the trimethyl hydrogenated-cyclic-alkyl ammonium iodide, are shown in Table III. Solubility data on these materials are found in Table IV. The high solubility of the simple amides disappears with the substitution of the ethanol groups for hydrogen on the amide nitrogen in the diethanolamides. The diethanolamides of coconut acid exhibit superior solubility, probably reflecting their lower average mol wt.

Conclusions

Amides prepared from hydrogenated cyclic acids possess unusually low mp, high solubility, and good compatibility with synthetic resins, which suggest their utility as mutual solvents for waxes and resins. Nitriles of hydrogenated cyclic acids and monomer acids, as well as the morpholides of the two acid mixtures, are compatible with polyvinyl chloride-vinyl acetate copolymer and may have potential as plasticizers.

The amine of hydrogenated cyclic acids and its N,N-dimethyl derivative provide amines of high mol wt and of extremely low fp.

The surface-active materials appear on the whole to be similar to other fat-derived substances.

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[Received January 10, 1962]

Reactions Between Zinc Chloride and Surfactant Solutions[1]

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Abstract

Formation of precipitates or soluble complexes between solutions of zinc chloride and surfactants was investigated by means of pH and conductivity titrations. Precipitates were characterized by chemical analysis and X-ray diffraction.

Triton X-102 and zinc chloride appear not to react. Sodium dodecyl sulfate likewise appears non-reactive, but on addition of alkali a basic salt is formed at a pH between 7.9 and 8.5 which, however, does not precipitate if the concentration of sodium dodecyl sulfate is above the critical micelle concentration. The precipitate has a marked destabilizing action on oil-in-water emulsions. With the sodium salt of Empol 1022 the normal zinc salt precipitates on addition of the stoichiometric amount of zinc chloride.

Tamol 731 is neutralized in two steps by hydrochloric acid, the pH at the two endpoints being 7.0 and 3.3. It apparently forms a soluble complex with zinc ion which is not precipitated even in alkaline solutions.

Introduction

THE MAJOR PRACTICAL PROBLEM to which the present work should have application is that addition of zinc oxide to bodied linseed oil emulsions raises serious stability problems. In order to provide background information for the solution of this problem it was considered important to study the types of interaction which might occur between zinc oxide or zinc ion and a variety of surfactants of types found in emulsion paints.

Reaction between residual fatty acids and zinc oxide can lead to formation of zinc soaps which are stabilizers for W-O emulsions and would consequently have an adverse effect on the original O-W dispersion.

Zinc oxide itself, depending on its method of preparation and incorporation, may stabilize either O-W or W-O emulsions (1). Loss of stabilizer by adsorption on the metal oxide may reduce the concentration in solution to so low a value that instability results. The same effect could also result if the surfactant reacted chemically with the metal oxide, or if zinc ion furnished by solubility of zinc oxide either precipitates the stabilizer or reduces its concentration by formation of a soluble complex. Any or all of these processes may be the explanation for the common observation that larger quantities of surfactants are required to form stable linseed oil emulsions when driers or pigments are present than in their absence. Consequently this work was undertaken to explore the possible effects of zinc ion in O-W emulsions containing a number of common stabilizing agents.

Materials and Apparatus

All inorganic chemicals used were Baker and Adamson, reagent grade. Standard solutions of zinc chloride were prepared by adding a very slight excess of the acid to a known wt of zinc oxide dried at 110C.

Pure sodium dodecyl sulfate (SDS) was used as a stabilizing agent, either the same sample prepared by Phansalkar (2) or a slightly less pure preparation by H. M. Princen from combined lauryl alcohol fractions of mp 23.40 and 23.71C. The two preparations of SDS gave identical X-ray diffraction patterns, and were freshly extracted with ether before use.

Other surfactants were used directly as received without further purification. Triton X-102[3] and Tamol 731-25%[4] were supplied by the Rohm and Haas Co.

[3] Triton X-102 is an alkyl aryl polyether in which the polyoxyethylene chain has a length of twelve to thirteen carbon atoms.
[4] In this paper per cent Tamol is in terms of a 100% product and not in terms of the 25% solution as which it is supplied. Tamol is described as being the sodium salt of a carboxylated polyelectrolyte.

Sodium dimerate is the sodium salt of Empol 1022 which is reportedly (3) a mixture of 3% monomer, 26% trimer, and 71% dimer of unsaturated acids of 18 carbon chain length. Titration with 0.3 N sodium hydroxide (4) gave an equivalent weight of 296, leading to a calculated mol wt of 659, assuming MW = Eq. Wt. × (1 × 0.03 + 2 × 0.71 + 3 × 0.26). The sodium salt was prepared by adding the stoichiometric amt of 1.0 N sodium hydroxide to a weighed amt of the acid, and heating at 100C for about 2 hr. M/20 solutions so prepared had a pH of 9.5 to 11.0 depending on the detailed procedure followed in their preparation.

A Model G Beckman pH meter with either No. 290 or No. 40498 glass electrode was used for determination of pH. Bottle titrations were made at room temp on solutions made up to const volume (generally 15 ml) with a fixed volume of titrant (generally 10 ml) and varying volumes of water and titrating agent, equilibrated 24 hr or longer before determination of pH. Continuous titrations were made at 25.6C in a specially constructed titration vessel about 11 cm high permitting introduction of either a glass electrode or a conductivity cell. Stirring and exclusion of oxygen and carbon dioxide were both accomplished by bubbling a stream of purified nitrogen through the solution, stopping it momentarily when readings were taken, and making further addition of titrating solution only after two successive readings were identical. Titration samples were usually 30 ml.

