is placed only in the first tube, we may calculate from Nichols' equation 5 (9) that in a 50-tube instrument 123 transfers would be applied before the fraction which corresponds to the point of intersection of the curves, i.e., the fraction in the distribution of a two-component system which contains equal amounts of each component, leaves the instrument. With a 100-tube instrument 245 transfers would be applied; with a 200-tube instrument, 490 transfers, which checks our experimental value in Figure 1. Then if equal amounts of linoleate and linolenate are present in the starting mixtures and if the fractions are divided at the intersection point, we may calculate from the equations of Lancaster *et al.* (7) that each component from the 50-tube instrument would contain 4.5% of the other component as impurity. Each component from the 100-tube instrument would contain 0.8% of the other component. Greater purity can be achieved by starting with material enriched in the desired component, by discarding the small fractions near the intersection point of the curves, or by using a smaller ratio of upper-to-lower-solvent volumes.

Summary

Acetonitrile-pentane-hexane makes a desirable solvent system for preparation of pure methyl esters because of its immiscibility, selectivity toward unsaturation, low boiling point, stability, and ease of recovery. Since separated esters are removed from the apparatus dissolved in the pentane-hexane layer, successive batches may be fractionated without removing the acetonitrile layer from the instrument. Applications have been illustrated for the preparation of methyl linolenate from an 85% linolenate concentrate, methyl linoleate from safflower esters, and methyl arachidonate from pig liver lipids.

This procedure provides a source of "natural" fatty acids with the double bond configuration unchanged, in contrast to those from the conventional bromination-debromination process. Automation of the process is completed by use of a recording refractometer which monitors concentration of solutions issuing from the extractor. Resolutions to be anticipated with lesser numbers of extraction tubes than 200 are calculated for an equal mixture of linoleate and linolenate.

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Theory of the Washing Process[1]

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THE SOIL usually occurring on the textiles to be washed is a complicated mixture of very different components. For the sake of simplicity, they may be subdivided into materials which are liquid at the washing temperature and others which are solid under the same conditions. Regarding the washing process theoretically, it is useful to consider the displacement of both types of soil separately because they are taken away from the textile fibers by quite different mechanisms.

Liquid soil, or as we may call it, oily soil is chiefly displaced by preferential wetting. It has been shown by microscopic observations that the oil originally spread over the fiber as a thin and nearly uniform layer is pushed together to form spherical droplets after immersion in the washing liquor. From a detailed study of this process it follows that the preferential wetting is governed by the interfacial tension σ_{AB} between the oil and the washing liquor as well as by the difference Δj between the adhesion tensions for the washing liquor/fiber and for the oil/fiber interfaces. If Δj is greater than σ_{AB}, the droplets are spontaneously detached. The work A_W done by the system during this process is given by the following formula derived by Kling and Koppe (6):

$$- A_W \simeq F (\Delta j - \sigma_{AB}), \tag{1}$$

where F is the area exempted from the oil.

In most of the practical cases however Δj is smaller than σ_{AB}. The oily droplets attain equilibrium in the form of spherical segments with a definite contact angle. A "residual work of washing" A_R must then be done to detach the soil completely. For A_R the following equation has been derived (7):

$$A_R = y \cdot \sigma_{AB} \tag{2}$$

y is a function of the contact angle, which in turn is correlated to Δj and σ_{AB} by the Young relation. The function is expressed by the following equation:

$$y = \sqrt[3]{4} - \sqrt[3]{2 - 3 x_0 + x_0^3} \tag{2a}$$

where $x_0 = - \Delta j / \sigma_{AB}$. The term A_R as calculated by the equations (2) and (2a) is related to an oil drop of the volume

$$v = 1/ 3 \sqrt{\pi}) \text{ cm}^3$$

The equations (2) and (2a) permit expression of the effectiveness of a detergent in removing oily soil by physically defined and measurable quantities, *i.e.*, Δj and σ_{AB}. This may be demonstrated by measurements with a model system, namely, a foil made from poly-ε-caprolactam, liquid paraffin, and aqueous solutions of sodium dodecylsulfate. Figure 1 shows, as

