capable of giving an enormous amount of information even when the exact natures of the components are unknown. Chromatograms of the type of product which you like and those you do not like may indicate a trend which will enable you to obtain your ideal material.

CONCLUSION

The perfumer naturally wants the raw material which will give him maximum results and he wants the material to be identical with each delivery. He, the perfumer, can do a lot to help the supplier to bring about this highly desirable state of affairs. Finally, can I just say that the number of times when you find you really need a pure compound will be relatively small. That master perfumer—nature—never offers a pure chemical to us, she always shades it off with blending agents.

[*Received : 25th August 1959*]

REFERENCES

[1] Krajkeman, A. J. *J. Soc. Cosmetic Chem.*, **7** (1956) 38.
[2] Mitchell, W. *Perfumery Essent. Oil Record*, **21** (1950) 41.

AMPHOLYTIC SURFACE ACTIVE AGENTS

C. D. MOORE, F.R.I.C.*

Based on a lecture delivered before the Society on 16th March 1959.

The general characteristics of surface active ampholytes are discussed with particular reference to their similarities and dissimilarities to the better-known types of the surface active agents. A re-classification of the long chain betaines is proposed, and the reasons for this suggested change are given.

AMPHOLYTIC SURFACE active agents have been known for a considerable time, but they have remained little more than chemical curiosities until very recently, owing to the difficulty of procuring suitable intermediates for their manufacture. The situation has changed radically over the last few years, due principally to the pioneering work on Fat and Petroleum Chemicals, carried out mostly in the U.S.A. At the time of writing, however, it would be fair to say that owing to the still comparative novelty of the Ampholytics, little is yet known regarding their practical application.

---

* Glovers (Chemicals) Ltd., Leeds, Yorks.

Consequently, discussion must mainly be confined to a description of their properties, and it will be a question for the expert in any field to apply them to his particular problem.

General structure of ampholytic surface active agents

The older surface active agents can be divided into three classes: (a) Anion active, (b) cation active, and (c) non-ionic. The first two classes are analogous with the inorganic salts, and depend for their properties on whether the long chain fatty radical resides in the anion or cation; the solubilizing counter ion when small, such as Na^+, NH_4^+, Halogen$^-$, $SO_3CH_3^-$ having little effect except that of promoting solubility. The non-ionic surface active agents depend on their solubility on a plurality of hydroxyl or ether linkages, being hydrated by means of hydrogen bonding with water, or to a much lesser extent polyoxonium hydrate formation.

By analogy with the inorganic salts, it would seem that ampholytic surface active agents corresponding to the amphoteric inorganic salts should be possible. While strict analogy is not feasible, this effect may be simulated by placing in the molecule various groups of opposite characteristics, for example,— NH_2 and — COOH, the effect of these groups being accentuated under proper conditions of *p*H, — NH_2, for example, being a base, most noticeable in acid media, and — COOH an acid, in basic solution. As the opposing ionic effect will be mostly suppressed under conditions ideal to the other radical, the attached fatty chain will be converted from the anion to the cation and vice versa, according to the *p*H of the solution, and thus become anion-active or cation-active. In aqueous solution, when unaffected by external agents controlling *p*H, the basic and acidic radicals neutralize each other as, for example, in amino acids; this condition is known as the isoelectric point, and is common to all amphoteric surface active agents. The isoelectric point is dependent on the relative strengths of the radicals of opposing polarity or numerical dissimilarity, and may vary from the very acid to the quite strongly basic side. It must be realized that there is not only an isoelectric point, but in many cases a broad zone in which an ampholyte may be practically isoelectric. An extreme case of this effect may be exemplified by reference to the simple amino acid glycine, between the *p*H values of 4·3 and 7·7 species other than the zwitterion represent less than two per cent of the whole. There is little doubt that this state of affairs exists in the surface active members, though generally to a less degree. From the above description there is every reason for stating that the ampholytic surface active agents show anion or cation active properties according to *p*H, but it is felt that there is no justification in comparing these products at their neutral points with the non-ionics, as is so often done. To consider them in this light is bound to be misleading because, while the net charge at the isoelectric point will be nil, the gross charge, of course, will remain high.