Most conductivity measurements were made with a Leeds and Northrup audio oscillator, certified resistance box, and a student type Kohlrausch bridge, although a few were made with a Jones conductivity bridge.

X-ray diffraction patterns were obtained with a North American Philips X-ray spectrometer coupled to a Brown Elektronic recorder. Values of the Bragg spacings were appropriately corrected for recorder lag.

Results and Discussion

Triton X-102. Conductivity and pH measurements were made on M/80 zinc chloride solutions equilibrated with M/20 Triton solutions (calculated from the wt on the basis of 100% purity and an assumed mol wt of 756), and water over a range of concentration up to a molar ratio of Triton to zinc of two to one. Both the pH and conductivity of the zinc chloride solution remained constant regardless of whether it was diluted with water or with Triton solution. Hence it appears that zinc chloride does not form complexes or otherwise react with Triton X-102 at these dilutions over this concentration range.

Sodium Dodecyl Sulfate. Conductivity and pH measurements were made on 10 ml of M/120 zinc chloride solutions equilibrated with 5 ml of solution varying from pure water to M/20 SDS solution. The pH of all the mixed solutions was 3.14, suggesting that there is no specific reaction between zinc ions and dodecyl sulfate ions. The specific conductivity increased linearly with increasing concentration of SDS in the zinc chloride solution but at a slightly slower rate than on addition of SDS to water alone. Such linearity of behavior would not be expected if soluble complexes were formed between zinc ions and dodecyl sulfate ions. The lower rate of increase in the zinc chloride solution is likely to be due to differences in the viscosity and ionic strength of the two solutions (5) rather than to any tendency toward specific complex formation.

TABLE I
Initial Composition of SDS-ZnCl₂-HCl Systems Titrated with NaOH

| System | SDS | | HCl + ZnCl₂ | | | Water |
	Vol, ml	Conc. M	Vol, ml	Conc. of HCl, M	Conc. of ZnCl₂, M	Vol, ml
For fig. 1, SDS above cmc						
I	25	0.0200	5	0.0104	0	0
II	25	0.0200	5	0.0104	0.0050	0
III	0	......	5	0.0104	0.0050	25
IV	25	0.0200 a	5	0.0104	0.0050	0
For fig. 2, SDS below cmc						
I'	25	0.00400	5	0.00210	0	0
II'	25	0.00400	5	0.00210	0.00100	0
III'	0	......	5	0.00210	0.00100	25

a System IV contained no SDS but instead 25 ml of 0.0200 M NaCl.

To study the effect of alkali in this system pH titrations were carried out by the continuous technique on solutions of zinc chloride and hydrochloric acid, with and without SDS, using 0.00520 M sodium hydroxide for titrations above the critical micelle concentration (cmc) of SDS, and 0.00104 M below the cmc. The compositions of the systems used are given in Table I, and the results of the titrations are shown in Figures 1 and 2.

When alkali is added to these systems either zinc hydroxide or a basic zinc dodecyl sulfate may precipitate, but if the concentration of SDS is above the cmc the precipitate may be solubilized or peptized. The results reported in Figures 1 and 2 show that in the absence of SDS zinc hydroxide precipitates as expected. Below the cmc of SDS addition of NaOH results in the appearance of a precipitate, which is later shown to be a basic zinc dodecyl sulfate, but above the cmc no precipitation is observed although reaction still occurs to form the basic salt.

Thus, zinc chloride + hydrochloric acid on addition of sodium hydroxide forms a visible precipitate of zinc hydroxide at a pH between 7 and 8 (Curve III of Fig. 1), the pH not rising to 8.6 until sufficient sodium hydroxide has been added to precipitate all the zinc. A similar result is obtained at a lower zinc concentration (III' of Fig. 2), although here precipitation does not begin until a pH of about 7.5, the bulk occurring at around 8.2, and being completed about a pH of 8.4 to 8.5 after addition of 20 to 21 ml of alkali. When SDS is present above
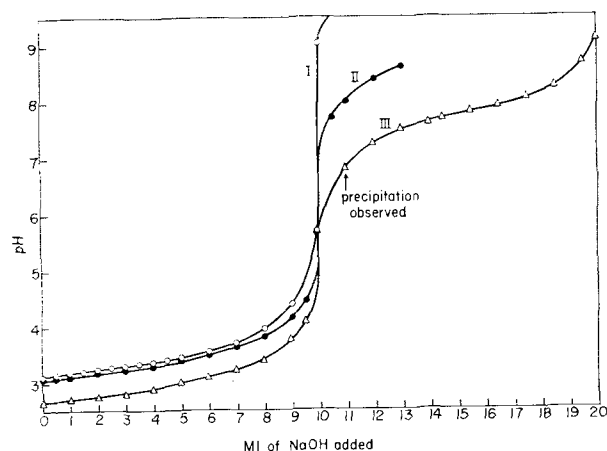

FIG. 1. Titration curves of zinc chloride and sodium dodecyl sulfate above the critical micelle concentration of sodium hydroxide.