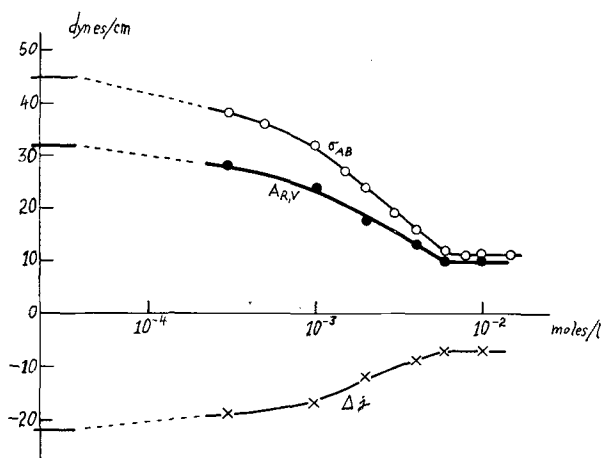FIG. 1. Interfacial tension σ_{AB}, difference of the adhesion tensions Δj, and residual work of washing A_R for the system poly-ε-caprolactam foil, liquid paraffin, aqueous sodium dodecyl sulfate solution, as a function of the concentration of the detergent.

functions of the concentration of the detergent, the interfacial tension σ_{AB} measured by the Wilhelmy method, the difference Δj of the adhesion tensions determined by the method described by Guastalla (4), and the residual work of washing A_R calculated by the equations mentioned before. A_R is lowered with increasing concentration, indicating the growing washing power of the solution.

THEORETICAL considerations on the removal of solid soil particles are more difficult. The fundamental question is what forces are effective between the fiber and the soil particles immersed in a washing liquid
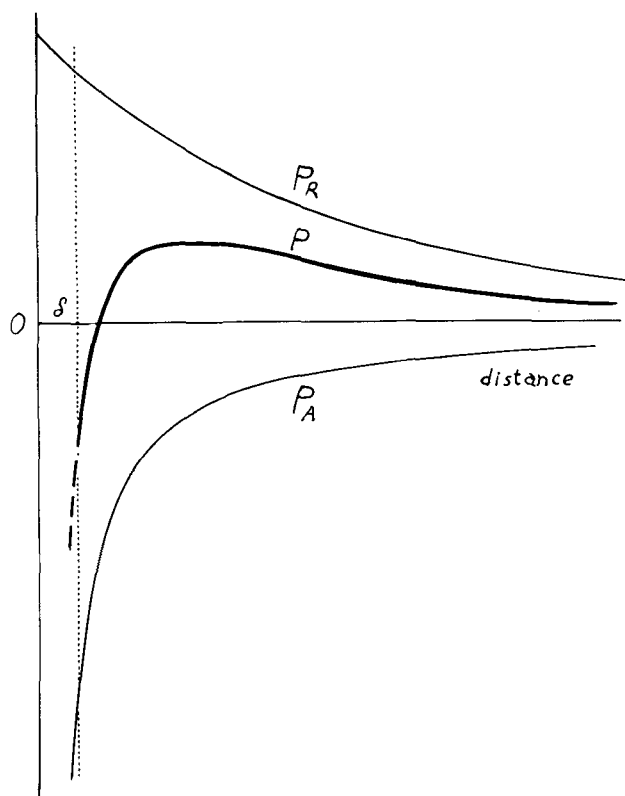

FIG. 2. Electrical repulsive energy P_R, v.d. Waals attractive energy P_A, and the resultant potential energy P of a soil particle as a function of the distance from the fiber surface, schematically.

and in what manner they are influenced by detergents. London—v.d. Waals attraction and electrical repulsion caused by the mutual interaction of the electrical double layers are of primary importance. By calculating these forces or the corresponding potential energies as functions of the distance between fiber and soil particle by means of the theories derived by Derjaguin and Landau (3) as well as by Verwey and Overbeek (12), one generally obtains a resultant curve that shows a minimum at the shortest distance δ which is possible and surpassing a maximum at a certain greater distance (Figure 2). Hence the particles have to surpass an energy barrier when they are removed as well as when they are redesposited (8).

