3.6 ± 0.2	−69 ± 4
Glass	3.2 ± 0.1	−62 ± 2

[a] 95% Confidence limits.

Particle mobilities in test dispersions were measured at 100 magnification. Particle size and shape apparently had no significant effect on mobility as viewed in the field. To obtain one mobility value used in calculating the average, the time required for the particle to move 100 units on the microscope ocular scale (1 unit = 3.2 μ) was measured 10 times with field strength noted for each. The avg of these 10 measurements was taken as a single determination. Thus, each of the 26 observations for Nujol involve 10 measurements of particles over the 100 scale unit distance, and so on throughout the data. Mobility units are μ/sec/volt/cm and indicated is direction of motion: towards anode (negative particles) or towards cathode (positive particles).

Zeta Potentials were calculated by equation 1, assuming the dielectric constant and viscosity of the relatively dilute test solutions are equivalent to that for pure water. In calculations, adjustment was made for the 3.2 μ diam particle measured. Zeta potential values are given in mv. The sign of potential indicates particle charge: (−) negative, (+) positive.

Data and Discussion

Particle Mobilities in Deionized Water. Consistent with the literature, Nujol, triolein, and glass particles were negatively charged in deionized water and yielded the following mobilities and zeta potential values in Table I.

Statistically, triolein motion is most rapid and glass least rapid of the three particle types. Mobilities in water are highly sensitive to trace impurities (4) and numerous observations (26–77) were required to show differences at the 5% significance level. Nujol and glass mobilities agree well with literature values: Powell and Alexander (4) reported 4.0 ± 0.5 for Nujol and Karpova (5) obtained 3.0 μ/sec/v/cm for glass. No triolein mobilities were found in the literature.

Glass particles measured were irregular, while the oils were spherical. However, glass mobilities were

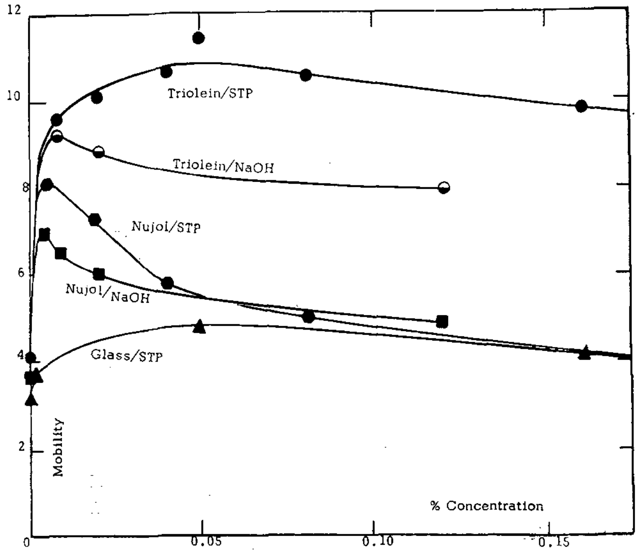


FIG. 2. Particle mobilities in Alkaline electrotype solutions.

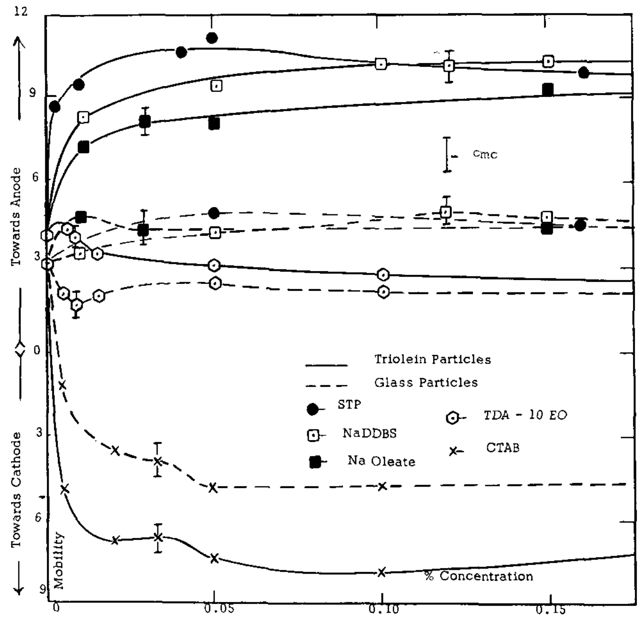


FIG. 3. Effect on detergent type.