  I. 25 ml 0.02 M SDS plus 5 ml 0.0104 M HCl with 0.0052 M NaOH.
 II. 25 ml 0.02 M SDS plus 5 ml mixed solution (0.0104 M HCl and 0.005 M ZnCl₂) with 0.0052 M NaOH.
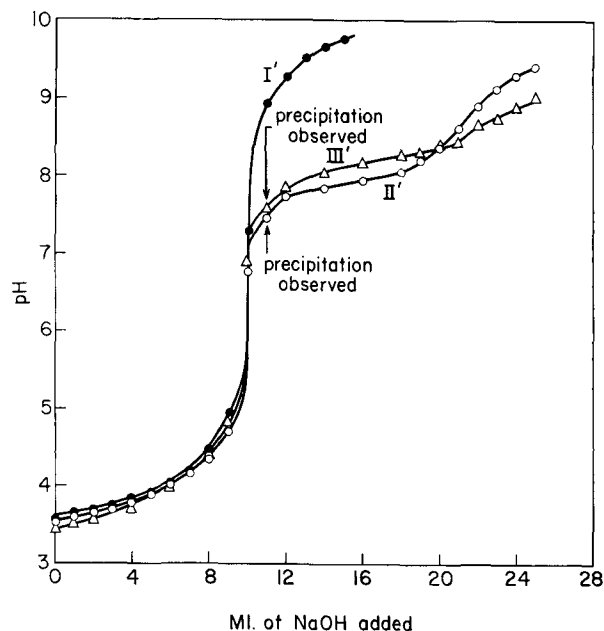III. 25 ml water plus 5 ml mixed solution (0.0104 M HCl and 0.005 M ZnCl₂) with 0.0052 M NaOH.

FIG. 2. Titration curves of zinc chloride and sodium dodecyl sulfate below the critical micelle concentration with sodium hydroxide.

I. 25 ml 0.004 M SDS plus 5 ml 0.0021 M HCl with 0.00104 M NaOH.

II. 25 ml 0.004 M SDS plus 5 ml mixed solution (0.0021 M HCl and 0.001 M ZnCl₂) with 0.00104 M NaOH.

III. 25 ml. water plus 5 ml mixed solution (0.0021 M HCl and 0.001 M ZnCl₂) with 0.00104 M NaOH.

the cmc (Curve II of Fig. 1), the pH rises well above that at which zinc hydroxide precipitates (about 7) with no indication of reaction. Not until a pH around 7.5 is reached does the curve flatten, indicative of consumption of alkali in the formation of an alkali-containing salt, but no visible precipitation is observed.

That the non-appearance of a precipitate is caused by reduction of zinc ion concentration due to complexing with SDS is ruled out by the pH and conductivity results on SDS-zinc ion solutions reported above. That it is not due to increase of the solubility of zinc hydroxide because of the increased ionic strength due to the presence of the 0.02 M SDS was shown by substituting sodium chloride for SDS. When this was done the resultant curve was virtually indistinguishable from that of zinc chloride + hydrochloric acid (III of Fig. 1) except for a slightly sharper endpoint, with visible precipitation evident between pH 7 and 8.5. Hence the non-occurrence of precipitation in the presence of SDS above the cmc must be due to peptization or solubilization of the precipitate by the SDS micelles.

This explanation was confirmed by the observation that if SDS was present below the cmc addition of sodium hydroxide to zinc chloride + hydrchloric acid did result in formation of a precipitate with consumption of alkali at a pH around 7.9 (Curve II' of Fig. 2). In the particular system studied the concentration of SDS at the endpoint is 0.0025 M while the cmc in water is at 0.0081 M (6). Even in the zinc chloride solution the concentration of SDS is still well below the cmc since in this case zinc chloride is 0.000125 M and sodium chloride 0.00026 M, while Shinoda (7) found that 0.05 M sodium chloride or 0.005 M zinc chloride was necessary to decrease the cmc of SDS to about 0.0024 M. That precipitation in this case occurs at a lower pH (7.9) in the presence

of SDS (Curve II' of Fig. 2) than with the same concentration of zinc alone (at a pH of 8.2, Curve III' of Fig. 2) shows that the precipitate when SDS is present is not simply zinc hydroxide, but is probably a basic zinc salt of the dodecyl sulfate.

The buffer region corresponding to precipitation of basic dodecyl sulfate salt lies below the pH at which zinc hydroxide precipitates when the concentration of SDS is below the cmc (Fig. 2), and above it when SDS is above the cmc (Fig. 1). Hence, above the cmc of SDS, zinc ions must have been solubilized or made unavailable by the micelles prior to formation of the basic salt at a higher pH, formation of a soluble complex ion with simple dodecyl sulfate ion being excluded by the consideration that below the cmc zinc hydroxide precipitated even though the dodecyl sulfate ion was present.

Nature of the Precipitate in Sodium Dodecyl Sulfate Systems. The nature of the precipitate resulting from addition of sodium hydroxide to solutions of zinc chloride, hydrochloric acid, and SDS was studied by X-ray diffraction as well as by direct chemical analysis. Both methods suggest that it is a basic zinc dodecyl sulfate of probable empirical formula $Zn_3(OH)_5(DS)$.