From a practical point of view, the most interesting question is in what manner these curves, particularly the heights of the energy barriers for the removal and the redeposition, are influenced by detergents.

By adsorption of anionic detergents the negative interfacial potential ψ_0 washing liquor/fiber and washing liquor/soil is increased. Figure 3 shows, by
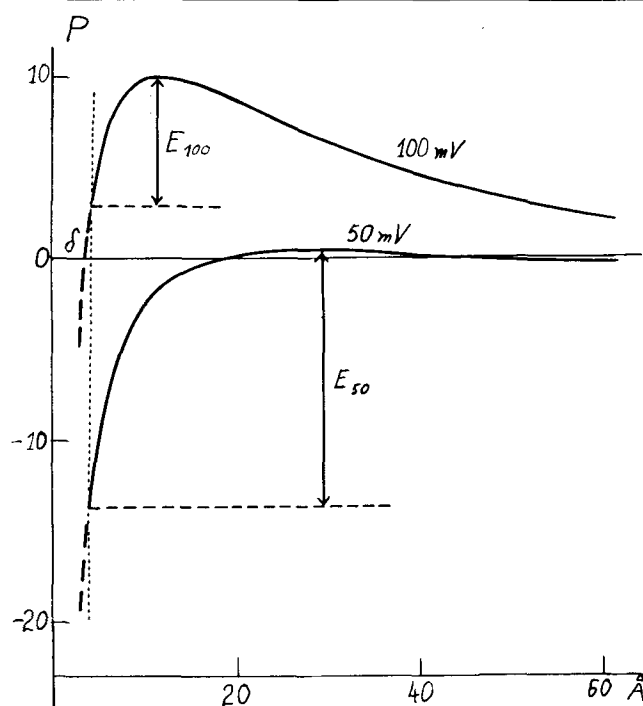

FIG. 3. Energy barriers E_{50} and E_{100}, to be surpassed at the removal of a soil particle, for interfacial potentials $\psi_0 = 50$ mV and 100 mV respectively. A spherical soil particle with a diameter of 10^{-5} cm., a total electrolyte concentration of 10^{-2} moles/l., and univalent ions have been assumed in calculating the curves.

using an example calculated with concrete quantities, how the curves are shifted if the potential ψ_0 is raised from 50 to 100 mV. The energy barrier for removing the soil particle is decreased while that for the redeposition is increased. A favorable influence on the washing process results.

The total electrolyte concentration of the washing liquor also influences the curves. For example, increasing the electrolyte concentration from 10^{-2} to 10^{-1} moles/l. causes a lowering of the energy barriers both for the soil removal and for the redeposition and therefore a promotion of these processes (Figure 4).