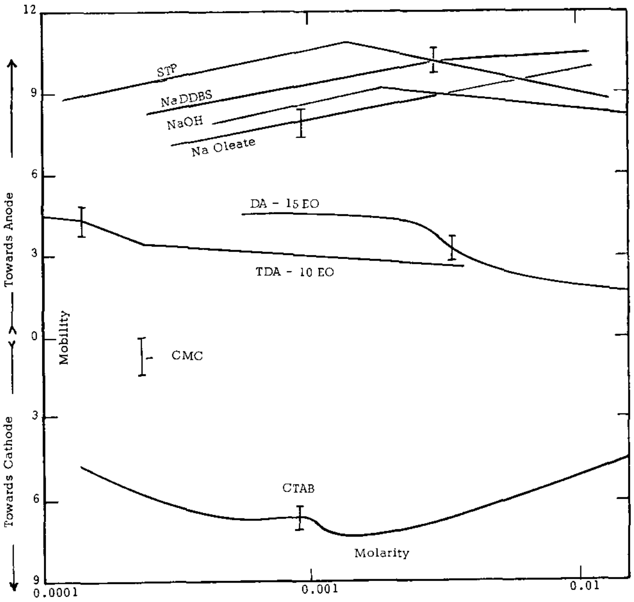


FIG. 4. Triolein mobility vs. log surfactant concn.

apparently independent of shape in the 2–4 μ diam size measured. Karpova (5) investigated spherical and irregular glass particles in water and electrolyte solutions, and found mobilities varied little with size and shape in the 4–20 μ range. Zeta potentials of triolein, Nujol and glass particles are similar in spite of the different chemical nature of the surfaces involved. It is difficult to accept the possibility that all three substances adsorb hydroxyl ions from water dissociation to the same extent. A more likely explanation is that the similar charge arises from contact electrification or transfer of electrons from water across the interfacial boundary (6). The charge transfer may be caused by differences between work functions of the two phases. Thus, the three particles types are negative partners since they tend to retain their electrons more tenaciously than water. With addition of solute, however, the charge effects and zeta potentials are determined by adsorption.

Electrolyte Effects. Mobility towards the anode, hence surface charge and negative zeta potential, are increased for Nujol, triolein, and glass by addition of alkaline electrolyte builders (Fig. 2). The effect is greatest for triolein, next Nujol, and glass is least sensitive. This trend is the same as found in pure water.

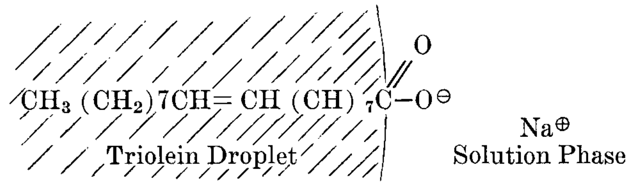
With both triolein and Nujol, mobility increased more from tripolyphosphate addition than from NaOH. This suggests polyvalent tripolyphosphate anions are adsorbed to give a higher surface charge relative to that from OH^- ions.

The mobility-concn curves show rapidly increasing mobilities at low electrolyte concn, reaching a maximum, then decreasing moderately at elevated concn. The rising portion of the curve is attributed to increasing charge density, while the maxima and decreasing portions are attributed to double layer compression from increasing gegenion concn. The maxima are less pronounced with triolein than Nujol, indicating stronger anion adsorption, and more effective screening by polyphosphate anions is particularly effective. The loose attachment of polyphosphate ions on Nujol accounts for greater sensitivity to gegenion effects. Mobility maxima depend more on gegenion concentration for Nujol and more on anion concentration in the case of triolein. In STP solutions, glass mobilities are ca. half those with triolein. This agrees with other findings (5,7) for glass or clay and oil particles. Glass apparently has relatively little tendency to sorb negative ions.