Figure 3 shows the X-ray diffraction patterns of SDS, zinc dodecyl sulfate, and three precipitates obtained by adding sodium hydroxide to solutions of zinc chloride, hydrochloric acid and SDS. Precipitate I was formed below the cmc (Curve II' of Fig. 2), precipitate II from a very concentrated solution (10 g SDS, 25 ml alcohol, 18 ml water), and precipitate III by solution of II and reprecipitation under the same conditions as I. In addition, diffraction patterns were determined for zinc oxide and for the solid separated from a sol prepared by neutralizing zinc nitrate solution with ammonia. Both these patterns agreed completely with the ASTM pattern for zinc oxide, showing that although zinc hydroxide may be the precipitating species in this case the resultant suspended solid is zinc oxide (8). Zinc dodecyl sulfate was prepared by the method of Lottermoser and Füschel (9) since its solubility prevented preparation by the precipitation method (10). Not only was it soluble in the alcohol-water solution mentioned above but also in water solution alone, even after dilution to 2 liters.

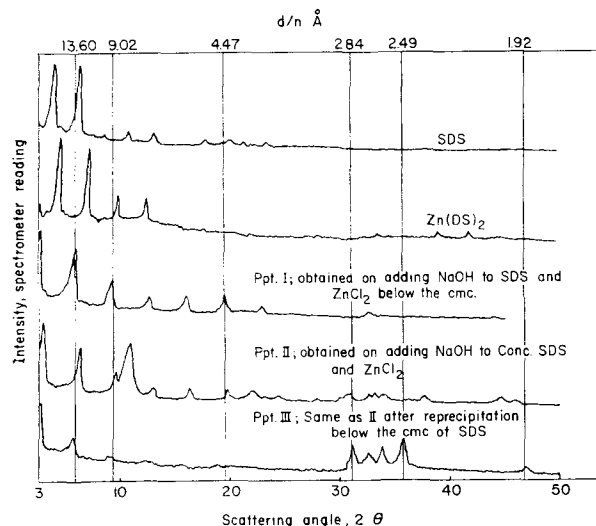It is evident that none of the precipitates from the

FIG. 3. Diffraction patterns of sodium dodecyl sulfate, zinc dodecyl sulfate, and alkaline precipitates.

SDS systems gave diffraction patterns indicating the presence of detectable amounts of sodium or zinc dodecyl sulfate, nor do they at all resemble that of zinc oxide. None of the patterns from the precipitates are identical, although all have a long spacing indicative of the inclusion of a dodecyl sulfate residue in the precipitated solid. The non-identity of the three diffraction patterns might be due to varying ratios of zinc, hydroxyl, and dodecyl sulfate dependent on the precipitation conditions, although if this were the case precipitates I and III would be expected to be identical. It seems more likely that polymorphism, varying hydration, and possible trace impurities are responsible for the observed variations in the diffraction patterns (11).

Analysis of the precipitates for zinc could not be carried out by the usual ferrocyanide titration (12) since the diphenylamine sulfonate indicator did not work in the presence of SDS. Consequently, the method used was that of Lottermoser and Füschel (9), involving hydrolysis of the precipitate, followed by gravimetric determination of sulfate as barium sulfate, and ferrocyanide titration of the zinc after removal of sulfate. Hydroxyl was determined by difference. Treated in this way the empirical composition of precipitate I could be represented as

$$Zn_3(OH)_5(DS) \cdot 2H_2O$$
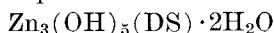
and that of II as $Zn_3(OH)_5(DS)$, duplicate analyses agreeing within 1%.

Effect of Basic Zinc Dodecyl Sulfate on Emulsion Stability. Since the basic salt forms at a lower pH than zinc hydroxide itself, it seems likely that addition of zinc oxide to a system containing SDS would result in metathesis of the zinc oxide on the surface to form a precipitate of composition similar to that found above. Such a precipitate might well promote the formation of W-O emulsions thus tending to destabilize an existing O-W emulsion. Moreover, loss of the soluble emulsifier (SDS) due to formation of this precipitate would also have a destabilizing effect.

That basic zinc dodecyl sulfate does indeed have a deleterious effect on the stability of both Nujol and M 37 oil[5] emulsions is shown by the following results. Attempts to prepare 50 volume percent oil-water emulsions with 1% of the basic salt by first stirring at 5000 r.p.m. with a Brookfield Counter-rotating (BCR) mixer and then passing six times through a Cenco Hand Homogenizer were totally unsuccessful even though with zinc oxide itself some emulsification to form very unstable, very dilute O-W emulsion was observed. Even more significant is the effect of incorporating the basic salt (precipitates I and II) into O-W emulsions stabilized with SDS. In these experiments emulsions of Nujol and M 37 oil in water were prepared by stirring 25 ml of oil with 75 ml of 1% SDS solution at 5000 r.p.m. with the BCR mixer (10 min for Nujol; 30 for M 37 oil), followed by passing each five times through the Cenco Hand Homogenizer. Duplicate 30 ml samples of each were then taken and stirred for five min at 5000 r.p.m. with the BCR mixer, one with and one without 0.13 g of the basic zinc dodecyl sulfate precipitate. The foam collapsed completely within ten min in both emulsions containing the precipitate whereas it remained unchanged in the control samples. After a few days both emulsions containing precipitate had separated appreciable quantities of free