Finally the hydration shell produced by the detergent adsorbed on the fiber and on the soil particle re-
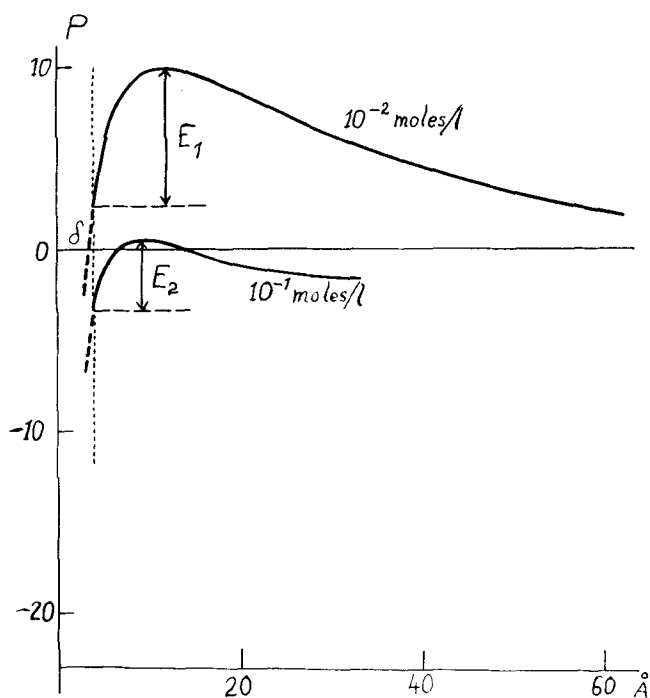
FIG. 4. Energy barriers E_1 and E_2 at electrolyte concentrations $c = 10^{-2}$ and 10^{-1} moles/l., respectively, for $\psi_0 = 100$ mV.
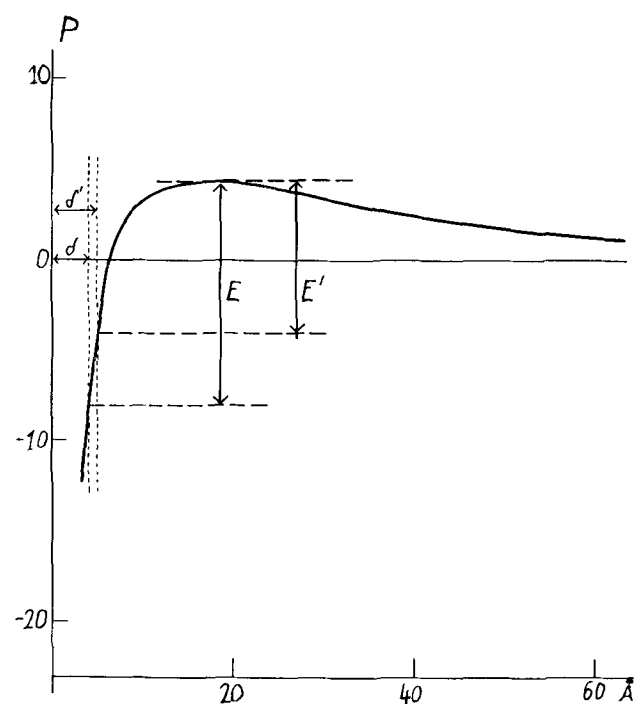

FIG. 5. Energy barriers E and E' for minimum distances of $\delta = 4$ Å and $\delta' = 5$ Å, respectively, $\psi_0 = 75$ mV, $c = 10^{-2}$ moles/l.

sults in an enlargement of the minimum distance and, as a consequence, in a reduction of the energy barrier the soil particle has to surpass when moving away from the fiber (Figure 5).

For a further development of the theory, certain refinements are necessary, which can only be mentioned but not explained. For example, the fact that the interfacial potentials on the fiber and on the soil usually have different values has to be allowed for. The theory of dispersion forces proposed by London (11) must be modified by recent theories of Casimer and Polder (2) as well as by those of Lifschitz (10). Some corrections of the Gouy-Chapman theory of the electric double layer should be applied. Finally it will be necessary to investigate the properties of the hydration shells, the influence of which has been expressed provisionally by the term δ. Such investigations have been started by recent work (9)

concerned with the influence of detergents on the stability of hydrophobic sols at high ionic strength.

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Preparation of 8t,10t-Octadecadienoic Acid [1]

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SMIT (1) ISOLATED a conjugated linoleic acid (m.p. 56°) by debromination of a tetrabromostearic acid, which had a melting point of 124°. The latter was isolated by them from the brominated products obtained by brominating the distillate of the fatty acid from castor oil. They assigned a structure of 9,11-octadecadienoic acid to this fatty acid and believed it to be elaidinized.

von Mikush (2) distilled the fatty acids obtained from castor oil according to the method of Scheiber (3) and brominated the distilled fatty acids in petroleum ether at −20°. From the bromination product he isolated tetrabromostearic acids of different melting points. Upon debromination of one of these tetrabromostearic acids (m.p. 124°) with zinc in ethanol and by crystallization of the resultant product from aqueous ethanol, he isolated an acid which melted at 55.5–56.5°. This acid was assigned a *trans-trans* structure on the basis of diene and pentadiene values and