

MODIFICATION OF ORGANIC REAGENTS BY THE FORMATION OF IONIC ASSOCIATES WITH SURFACE-ACTIVE SUBSTANCE

Salixova Ozoda Abdullayeva

Candidate of Technical Sciences,

Associate Professor of the Tashkent Institute of Chemical Technology.

E-mail: ozodaxon.salihova@gmail.com

Sidikova Gulchekhra Abdujalolovna

Senior Lecturer, Tashkent Institute of Chemical Technology.

E-mail: gulihonsidikova@gmail.com

ANNOTATION

Obtaining ion associates is one of the main ways of modifying electronegative or electropositive organic reagents with surfactant ions having an opposite charge. This path is typical for ionic surfactants and reagents that give ions in aqueous solutions. The formation of the corresponding ion associates can be predicted. For a long time it was believed that due to the high dielectric constant of water in aqueous solutions, the formation of ion pairs is unlikely. Surfactant ions interact with an organic reagent through an analytical-active group, so there is no competition with the formation of a reagent complex with a metal ion. This makes it possible to create a large number of practically new, more effective modified reagents from known organic reagents. This path is typical for ionic surfactants and chromophore polydentate chelating or, in general, complexing reagents.

Keywords: reagent, ionogenic, carbon, heterocyclic amines, ionic associates, trimethylcetylammmonium, sulfophthalein indicator, phenolcarboxylic acids, triphenylmethane.

INTRODUCTION

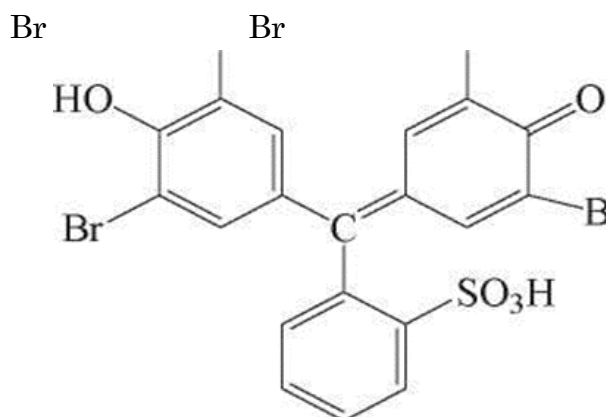
To modify organic reagents with negatively charged analytical-active groups, long-chain cationic surfactants containing at least 12 carbon atoms in the alkyl radical are used - salts of quaternary ammonium bases (for example, trimethylcetylammmonium bromide), alkylpyridinium salts (N chloride -cetylpyridinium) and other heterocyclic amines, primary, secondary and tertiary amines capable of being protonated in water to form cations. The modification of organic reagents of these classes is based on the concept of the formation of ion pairs (ion associates).

Reaction scheme for $R(OH)_2$ reagent with one functional-analytical group and one analytical-active group (AAF) ($-CO_2H$, $-OH$, $-SO_3H$) cationic surface-active substance can be written as follows:



The reagents of the classes of sulfophthalein indicators, phenolcarboxylic acids of the triphenylmethane series, and also some other classes of organic reagents have been most fully studied and most effective for analytical purposes.

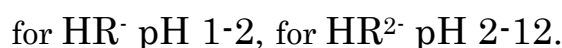
The formation of associates with superactive substances can be considered using the example of bromophenol blue - sulfophthalein indicator:



In aqueous solutions of the indicator, depending on pH, the following equilibria exist:



The optimal intervals for the existence of individual anionic forms of the indicator are as follows:



Adding to the solution of this compound cationic superactive substances with the length of the hydrocarbon radical C12 - C16 and a concentration significantly lower than the cmc (10^{-6} - 10^{-4} mol / dm³) in the pH range corresponding to the equilibrium between the forms HR⁻ and R²⁻, leads to a clearly fixed bathochromic shift of the absorption band of the R²⁻ form by 15-20 nm. The maximum wavelength (λ_{max}) for the form R²⁻.

BPS is equal to 590 nm, and for the same form in the presence of cetylpyridinium or cetyltrimethylammonium λ_{max} is 605 nm. It has been established that with an increase in the length of the non-polar hydrocarbon radical, the stability of the associates increases. This fact is interpreted as a result of participation in the binding of counterions not only electrostatic, but also hydrophobic interaction.