5 M 37 oil is a heat-bodied linseed oil widely used in the coating industry.
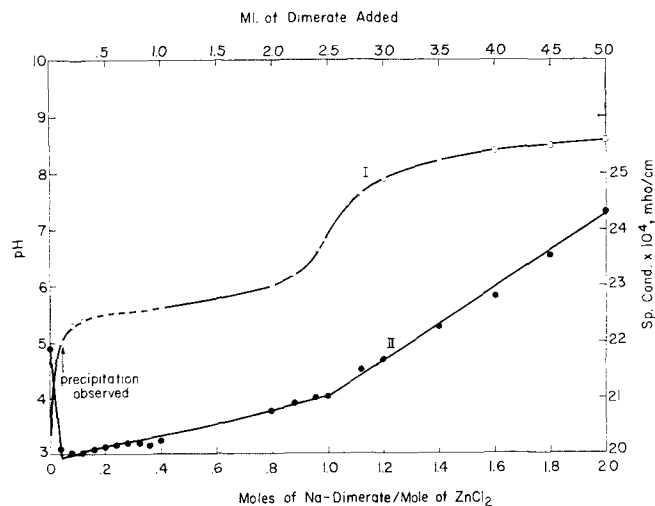

FIG. 4. Conductometric and pH titration of M/80 zinc chloride with M/20 sodium dimerate; I pH titration curve; II conductometric titration curve.

oil whereas the controls remained unchanged from their original appearance. Hence it seems that formation of this basic salt on the surface of zinc oxide suspended in SDS solutions is likely to be an important factor contributing to the instability of emulsions containing these ingredients.

Sodium Dimerate. The pH and conductivity were determined of solutions of M/20 and M/80 sodium dimerate titrated with M/80 and M/400 zinc chloride solution up to a molar ratio of four moles dimerate per mole of zinc, typical results being shown in Figure 4. The pH rises rapidly at first due to neutralization of the slight excess of hydrochloric acid in the zinc chloride by the strongly alkaline dimerate solution, then very slowly while a precipitate is forming, and rapidly after the stoichiometric amt of dimerate has been added at a one to one molar ratio of zinc to dimer acid. Thus it seems likely that the precipitate is normal zinc dimerate and neither zinc hydroxide nor a basic zinc dimerate salt. Since precipitation of zinc hydroxide under these conditions requires a pH of 7.2 or higher, and this precipitate forms at a pH of 5.5 to 6, it also appears that zinc dimerate is less soluble than zinc hydroxide.

The conductivity data likewise suggest that the precipitate formed on adding sodium dimerate to zinc chloride solution is the normal zinc dimerate. The specific conductance first drops rapidly on addition of sodium dimerate because of neutralization of the highly conducting hydrochloric acid in the zinc chloride solution by the sodium hydroxide present in the sodium dimerate solution. Thereafter, the conductance increases slowly on addition of further dimerate over the range where precipitation of zinc dimerate occurs, the reaction here being $ZnCl_2 + Na_2Dm (NaOH) \rightarrow ZnDm + NaOH + 2 NaCl$. When precipitation of zinc dimerate is complete the conductance increases at a more rapid rate on addition of further sodium dimerate. As in the pH curve, so here, the change of slope occurs exactly at an equimolar ratio of zinc to dimerate.

These reactions are likely to be involved whenever zinc oxide is added to emulsions containing sodium dimerate as one of the stabilizers. Zinc ion furnished by the zinc oxide would be sufficient to cause the precipitation of zinc dimerate in the solution, as well as the formation of a coating of precipitated zinc

TABLE II
Data from Titration Curves of Tamol with HCl

System	Ml at 1st endpoint	Ml at 2nd endpoint	Eq wt	pH at 1st endpoint	pH at 2nd endpoint	pK₂ᵃ	pK_b
20 ml 1.00% Tamol c—1.03 N HCl	0.30	0.91	647	7.0	3.0	9.3	4.2
10 ml 1.00% Tamol d—0.515 N HCl	0.30	0.92	647	7.25	3.3	9.75	4.55
10 ml 3.133% Tamol d, e—0.1400 N HCl	3.40	10.60	658	7.0	3.5	10.1	4.5
25 ml 0.626% Tamol c—0.193 N HCl	1.20	3.60	676	7.0	3.3	9.9	4.5

a, b These values actually are, respectively, the pH at the points of half neutralization between initial Tamol and the first endpoint and between the first and second endpoints. If Tamol could be treated as a monomeric diprotic weak acid analogous to H₂CO₃ these values would then correspond approximately to the first and second acid dissociation constants.
c Titrations made by the continuous technique.
d Titrations made by the bottle technique.
e For purposes of molecular comparisons which become of interest in connection with possible reactions with zinc chloride it should be noted that a 3.133 wt % solution of Tamol is 0.0477 N if the equivalent wt is taken as 657 from the first endpoint in the titration curve.

dimerate on the surface of the zinc oxide particles. This latter might be adherent and stop the reaction, or it might continue to slough off, with resultant formation of more zinc dimerate until all the sodium dimerate was exhausted. Here again, then, as in the SDS case, zinc oxide may have a destabilizing effect on the practical oil-in-water emulsion system by removing one of the stabilizing agents through precipitation, and by forming a finely divided solid which presumptively would promote formation of a water-in-oil emulsion.