Surfactant Effects. Electrophoretic properties are determined by the surfactant ionic charge or type and the sorbing tendency of the particle.

Anionic surfactants such as sodium dodecylbenzenesulfonate (NaDDBS) and sodium oleate, are strongly sorbed by triolein and yielded high negative zeta potentials (−106 to −147 mv) Figures 3 and 4. NaDDBS imparts higher mobility than sodium oleate.

The lipophile chains of surfactant anions are sorbed into the triolein droplet interior through van der Waals' attraction. Negatively charged polar groups extend into the solution. Surfactant anions are therefore potential-determining while sodium ions are the gegenions, e.g., schematically:



Triolein mobility-concentration curves resemble Langmuir adsorption curves. Mobility increases rapidly at first over a relatively narrow concn range. Mobilities are essentially linear with respect to log concn (Fig. 4). Mobility was not depressed at high agent concn as found for alkaline electrolytes with triolein. The internally sorbed surfactant anions are relatively fixed and therefore are more impervious to gegenion penetration than are simple electrolyte anions. No discontinuities in the triolein mobility curves occurred at cmc where mobilities already were essentially constant. The initial levelling off of the curves apparently occur at very low concn (well below the cmc's) where the sorption approaches a monolayer. Monolayer coverage is estimated to occur in the 0.0001% surfactant concn range.

Anionic surfactants increased glass particle mobility to only a slight extent, values again falling at ca. half the triolein mobilities. Glass shows relatively little tendency to adsorb negative ions, including surfactant types. As with STP, the anionic surf-

TABLE II

Triolein Mobility Data for Tripolyphosphate-Surfactant Systems

Agent[a]	Mobility	Zeta (mv) Potential
STP	9.4 ± 0.6	−133
Decanol (DA)−10 EO	1.50 ± 0.04	− 29
DA-10 EO/STP[b], 1:2 mole ratio	8.9 ± 0.3	−126
NaDDBS	10.4 ± 0.2	−147
NaDDBS/STP[c], 1:2 mole ratio	9.2 ± 0.1	−131

[a] Total agent concn = 0.25%.
[b] STP at 0.14%, DA-10 EO at 0.11% concn.
[c] STP at 0.17%, NaDDBS at 0.08% concn.

TABLE III

Mobility—Zeta Potential Data—Range Basis

Triolein

Agent	Charge	Mobility[a]	Zeta[b]
Deionized Water	(−)	4.1	−79
NaOH	(−)	7.8– 9.2	−111 to −131
STP	(−)	8.7–11.3	−124 to −160
NaDDBS	(−)	8.4–10.4	−120 to −147
Na Oleate	(−)	7.4– 9.8	−106 to −139
TDA—10 EO	(−)	2.6– 4.6	− 50 to − 88
CTAB	(+)	4.8– 7.4	+ 69 to +105

Glass

Agent	Charge	Mobility	Zeta
Deionized Water	(−)	3.2	−62
NaOH	(−)	—	—
STP	(−)	3.7–4.8	−53 to −67
NaDDBS	(−)	3.6–4.7	−52 to −65
Na Oleate	(−)	4.2–5.0	−60 to −70
TDA—10 EO	(−)	1.7–2.5	−33 to −48
CTAB	(+)	1.1–4.8	+16 to +68

[a] μ/sec/v/cm.
[b] mv.

actants did not significantly alter the zeta potential of glass.

Nonionic detergents reduced the mobility of both triolein and glass (Fig. 3 and 4). The particles became less negatively charged from the slight cationic character of sorbed polyethenoxy groups. Cmc is especially significant for nonionic agents. With triolein, mobilities were essentially constant up to cmc, then decreased rapidly near cmc, and again became relatively constant at higher concn. With glass, mobilities decreased to a minimum at cmc then increased at concn above cmc. The differing character of the mobility curves suggests different adsorption mechanisms. Thus, triolein probably sorbs nonionics through the hydrocarbon chain with the polyethenoxy chain solution oriented. Glass, on the other hand, apparently sorbs the slightly cationic ethoxyls first and mobility diminishes. Above cmc, the micellar solubilizing action removes some of the sorbed molecules, since these are weakly held by the glass, and mobility then increases slightly.