The number of ampholytic surface active agents possible is legion, due to being polyfunctional compounds, and, in practice, is only limited by the availability of suitable intermediates. The ampholytics are not confined to the derivatives of carbon and nitrogen, but may also be derivatives of sulphur, phosphorus, arsenic, etc., and for special purposes these derivatives may appear in commerce in due course ; in this discussion, however, we will confine ourselves to the compounds which are articles of commerce.

The ampholytic surface active agents in commerce are broadly based on two types of structure :

(a) Long chain *N* substituted amino acids, and
(b) long chain betaines.

In respect of the betaines, we feel that we should follow conventional ideas on these products, and include them in our discussions, but in future they would better be ascribed to a new class of surface active agent.

Products in class (a) are, for example, the *Amphionics*, *Deriphats*, *Tegos*, and in class (b) examples are *Ambiterics*, *Miranols* and *Amfaides*.

To illustrate the major points concerning ampholytes it would be better to discuss a limited number of examples at some length from each class of structure, referring to them under their chemical names. From class (a) we will discuss the β alkyl aminopropionic acids, and from (b) the straight chain betaines.

β ALKYL AMINOPROPIONIC ACIDS

The alkyl aminopropionic acids are obviously long chain derivatives of the amino acid alanine or β aminopropionic acid, and consequently they would be expected to behave in a similar manner, under many conditions, to the parent acid.

Effects of p*H*

The amino acids, with change of *p*H from one side to the other, pass through their isoelectric points, and at this point the amino acids exist in their zwitterion form. The isoelectric point occurs for the β alkyl aminopropionic acids at *p*H 4·3, and this suggests that the acidic strength is slightly greater than the basic strength ; it is, in fact, difficult to find an amino acid derivative which has the isoelectric point at *p*H 7·3. On each side of *p*H 4·3, of course, the anion or cation properties begin to appear, and in the case of the alkyl amino propionates are fully developed at *p*H 2 and *p*H 11, when the opposing effect is virtually suppressed.

Solubility

As pointed out previously, the β alkyl aminopropionic acids are typical amino acids, and therefore one would expect at the isoelectric point a region of lower solubility; this is, in fact, noticeable with this particular class. For instance, the dodecyl compound has a solubility at 20° C. of the order of 0·25 per cent at the isoelectric point, whereas the sodium salt with a natural *p*H of about 11·0 is extremely soluble, and at the other extreme the aminosulphamic acid salt at a *p*H of about 3·0 has a solubility greater than 5·0 per cent. Although there is obviously a considerable reduction in solubility in the zwitterion form, there is adequate solubility to provide most surface active characteristics, and in any case the solubility increases greatly with rise in temperature.

The hexadecyl compound has, as expected, lower solubility characteristics, and at the isoelectric point has a solubility of only 0·04 per cent, and the aminosulphamic acid salt a solubility of 0·02 per cent; the acetate is, however, much more soluble. The dodecyl and hexadecyl compounds' solubility increases with rise in temperature.

Surface Active Characteristics

The surface tension reducing properties have been indicated by Anderson, *et al.*[1,2], for instance, the dodecyl compound at a concentration of 0·1 per cent has an interfacial tension of less than 2 dynes/cm., and a surface tension of about 25 dynes/cm. This compound is, therefore, an exceptionally powerful wetting agent, and is approching the sulphosuccinates in this respect. The values given are fairly independent of *p*H, and our own tests on the comparative wetting times in relation to *p*H, using a sinking method, indicate that there is little variation over the *p*H range 3·5 to 10·1. This statement applies also to the hexadecyl compound where it has sufficient solubility to enable the data to be obtained.

The dodecyl amino acid is an excellent foam producer, the sodium salt being about twice as efficient in this respect as pure sodium laurate. Decrease in *p*H has some detrimental effect on the foaming properties to the extent that foam trials on the free acid show its foaming properties to be only about two-thirds that of the sodium salt, while the sulphamic acid salt of this compound is only about half as effective a foamer as the sodium salt. Hard water has little effect on the foaming power of the dodecyl compound, as is shown by the fact that foaming efficiency is reduced by only 10 per cent if water at 40° hardness is substituted for distilled water in the foaming trials. The hexadecyl amino acid has far less foaming power than the dodecyl compound, as is expected, and the foaming power of the sodium salt is completely repressed in water at 40° hardness, although the free acid is not so affected. Lack of solubility of the sulphamic acid salt of this compound renders foaming trials difficult, and its intrinsic lack of foaming makes it unsuitable as a foam-producing agent in any case. It must be realized that all long chain amino acids are not as resistant to hard water as the best amino propionates. Those based on α amino acids, and derivatives of dicarboxylic acids in which the carboxyls are in close proximity, such as those derived from aspartic acid, can show very high sensitivity to calcium and magnesium ions.