Tamol 731-25%. In order to understand the reactions of Tamol with zinc ion, it was first necessary to carry out a number of experiments on Tamol itself. As is shown by curves I and II of Figure 5, there are two distinct endpoints in the titration curve with hydrochloric acid, with changes of slope in the conductivity curve at corresponding concentrations. Both endpoints appear to be due to acidic groups constituting an integral part of the polymer molecule
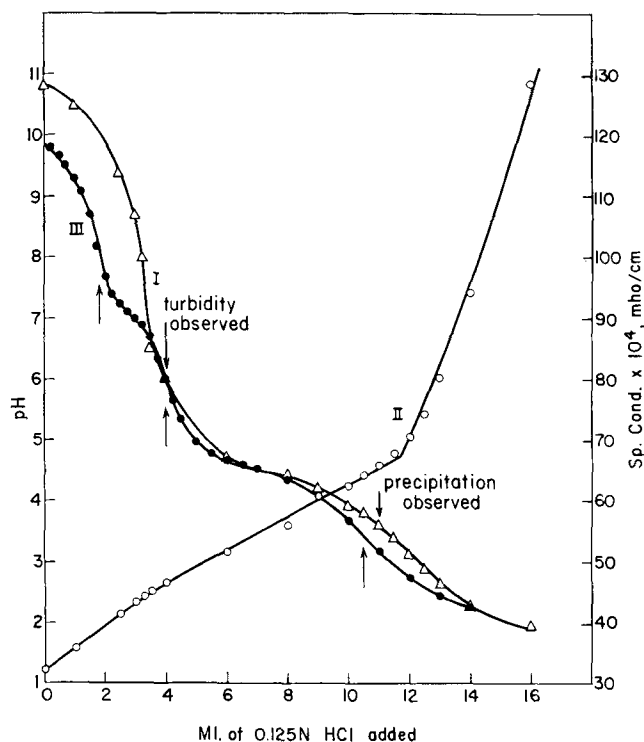

FIG. 5. Conductometric and pH titration of 3.133% Tamol with 0.140 M hydrochloric acid.
I. pH titration curve.
II. Conductometric titration curve.
III. pH titration of product prepared by neutralizing precipitated Tamol acid to a phenolphthalein endpoint with sodium hydroxide and adding sodium carbonate in amt equivalent to the acid required for the first endpoint on curve I.

rather than to alkaline impurities in the commercial preparation.

Characterizing data from the various titration curves are assembled in Table II. The first endpoint occurs at a pH of 7.0 and is accompanied by development of a slight turbidity in the solution while definite precipitation occurs at the second endpoint at a pH of about 3.2. If Tamol were a pure sodium polyacrylate there should be but a single endpoint in the curve despite the fact that the apparent dissociation constant of the acid decreases progressively with the degree of neutralization, because of cooperative effects arising from the close proximity of so many charged groups on the same chain (13). The pH of polyacrylic acid (13) appears to be slightly less than 3 in reasonable accord with the pH at the second endpoint in the present titration of Tamol with hydrochloric acid. The rapid increase in conductivity after the second endpoint is also consistent with the concept that the second endpoint corresponds to complete neutralization of the sodium carboxylate groups of a sodium polyacrylate.

The first endpoint at a pH of 7 can not be attributed to the presence of either sodium hydroxide or sodium carbonate as impurities in the sample. The initial concentration of hydroxyl ion, calculated from the amt of acid required to reach the first endpoint, would correspond to an initial pH of 12.0 whereas the actual value is only 10.9. Even more conclusive is the fact that the conductivity increases continuously with addition of hydrochloric acid whereas it would have to fall at the beginning if the reaction were one of neutralization of hydrochloric acid by sodium hydroxide.

The observed pH of 7 at the first endpoint is too low to correspond to formation of bicarbonate and too high for neutralization to carbon dioxide. Moreover, if it were taken as the bicarbonate endpoint another endpoint corresponding to formation of carbon dioxide would be expected after addition of 6.80 ml of acid while if it were assumed to be the carbon dioxide endpoint then another endpoint due to carbonate would be expected at half the volume, i.e., 1.70 ml. In neither case is there any indication experimentally of an endpoint at these volumes.

Curve III of Figure 5 shows that had sodium carbonate acutally been present in the sample the expected endpoints would have been found on the titration curve. Here free Tamol acid was prepared by acidification of Tamol, filtration, and washing free of any low mol wt salts or contaminants. The precipitated acid was then neutralized with sodium hydroxide to the phenolphthalein endpoint (Curve I of Fig. 6), and then just that amount of sodium carbonate added equivalent to the acid consumption of the original Tamol sample to the first endpoint. When this sample was titrated with hydrochloric

acid (Curve III of Fig. 5) it showed three distinct endpoints (marked by strokes on the graph), the first two at the expected positions for the stepwise neutralization of sodium carbonate, and the last coinciding with the second endpoint found for the original sample of Tamol.

Figure 6 shows the results of a titration of the precipitated and washed Tamol acid with sodium hydroxide (Curve I). The sharp endpoint in the curve at a pH of 8 agrees very well with the calculated value for titration of a weak acid of dissociation constant $10^{-4.5}$, the value obtained from the second endpoint of the original Tamol titration curve (I of Fig. 5, pK_2 of Table I). An additional endpoint would not be expected in this titration since according to the data of Table II the acidic group responsible for the first endpoint in the direct titration of Tamol with acid—assuming it to be a sodium salt—has a dissociation constant of only $10^{-9.8}$, too weak to detect on a direct titration with base. However, that the Tamol acid is still reacting with base beyond this endpoint is shown by the difference between its titration curve (I) and that of a sodium chloride solution of the same ionic strength (II of Fig. 6). In the latter case the pH rises rapidly and abruptly on addition of the first few drops of sodium hydroxide whereas in the case of the Tamol acid neutralized to its first endpoint addition of further base results in a much more gradual increase in pH, proving that some of the added base is still reacting with the Tamol.