Cationic Agent. Cetyltrimethylammonium bromide (CTAB) imparts a high positive charge and zeta potential to both triolein (69–105 mv) and glass (16–68 mv) surfaces. With initial CTAB addition, mobilities decrease rapidly to zero then reverse direction, i.e., particles move towards the cathode as the CTAB concn increases (Fig. 3). Extensive flocculation of glass was observed at 0.005% CTAB. The zero mobility or isoelectric point occurs in the range of 0.0001% CTAB concn and this corresponds roughly to the concn required for a monolayer. Mobility then increases towards the cathode up to ca. the cmc where inflection points are observed. Above cmc, mobilities remain essentially constant or decrease slightly. Cationic monomer concn apparently governs the electrophoretic effects from CTAB.

Glass yields somewhat lower mobilities than triolein but shows a much stronger tendency to sorb positive ions compared to negative ions. The surfactant cations apparently sorb on glass through their positive polar groups with hydrophobic surface at monolayer coverage. At higher than monolayer concn, multilayers result with cationic polar groups solution oriented to give the net positive charge. Above cmc, cationic monomers are incorporated into micelles so no further increase in mobility is observed.

The above effects apply also to triolein but in this case CTAB is assumed to be sorbed through the lipophile group. Additional adsorption beyond a monolayer may stem from increasing interfacial area resulting from particle size reduction. Such particle size reduction or emulsification is known to increase for surfactants up to the cmc, and remain essentially constant at higher concentrations.

Surfactant-builder combinations. Triolein mobility and zeta potential data for STP combined with anionic and nonionic surfactants are essentially that of the STP alone (Table II). The mobility depressant action of the nonionic surfactant is nullified by adsorbed tripolyphosphate ions. No synergism is apparent between active and builder.

Electrophoretic Data and Detergency

Electrophoretic data for triolein and glass have established the data in Table III. Anionic surfactants, STP, and NaOH yielded highest triolein mobilities and negative zeta potentials (−106 to −160 mv), but have little effect on the electrophoretic charge of glass. Nonionic surfactants slightly lowered mobility and zeta for triolein (−44 to −88 mv) and glass (−40 to −70 mv). The cationic agent produced high positive zeta potentials for both triolein (69–82 mv) and glass (16–68 mv). CTAB and synthetic anionic surfactants are relatively ineffective in removing fatty soil from glass, even at elevated temp. STP is effective at 75C, but yields little soil removal at 35C. Most effective detergents are nonionic surfactants and sodium oleate, over the entire temp range.

The high detergent action of nonionic surfactants shows that electrical charge is not requisite for detergency. These agents are also effective as emulsifiers and dispersants. It has already been suggested that solvation or envelopment of soil particles in micellae containing water molecules is a very important factor in soil removal and emulsification.

Electrical charge effects probably contribute to the activity of ionic agents, though they may not be necessary and sufficient causes for soil removal. With STP, e.g., activation energy in the form of heat was required for soil removal in addition to the electrical energy. The electrical charge effects apparently are more important in preventing flocculation and soil redeposition, once the soil is separated from the substrate. The importance of electrical charge effects in dispersion and emulsion technology is well established.

Summary and Conclusions

Electrophoretic mobilities and zeta potentials were established for triolein, Nujol, and glass particles in deionized water: 4.1, 3,6 and 3.2 μ/sec/v/cm, and −79, −69, and −62 mv, respectively. Adsorption of specific radicals determine the electrokinetic properties. Electrolyte and surfactant anions are preferentially sorbed to promote negative zeta potentials and increase mobilities particularly for triolein and Nujol. Glass mobilities and zeta potentials were ca. half of those found for triolein in alkaline electrolyte or anionic surfactant solutions.

With anionic surfactants, triolein mobilities are near maximum at cmc. Mobilities increased linearly

with log concn over a wide anionic concn range.

Nonionic surfactants lower mobility of both triolein and glass, thus have slight cationic character. Significant inflection points and minima at cmc were found in mobility-concn curves.