Critical Micelle Concentration

The β alkyl amino propionate salts are micelle forming at all *p*H's, and the critical micelle concentrations appear to be in line with those expected. For instance, potassium dodecyl alanate has a CMC of 0 0030 mol/l., as compared with potassium palmitate at 0·0022 mol/l., N dodecyl β alanine hydrochloride 0·010 and dodecyl trimethyl ammonium chloride 0·014 on the same terms.

Emulsification

The emulsification properties of the alkyl amino acids were assessed in the usual way with mineral and vegetable oils, fatty alcohols and acids using small proportions of ampholyte (i.e., 1 per cent on the oil) and repeating the trials at various *p*H values. In general, it is found that the amino acids are fair to good emulsifiers for fats and oils, except those of a paraffinic nature, for which type they are of little value. Both the dodecyl and hexadecyl compounds are particularly effective with fatty alcohols, but with vegetable oils, fatty acids, etc., the hexadecyl compound is the better of the two ; this is to be expected by analogy with commoner types of surfactants. Emulsions can be produced with the alkyl amino acids acting both as anionic or cationic emulsifiers, or at the isoelectric point, but as a general rule emulsions are more readily produced on the anionic side, i.e., with the ampholytes at fairly high *p*H. These results are in line with those obtained by using individual surface active agents of single effect.

It is possible, by adjustment of the *p*H, to change an emulsion based on ampholytes from anionic to cationic. This property, which is unique to the ampholytic surface active agents, could be extremely useful, because, as stated above, emulsions are more readily formed on the anionic side, and when the more difficult to obtain cationic emulsions are required, it is often a simple matter to prepare the emulsions anionically, and then by addition of the appropriate acid to alter the *p*H and render the emulsion cationic.

Solubilizing properties

As previously indicated, micelles are formed by the alkyl amino acids in solution at concentrations in accordance with that expected from their chain length and, by analogy with other types of surface active agents, they should show similar solubilization characteristics. Sodium laurate and sodium dodecyl amino propionate show characteristics and solubilizing power of the expected order when using geraniol and diphenyl methane as the solubilizates representing products of different polarity. 10 per cent solutions of sodium laurate and sodium dodecyl amino propionate will solubilize 4·4 per cent and 2·8 per cent of geraniol, and 1·4 and 2·3 per cent of diphenyl methane respectively. Similarity is also shown between the acetates and butyrates of dodecylamine and similar salts of dodecyl aminopropionic acid in their capacity to solubilize water in decanol. This is an example of inverted solubilization. The acetates and butyrates of both dodecylamine and dodecyl aminopropionic acid at 10 per cent in decanol, solubilized 5·2 and 4·4 per cent of water respectively.

Adsorption

The alkyl amino acids are adsorbed from solution most strongly at low *p*H, where they tend to simulate the effect of quaternary ammonium compounds in being fairly substantive, whereas at high *p*H they are adsorbed to a considerably lesser degree, as are anionic surface active agents.

It is realized, of course, that adsorption on human skin is a most important feature to the cosmetic chemist ; unfortunately, figures are not available for this, but guidance can be obtained by reference to results obtained in our laboratories by the use of cotton, wool, and human hair as the adsorbents.

Fig. 1, Curves A and B, clearly illustrates the marked adsorption effects at low *p*H, particularly on wool, and as the *p*H is increased an equally marked drop in adsorption, until it has reached a very small amount at *p*H 9·0 and is undetectable at *p*H 10·0. Adsorption on the much less polar material, cotton, is not so pronounced, but nevertheless follows the same pattern. With regard to adsorption on human hair, Curve C, it was found that at *p*H 2·5 the figure was close to that obtained with wool. Under our experimental conditions, it was not possible to obtain satisfactory results with human hair at higher *p*H values, but there is every reason to believe that hair will respond to ampholytes in a very similar way to wool.