Associates with surfactants also form phenolcarboxylic acids of the triphenylmethane series. A feature of this group of reagents is the existence of two cycles in the molecule due to intramolecular hydrogen bonding. The inclusion of carboxyl, as well as carbonyl and hydroxyl groups in these cycles is reflected in the specifics of their protolytic properties and the nature of changes in the absorption spectra. Depending on the pH in chromazurol solutions, the following series of protolytic equilibria is possible:

RESULTS

These equilibria have been fairly well studied; it was found that the proton of the sulfo group dissociates first, then the carboxyl group of cycle I, then the carboxyl group of cycle II; the last to dissociate is the hydroxyl group included in cycle I. When a surfactant is added to a solution containing the H₂R²⁻ form of the reagent, a bathochromic shift of the maximum by 10–15 nm and a slight increase in the absorption intensity are always observed. The absorption spectrum of the form doubly ionized by carboxyl groups in the presence of surface active substances is slightly shifted hypsochromic (5-10 nm), and the form dissociated by the oxy group is bathochromic (10-20 nm). It is shown that these changes in the spectra are due to the formation of associates.

The associates obtained with different forms of the reagent have the following composition: for $H3R^-$ - 1:1, for $H2R^{2-}$ - 1:2, for $HR3^-$ - 1:3, for $R4^-$ - 1:4. Thus, the number of attached surfactant cations corresponds to the number of dissociated acid groups of the reagent. The electrical neutrality of the associates was confirmed by electrophoresis. In addition, it was found that the reagents themselves are hydrophilically hydrated, while their associates are hydrophobically hydrated.

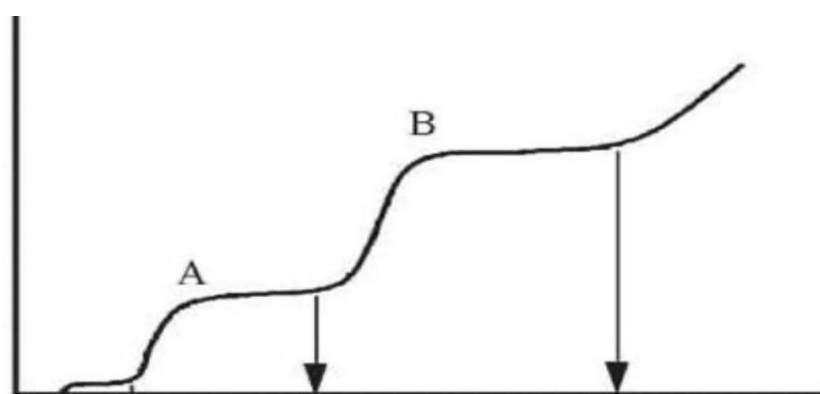
CONCLUSION

The study of the features of hydration of organic reagents modified with the help of surfactants showed that, upon the formation of an ion associate with surfactant, the reagent passes from a predominantly hydrophilic hydrated state into a hydrophobically hydrated one, characterized by a weakening of the interaction of a particle with water. A consequence of this may be a decrease in the polarity of the medium near the reagent molecule. A decrease in the hydration and polarity of the microenvironment of reagents modified with surfactants makes it possible to explain the direction of changes in a number of their characteristic properties: protolytic, complexing, solubility, extractability, etc.

Solubilization is the most important property of surfactants, which, like micellization, is associated with hydrophobic interactions. Solubilization is a phenomenon of a sharp increase in the solubility of low-polarity organic compounds in water in the presence of surfactants. As a result of solubilization, almost transparent thermodynamically equilibrium solutions are formed. The solubilization process is dynamic. A substance that dissolves in surfactant solutions is called a solubilisate (substrate).

Solubilization is usually expressed by analogy with solubility as the amount of a substance per unit volume of a surfactant solution, i.e., in mol / dm³, or attributed to one mole of micellar surfactant (the so-called molar solubilization) and expressed in mole of solubilisate / mol of surfactant .

The amount of solubilized substance, as a rule, increases with an increase in the surfactant concentration in the region of spherical micelles and increases abruptly upon transition from one form of micelles to another (for example, upon transition from spherical to spherical and then to lamellar (lamellar) micelles). The described regularity is illustrated by the molar solubilization isotherm.



Concentration field of active substance

Schematic representation of the molar solubilization isotherm

Solubilization begins to appear only after the first micelles are formed in the surfactant solution, which corresponds to CMC; After that, the molar solubilization begins to increase, since both the number of micelles and their size increase in this concentration range. After completion of the formation of spherical micelles (point A), molar solubilization remains constant up to the concentration when, at the second critical concentration of CMC2 micellization, spherical micelles do not begin to rearrange into spherocylindrical ones. After the formation of such micelles is completed (point B), solubilization remains constant in a certain range of concentrations until these micelles begin to rearrange into lamellar ones at the third critical concentration of CMC3 micellization. There is no solubilization limit in layered micelles, since the solubilize is located between the surfactant layers in the region of their hydrocarbon radicals, where an unlimited amount of the solubilized substance can be found.