Standard qualitative organic tests for phenolic groups and for nitrogen were negative, ruling out the possibility that the first endpoint in the initial Tamol titration curve is due to neutralization by acid of a phenolate or amide group present as a part of the polymer molecule. A test for phosphate (heating first with nitric acid and then with ammonium molybdate) was also negative. However, this cannot be regarded as conclusive since even after addition of a small amt of disodium hydrogen phosphate to Tamol no yellow color was obtained. Apparently, Tamol complexes with either phosphate or molybdate or both.

Hence, if Tamol is essentially a sodium polyacrylate type of polymer free of consequential amounts of simple alkaline impurities, it either contains the sodium salt of a very weakly acidic material present in amt equal to one half the quantity of carboxylate groups in the polymer chain, or is a copolymer of acrylic acid with some other monomer containing an acidic group weaker than carboxyl, or contains two-thirds of its sodium carboxylate groups closely spaced and one third at greater distances where they act more independently of each other, thus giving rise to a different effective acid dissociation constant than the first group. However, since L. H. Princen of the Northern Regional Laboratory of the Department of Agriculture at Peoria, Ill., has evidence suggesting that Tamol 731 is the sodium salt of a partial butyl ester of polymethylacrylic acid (personal communication) its true nature cannot be regarded as fully established despite the present work.

Reactions Between Tamol and Zinc Ion. Typical results of a series of conductometric and pH titrations of zinc chloride solution with Tamol are shown in Figure 7. No visible precipitation occurred even in experiments in which Tamol addition was continued until the pH rose to 10, although a faint turbidity was noticed in some of the solutions. Since zinc hydroxide precipitates at a pH between 7.2 and 8.0 in the absence of Tamol, the zinc must be tied up
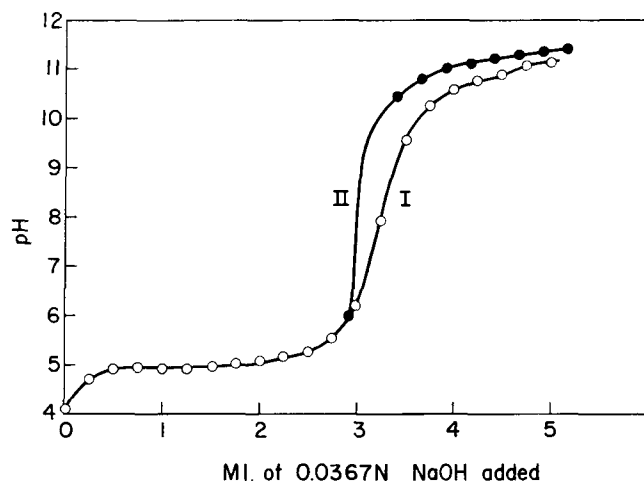

FIG. 6. Titration curve of 0.268% precipitated Tamol acid with 0.0367 M sodium hydroxide.

  I. NaOH added to Tamol in bottle titration
  II. NaOH in equivalent amt added to an equal volume of sodium chloride solution

in a soluble complex with Tamol, or as a solubilized precipitate with Tamol, with an equilibrium constant smaller than the solubility product of zinc hydroxide.

The initial rapid rise in pH and drop in conductivity on addition of Tamol may be attributed to neutralization of the excess hydrochloric acid in the zinc chloride solution by the hydroxide ion resulting from hydrolysis of the Tamol. Both pH and conductivity then increase very slowly over a range where Tamol is bound by the zinc, perhaps by a chelation reaction between the zinc and the polymer. After this reaction has proceeded to attainment of an equi-
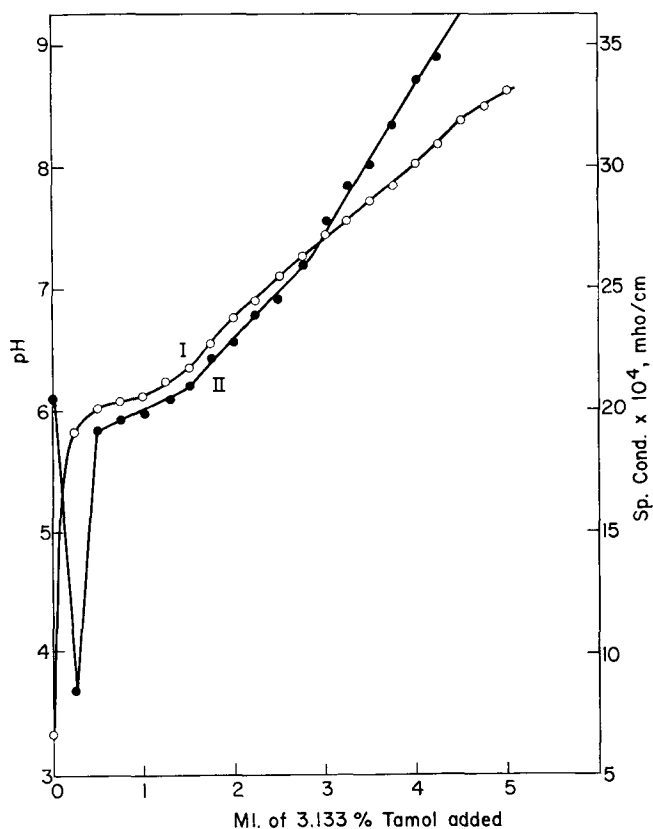

FIG. 7. Conductometric and pH titration of M/80 zinc chloride with 3.133% Tamol.