The flattening of Curve B is no doubt due to the fact that cotton is saturated with a cation active product at a much lower concentration than wool or hair. Actually the figures at *p*H 3·0 correspond well with those obtained when a normal quaternary ammonium compound is adsorbed on cotton.

Compatibilities

Of all the properties expected with ampholytic surfactants, compatibility with other types ranks with their change of activity in regard to *p*H as by far the most important.

Table 1 is a compatibility chart using dodecyl aminopropionic acid, as the ampholyte in the form of the acid salt (sulphamic), the zwitterion

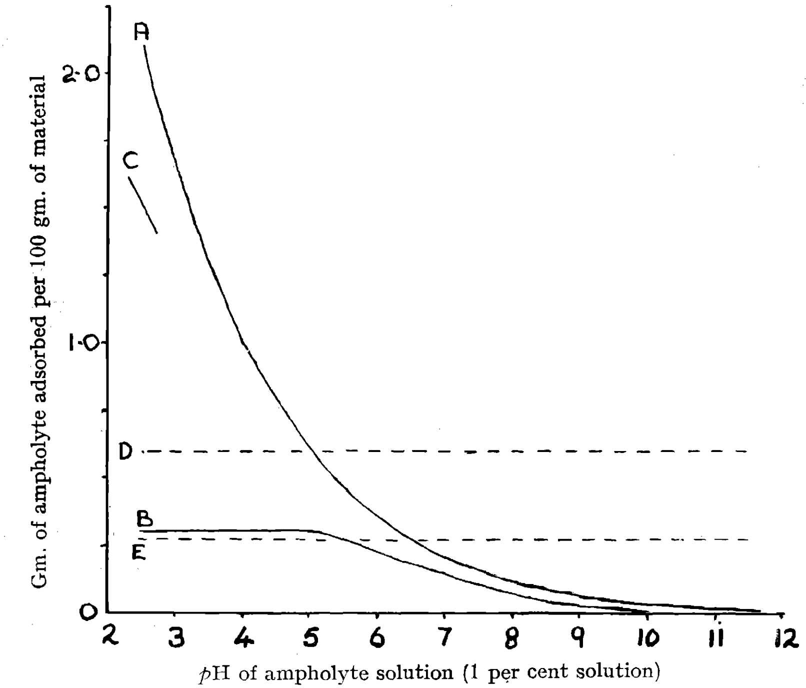

Fig. 1

Adsorption of ampholytes at various pH value.

A. Dodecyl amino propionic acid on wool.
B. Dodecyl amino propionic acid on cotton.
C. Dodecyl amino propionic acid on human hair.
D. Dodecyl betaine on wool.
E. Dodecyl betaine on cotton.

(isoelectric point) and the alkali salt (sodium). It will be noticed that compatibility with other surface active agents is almost universal, the only exception being incompatibility of the acid salt with anion active products. This is rather to be expected as the ampholyte, being only a comparatively weak base, is naturally strongly acid in solutions, with the result that in the case of admixture with soap, a precipitate of the free soap acid is formed.

Table 1

COMPATIBILITY IN SOLUTION

Alkylamino Acid	Anionics	Non-Ionics	Cationics
Acid Salt	Incompatible	Compatible	Compatible
Zwitterion	Compatible (Except Sulphonates)	Compatible	Compatible
Alkali Salt	Compatible	Compatible	Compatible

In the case of admixture with alkyl aryl sulphonates, the free sulphonic acid is formed and the sulphonic acid salt of the alkyl amino acid is not sufficiently ionized to be soluble.

The results shown in Table 1 were derived from trials carried out with stoichiometric quantities to obviate errors due to resolubilization, which is observed when either reagent is in excess, an error from which most solubility charts suffer.