1. For ionic surfactants, solubilization increases with an increase in the length of the hydrocarbon radical, for nonionic surfactants, with an increase in the number of oxyethylene units.
2. Compounds with a branched hydrocarbon chain have a greater solubilizing ability compared to aliphatic compounds with an equivalent chain length.
3. The solubilizing ability of a surfactant of one homologous series increases with an increase in the length of the hydrocarbon radical.
4. Solubilization increases when polar groups are introduced into the solubilize.
5. Increasing the temperature, as a rule, promotes solubilization. However, cases of a more complex effect of temperature on solubilization are known, especially in solutions of nonionic surfactants.
6. The amount of solubilization depends on the nature and structure of the surfactant and solubilize, the presence of foreign substances, including strong electrolytes.

The practical aspects of the application of solubilization are very wide. It is used in the textile industry to increase the solubility of dyes in water, in pharmacology, the production of polymers by emulsion polymerization, enzymatic catalysis.

Increase in the number of coordinated ligands. A typical example of this type of interaction is the reaction of complex formation of metal ions with phenolcarboxylic acids of the triphenylmethane series in the presence of surfactants. For chromazurol C in the pH range 1-8 in the absence of surfactants, the reaction product is formed during complexation with Al(III), Fe(III), Cu(II), Be(II) and Sc(III) with a molar ratio of M: R = 1:1 (Table 3). In the presence of surfactants, an intense band with X appears in the absorption spectra for CAS at 620 nm for Cu(II), 680 nm for Fe(III), 620 nm for Al(III), and 630 nm for Be(II). The values for different complexes varied in the range $(9.2-9.7) \times 10^4$. The study of complexation by the methods of equilibrium shift, variable concentrations, and physicochemical analysis showed that the products formed in the presence of surfactants have a greater number of coordinated ligands.

Molar ratios M: in the presence and absence of the field active substance(FAS)

Металл	рН	М:		FAS
		В отсутствие ПАВ	В присутствии ПАВ	
Be(II)	6	1 : 1	1:2	ЦП, ОП-10
Fe(III)	6	1 : 1	1:3	ЦП, ОП-7
Al(III)	6	1 : 1	1:3	ЦП, ОС-20
Sc(III)	7	1 : 1	1:3	ЦП, ОП-10
Cu(II)	6,5	1 : 1	1:2	ЦП, ОП-7

An increase in the number of coordinated ligands is observed for different types of OR. Indicative in this respect is the system Mo(VI) - bromopyrogallic red (BOD) - surfactant. In the absence of surfactants, molybdenum interacts very weakly with bromopyrogallic red, forming two complexes with $X_{max} = 540$ and 630 nm and molar ratios of components 1:1 and 1:2, respectively. The addition of CP (or other surfactants) leads to a sharp increase in the intensity of the absorption band with $X = 630$ nm, which is characteristic of the Mo(BOD)₂ complex. The absorption band of the 1 : 1 complex disappears completely.

The increase in the number of coordinated ligands observed in the presence of surfactants is explained by the loosening of the hydration shell of the metal ion due to the hydrophobic hydration of the complex.

LITERATURE

1. Будников Г. К. Модифицированные электроды для вольтамперометрии в химии, биологии и медицине / Г. К. Будников, Г. А. Евтюгин, В. Н. Май-стренко. - М. : БИНОМ. Лаборатория знаний, 2010.
2. Хандамов, Д. А., Муминов, С. З., Мирзакулов, Х. Ч., Салихова, О. А. Адсорбция метанола на модифицированных адсорбентах. *Universum: химия и биология*. 2019. , 12-15с.
3. Вережников В. Н. Коллоидная химия поверхностно-активных веществ / В. Н. Вережников, И. И. Гармашева, М. Ю. Крысин. - СПб. : Лань, 2015.
4. Волков В. А. Коллоидная химия. Поверхностные явления и дисперсные системы / В. А. Волков. - СПб. : Лань, 2015.
5. О.А.Салихова, Promising catalytic systems for the synthesis of cyclic ketones/ international conference on developments in education, sciences and Humanities. May -2022. Page No 351-354. <https://econferencezone.org>. Hamburg, Germany.
6. Гусев С. В. Некоторые экстракционные системы с ПАВ: применение и исследование / С. В. Гусев, О. С. Кудряшова // *Вестн. Перм. ун-та. Серия: Химия*. - 2013. - Т. 9, вып. 1. - С. 29-36.
7. Зиятдинова Г. К. Использование поверхностно-активных веществ в вольтамперометрическом анализе / Г. К. Зиятдинова, Э. Р. Зиганшина, Г. К. Будников // *Журн. аналит. химии*. - 2012. - Т. 67, №11. - С. 968-979.
8. Штыков С. Н. Химический анализ в нанореакторах / С. Н. Штыков // Там же. - 2002. - Т. 57, № 10. - С. 1018-10.