The cationic agent CTAB produced high positive charge and zeta potentials on triolein and glass. Inflection points were noted at cmc and, as with nonionics, mobility is relatively constant above cmc.

Surfactant-builder combinations yielded mobilities and zeta potentials essentially equal to those for builder alone; no synergism was evident. Oil droplets sorb surfactants through their hydrocarbon chains, and polar groups extending into the aqueous phase determine the sign and degree of charge. Glass has little tendency to adsorb negative ions, even those which are surface active. Surfactant cations are strongly adsorbed by glass and the adsorption apparently occurs with the positively charged polar group attaching to the glass. Nonionics behave like weak cationic agents, apparently attaching to glass through protonated ether oxygens which have a slight positive charge. Electrokinetic effects are not necessary and sufficient causes for fatty soil removal though they may be contributing factors, especially for ionic agents. The electrical properties are probably more important in suspending action and in preventing soil from redepositing on a surface once removed.

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Soybean Unsaponifiables: Chromatographic Investigation of Shell Drain Condensate from a Commercial Deodorizer

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Abstract

The shell drain condensate from a commercial soybean oil deodorizer was analyzed for nonpolar unsaponifiable constituents by liquid-liquid partition chromatography. A procedure for obtaining large quantities of these nonpolar constituents for flavor studies is described, and data on extraction techniques, purification, and analyses are presented. High-purity soy sterols can be obtained as a by-product.

Introduction

PREVIOUS work (4) indicated that the nonpolar constituents of soybean unsaponifiables, when added to freshly deodorized oils, were responsible for some of the oxidative flavor deterioration. Since unsaponifiables represent only about 1% (4,8) of soybean oils, further investigation of nonpolar consituents was hampered by the low concentration, usually less than 15%, in the total unsaponifiables. Adequate characterization and organoleptic study of nonpolar constituents require more sample than is ordinarily available from the usual quantitative procedure for the determination of unsaponifiables. This difficulty prompted an investigation of other starting materials for laboratory work.

Procedures

A commercial soybean oil shell drain condensate (SDC) was analyzed as a more concentrated source of unsaponifiables. SDC represents 7–10% of the deodorizer loss and contains constituents of low volatility that collect on the outer shell of a tray-type deodorizer (2). Such a deodorizer collects distillates of low volatility by allowing them to drain to the bottom where they are removed from the system as a green or brown oil.

Volatile and nonvolatile fractions were obtained upon distillation of the SDC in an Asco 50 Rota-Film molecular still at 200C and 4 μ. SDC, its fractions, and the unsaponifiables obtained from these fractions were analyzed by liquid-liquid chromatography, on 50-g silicic acid columns with 16% methanol (by wt of SiO_2) as the mobile phase and 2% methanol (by

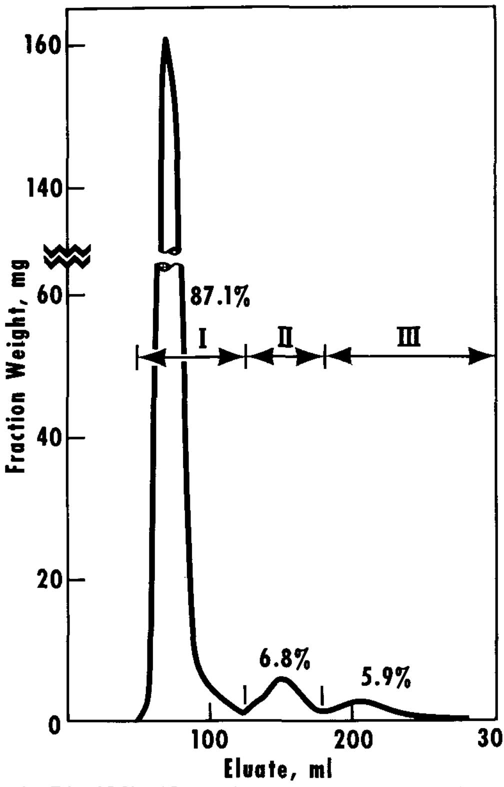

FIG. 1. Liquid-liquid partition chromatogram of shell drain condensate (SDC).

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