The reasons for compatibility of the alkaline or zwitterionic forms with cationics is simply due to the fact that the aminopropionic acids do not form insoluble salts with the quaternary cation, and are, therefore, not removed from the sphere of action. They do not modify or inactivate cationics in the process of admixture with them, except by micellular incorporation. This point is most important, and proof was obtained by preparation of hexadecyl trimethylammonium β N dodecylaminopropionate. This product, notwithstanding its very high molecular weight, was found to be soluble in water, but had quite different surface properties from a mixture of hexadecyl trimethylammonium bromide and dodecyl amino propionate, and unlike the mixture it was bacteriologically inactive, which suggested that its adsorption properties were entirely different. Tests on textile materials actually showed considerable adsorption of quaternary ammonium compounds in the presence of the ampholyte in its anionic form. This in itself is a proof that the cationic properties of the quaternary ammonium compounds are not being altered or modified, although it should be recognized that in the presence of a very large amount of an alkyl amino acid adsorption can be suppressed, but this is due to the commonly occurring phenomenon of micellular incorporation.

Compatibility with the various commonly occurring ions such as calcium, magnesium, copper, barium, aluminium, zinc and chromium is dependent on the pH of the solution. The alkali salts of the amino acids show naturally high pH's and consequently heavy metals come down as hydroxides in their presence, while at the neutral point or in acid solution few metals form precipitates. Indeed, it is difficult to find a salt which is precipitated anything like quantitatively, a matter of great value in practice, but a considerable nuisance in analysis. The tendency to precipitate with salts increases with increasing chain length in the ampholytes, as with any other series of surface active agent.

THE LONG CHAIN BETAINES

This type of surface active agent appears to have been almost universally accepted as a typical ampholyte.

We have recently felt that the betaine-like surface active agents must be reclassified, as they are increasingly unacceptable either in theory or on practical results as true ampholytes. This does not infer that the betaines are any the less interesting; indeed, they may in time prove to be one of the most useful types for the solution of problems outside the general run.

Our reasons for suggesting reclassification of the betaines and similar products are as follows:

The betaines are internal quaternary ammonium compounds, and thereby carry an integral positive charge which is characteristic of all onium compounds. Removal of these charges is normally accompanied by the degradation of these compounds. The nitrogen in the amino acids, however, carries no such permanent charge, in fact the amino group behaves like a typical amino group in that a positive charge may be added or removed according to the *p*H of the medium, in accordance with the Lowry–Brönsted concept of acids and bases. From an examination of the structure of betaines, it would appear that the transfer of a proton would not be possible, and in accordance with the above theory, betaines would not, therefore, be expected to behave as acids. Aceto-betaine, the parent member of the series, has been quoted as having a pK_1 value of 1·84, and a pK_2 value too large to measure.

The only conclusion reached from the above evidence was that the betaines, whilst being cationic in strongly acidic media, would not appear to be capable of acting as acids towards bases or, in other words, as anion active products. In view of the potential importance of surface active betaines, further investigation was deemed very necessary. Potentiometric studies of the behaviour of aceto and β propiobetaines, the parent substances, together with dodecyl betaine and dodecyl-β-propiobetaine, were carried out, and from the results of these studies no indication of amphoteric behaviour in aqueous media could be observed. Non-aqueous titrations carried out in a strongly basic medium, in attempts to augment any potential acidic behaviour, were negative. A true ampholyte, e.g., an amino acid, gave the expected results in both aqueous and non-aqueous media. A literature search failed to reveal any evidence of alkali metal or organic base salts of betaines having been prepared. As the isolation of an alkali metal or organic base salt would be added proof either way, an attempt was made to prepare suitable organic base salts. In all cases the betaines were recovered unchanged. From the foregoing evidence, it must be concluded that betaines, as a class, do not exhibit amphoteric properties, and alkaline solutions of betaines are simply solutions of the compounds in free alkali. Further physico-chemical evidence in support of this belief was gained from adsorption trials (*Fig. 1*). Such trials carried out on cotton and wool fibres gave constant adsorption figures irrespective of *p*H; these results are in line with those expected from compounds carrying an integral charge and unlike the result expected from an ampholyte; and indeed, obtained with the alkyl amino acids. Under the circumstances, the betaines, long recognized as typical ampholytes, would appear to be best classified as members of the cation active type. However, such a degree of difference exists between them and the ordinary quaternary ammonium compounds that some name seems to be required to cover the general class which includes their sulphur analogues, the thetines and the theoretical possibilities from phosphorus, arsenic, etc. We felt that a name should be coined, and propose that the general class of surface active agent based on the internal onium structure, if our views are accepted, should be called *Intronium Surface Active Agents.*

The betaines and allied surfactants actually appear to be so complimentary to the ampholytes, or in certain cases excellent alternatives, that there is no reason why they should not continue to be studied together, provided that recognition is clearly made of their different properties.