  I. pH titration curve.
  II. Conductometric titration curve.

librium concentration of the zinc-Tamol complex, further addition of Tamol increases both pH and conductivity fairly rapidly and smoothly except for an unexplained change of slope of the conductance curve at higher concentrations. That the "flat" in the pH curve is due to formation of a soluble complex rather than to formation of a precipitate which is subsequently solubilized is shown by the fact that precipitation of all the zinc present would have required addition of 5.25 ml of Tamol solution, whereas the actual "flat" ended after addition of 1.50 ml. Only 0.0716 meq. of Tamol ($1.50 \times 0.0313/657$) are used in forming the soluble complex with 0.25 meq. of zinc ion ($10.00 \times N/40$), where normalities in both cases are on a unit charge basis, although if Tamol is regarded as trivalent the equivalents of Tamol become very nearly equal to those of zinc.

The conclusion that Tamol and zinc ion form a sufficiently strong complex to prevent precipitation of zinc hydroxide was verified by a direct test in which 0.0600 N sodium hydroxide was added first to 25.00 ml of M/200 zinc chloride solution (pH 3.9), and then to another sample of the same solution to which 5.00 ml of 3.133% Tamol solution had been added. Where Tamol was present the solution was kept overnight and sufficient dilute hydrochloric acid added just before the titration with sodium hydroxide to reduce the pH to about 5, sufficient to prevent precipitation of zinc hydroxide but high enough to prevent decomposition of the Tamol to the free acid form. See Figure 8.

In the absence of Tamol the zinc is quantitatively precipitated at a pH of 7.2 to 8.0 before adding NaOH results in rapid increase of pH. With only 0.522% Tamol the pH rises continuously on added sodium hydroxide with no "flat" corresponding to
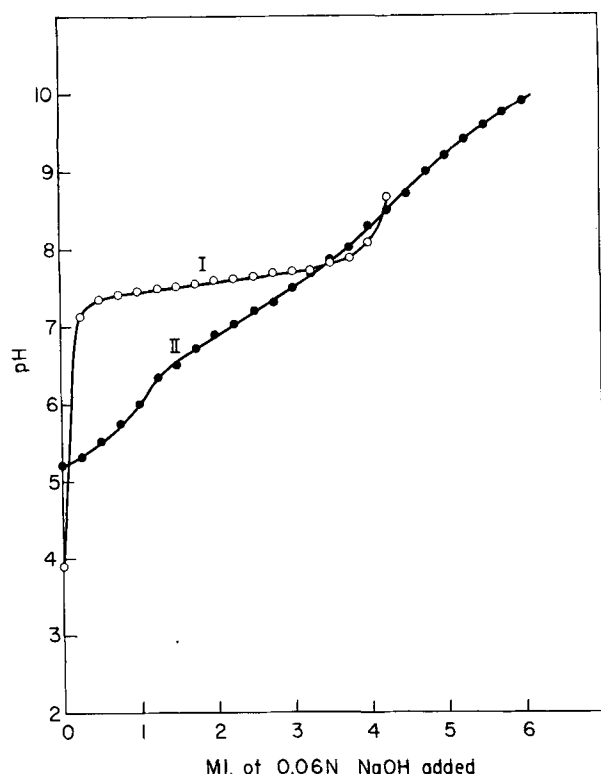
precipitation of zinc hydroxide, nor was any visible precipitation observed. Although the rate of rise is somewhat slower between pH 6.5 and 8.0, it is so rapid throughout that it seems unlikely that insoluble hydroxide or basic salt can be forming.

In contrast to the preceding behavior, addition of sodium hydroxide to a solution of Tamol and zinc chloride to which excess hydrochloric acid has been added gives a titration curve indicative of formation of a precipitate with consumption of alkali between pH 6.2 and 7.5, probably some basic salt of zinc and Tamol. The difference in behavior is most likely due to the fact that in the latter case the initial acidity of the solution is such that the Tamol is mostly precipitated, and so is not present in solution at a high enough concentration to react with the zinc and prevent its precipitation by the added hydroxide. Since at a pH of 6 a pure polyacrylate would still exist in the soluble salt form, this suggests the interesting possibility that it may not be the carboxylate groups giving an endpoint at pH 3.3 in the Tamol-hydrochloric acid titration curve which are responsible for the complexing power of the molecule for zinc ion but the other group which gives an endpoint at pH 7.

The fact that no precipitates formed in alkaline solutions containing Tamol indicates that the zinc ion concentration in equilibrium with the zinc-Tamol complex is lower than that in equilibrium with zinc hydroxide. Consequently, if equilibrium is established in emulsion systems containing Tamol to which zinc oxide is added, it would be expected that zinc oxide would dissolve until all the Tamol in the system had reacted with zinc ion, unless the Tamol is otherwise adsorbed or complexed with some other constituent of the system so as not to be free in solution. Hence destabilization by zinc oxide may involve removal of stabilizing agent from the system although here the species formed appears to be soluble. It is also quite possible that the complex which is formed may be surface-active and by adsorption at the oil-water interface promote formation of a water-in-oil emulsion.

Acknowledgments

FIG. 8. Titration curves of zinc chloride and of zinc chloride plus Tamol with sodium hydroxide.

I. 25 ml M/200 ZnCl₂ with 0.06 M NaOH.

II. 25 ml M/200 ZnCl₂ with 5 ml 3.133% Tamol with 0.06 M NaOH.

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[Received November 24, 1961]