An indication of the type of properties expected from the Intronium compounds can be gained by a study of the dodecyl and hexadecyl betaines.

Surface Active Characteristics

While not as effective wetting agents as the alkyl amino acids, the betaines are nevertheless of value in this capacity; the dodecyl compounds, for instance, being comparable in wetting power with well-known secondary alcohol sulphates. Little change in wetting power is noticed over a *p*H range of 3·0 to 10; if anything, the betaines act as slightly better wetters at a lower *p*H than they do at high.

The foaming capacity of the betaines is very similar to that of the alkyl amino acids, but the effect of *p*H is reversed and to a large extent levelled out. Whereas with the dodecyl amino acid a 50 per cent loss in foaming power was evident in the change from sodium salt to sulphamic acid salt, in the case of the dodecyl betaine, only about a 10 per cent loss in foaming power occurs, and that in the other direction, i.e., in the change from low to high *p*H. The even production of foam, together with an even level of wetting power throughout the entire practical *p*H range, is further support for the contention made above regarding betaines. In common with all other surfactants, the hexadecyl compound is well above the optimum chain length required for maximum foaming, but it is, for all that, a considerably better foaming agent than could be expected from a compound of such a chain length. Hard water is totally without effect on the foaming properties of the betaines, no difference being observed in our trials between the foam produced in distilled water and that produced in water at 40° hardness over the whole *p*H range.

Emulsification trials of the kind performed with the alkyl amino acids showed the betaines to have similar properties. While extremely poor emulsions of paraffin oils and waxes were possible, with vegetable oils and fatty alcohols, minor proportions of the betaines were capable of producing effective emulsions. The hexadecyl compound behaved normally in showing superiority over the dodecyl type as an emulsifying agent.

Compatibilities

A compatibility chart drawn up for the betaines would be similar to the one in Table 1. The betaines are thus compatible at all *p*H values with all classes of surfactants, with the single exception that an acid betaine will form a precipitate on addition to anionics.

Acid and neutral solutions of the betaines are compatible in all proportions with solutions of salts of calcium, magnesium, barium, aluminium, copper, nickel, zinc and chromium. Like the alkyl amino acids, at high *p*H the betaines will precipitate the heavy metals from solution. The hexadecyl compound was found, in our trials, to have identical compatibility properties with the dodecyl compound, and this is a point of divergence from the similarities observed between the alkyl amino acids and the betaines, and of surface active agents in general.

Having now described the betaines at some length, we can examine further properties of the long chain amino acids and betaines together.

Physiological Properties

The effect on skin of the alkyl amino acids depends upon *p*H, but examination of the results available indicate that on the alkaline side they are of a similar order to an ordinary soap of the same chain length, while on the acid side they show irritation effects comparable with those of the quaternary ammonium compounds. At neutrality (*p*H 7), skin irritation is reduced to the minimum. The triethanolamine salts appear particularly free of irritancy. The effect of the betaines on the skin has not yet been completely investigated, but it is possible to say at this stage that, in general, irritant effects are quite low.

Preservation

The preservation of preparations containing surface active agents from attack by microbiological organisms sometimes presents difficulties. We have examined this problem in our laboratories, using both dodecyl and hexadecyl amino propionates and betaines against aspergillus niger as an example of a vigorous growing and difficult organism to preserve against. At the natural high *p*H of the alkali salts, growth is inhibited to a large extent by the very alkalinity of the material. At concentrations of 1 per cent and 5 per cent in an artificially contaminated emulsion at *p*H 7 there was no growth at the high concentration and only slight growth at the lower. This also appertained at a *p*H of 3·5. Wherever slight growth took place it was easily controlled by the addition of a preservative such as 0·2 per cent of *p*-hydroxy ethyl benzoate. These particular surface active agents, therefore, could almost be said to be self-preserving against moulds, as the media used were prepared to simulate a cosmetic preparation which had been exposed to contamination with proteinous and other growth-supporting factors. Sabaraud's Maltose Agar media was the contaminant, and consequently the creams were far more contaminated than is ever likely to be met with in practice.

Bacteriological Aspects

The compatibility of ampholytic and intronium surface active agents with other surface active agents is a property which can be utilized in germicidal preparations, which have hitherto been impossible when using the better-known surface active agents.

A fuller report on this subject will be found elsewhere[8], but, briefly, the following points will be of interest :

It must be realized that when the article referred to above was written, the betaines were still considered as true ampholytes ; this, however, does not affect the published results or opinions to any great degree.

(a) In mixtures of alkyl amino acids with quaternary ammonium compounds, the high activity of the quaternary is maintained against the Gram positive organisms even when the alkyl amino acid is present as its sodium salt, and consequently in its anion active form. Under normal circumstances cation and anion active materials are incompatible and precipitate. It was generally thought that loss of bacterial activity in such circumstances was due to removal of the active constituent from the aqueous phase. This we felt was only half the truth. If, in fact, the precipitate had in some way been soluble, it would still have been inactive because of balance in the anion and cation. The bacteriological inactivity of the soluble hexadecyltrimethylammonium-β-*N*-dodecylaminopropionate was a proof of this supposition. Gram negative organisms are intrinsically more resistant to quaternary ammonium compounds as is well known, and they do not adsorb a quaternary ammonium compound as readily, consequently they are more sensitive to competition from other surface active agents. However, up to four times the amount of dodecylaminopropionate may still be added to a quaternary ammonium compound before the activity returns to the original figure.

The dodecyl compound is most useful for work with germicides, not only because of its higher intrinsic solubility, but also because it enhances the activity of the quaternary ammonium compound in certain proportions.

(b) In mixtures of quaternary ammonium compounds with long chain betaines against Gram positive organisms, there is no observed loss of activity in the quaternary ammonium compound, and against Gram negative organisms an increase in activity is observed, and this increase is maintained at a higher level than expected from the quaternary ammonium compound alone. This continued increase in activity may be due to the imposition of some antibacterial activity of the betaine type itself upon the whole.

(c) The alkali salts of alkyl amino acids in combination with phenols give results rather like those expected by solubilization in saponaceous materials, but, of course, inactivation by hard water is resisted to a large extent, particularly with the dodecyl compound.

(d) The betaines are particularly interesting solubilizing agents for phenols as they increase the activity of the phenol considerably, and the activity of the mixture does not fall to zero even with high proportions of betaines, as is the case with soaps.

It may be asked why a product like a betaine, in admixture with a phenol, should maintain activity at high concentrations of betaine contrary to expectations, when one considers the competing factor of micellular incorporation. This may be due to the fact that phenols apparently form some type of addition compound with betaines, and consequently the whole addition compound is probably acting as a bacteriocide in this case.

CONCLUSION

It is clear from the foregoing that the ampholytes and similar products have great potentialities, especially if one considers their properties and likely advantages in the proper light, and not merely regards them as slightly improved substitutes for standard type surface active agents. To reiterate, the most important potential characteristics of the ampholytes are that not only can one apply to them the very useful rules in regard to hydrophile/lipophile balance, but it is possible, even at this early stage, for one to make a semi-quantitative estimation regarding the effect of the anion/cation balance and the positioning of the isoelectric point. For instance, the isoelectric point may in many cases be approximately estimated from the relative acidic and basic strengths of the polar constituents, and as sufficient data becomes available it should ultimately be possible, by a combination of hydrophile/lipophile and anion/cation balances, to specify considerably more accurately than hitherto the exact type of surface active agent required for a particular purpose.

I wish to acknowledge the considerable advice and help afforded to me during the preparation of this lecture by my colleagues, M. Bell and R. B. Hardwick.

[*Received : 28th May* ***1959***]

REFERENCES

[1] Anderson, D. L. *J. Am. Oil Chemists' Soc.*, **34** (1957) 188.
[2] Anderson, D. L. *Am. Perfumer Aromat.*, **72** (1958) (No. 4) 59.
[3] Moore, C. D., and Hardwick, R. B. *Mfg. Chemist*, **29** (1958) 194.