Journal of Analytical Chemistry, Vol. 55, No. 7, 2000, pp. 608–614. Translated from Zhurnal Analiticheskoi Khimii, Vol. 55, No. 7, 2000, pp. 679–686.

REVIEW

Surfactants in Analysis: Progress and Development Trends

S. N. Shtykov

Department of Chemistry, Saratov State University, Astrakhanskaya ul. 83, Saratov, 410026 Russia

Received July 22, 1999; in final form, November 2, 1999

Abstract—The history of the application of surfactants in analysis; physicochemical principles for modification of analytical systems using surfactant ions and surfactant-based microheterogeneous organized systems; and the progress and trends in the further application of surfactants to the separation, preconcentration, and determination of organic and inorganic compounds are considered.

Surfactants have been used in analytical chemistry for more than 30 years. In some cases, the application of surfactants not only improved the performance of the known separation, preconcentration, and determination methods, but gave rise to their new versions as well. The methods like micellar versions of solvent extraction, liquid chromatography, electrokinetic chromatography, and room-temperature phosphorescence [1–3] are most widely known. The achievements due to the use of surfactants in some methods of analysis, separation, and preconcentration were discussed in part in the monograph [1] and reviews [2–10]. However, little has been reported about the history and trends in this field of analytical chemistry. These aspects are the subject of this paper.

SPECIATION AND PHYSICOCHEMICAL PROPERTIES OF SURFACTANTS IN SOLUTION

A brief consideration of this problem is necessary because of the fact that different forms of surfactants imply different mechanisms of influence on the analytical forms of reactants. It is known that amphiphilic species of commonly used anionic, cationic, and nonionic surfactants exhibit slight (10^{-4}–10^{-2} M) ionic or molecular water solubility [1]. A further increase in the surfactant concentration results in spontaneous self-association of individual ions or molecules into micelles and a drastic increase in the overall water solubility of the surfactant. In the case of ionic surfactants, this takes place at a certain temperature called the Kraft point. The lowest surfactant concentration at which micelle formation occurs is called critical micelle concentration (CMC). From here on, we will not consider all amphiphilic molecules capable of changing the surface tension when adsorbed at the water–air interface but only micelle-forming ones; that is, the molecules spontaneously forming organized assemblies, or micelles, in the solution bulk [1].

The micelles formed at the critical micelle concentration are spherical [1]. When the micelles are affected by electrolytes or other additives or when the surfactant concentration in water is more than ten times higher than CMC, the spherical micelles, as a rule, are transformed into cylindrical ones (CMC_2), and the solubility further increases [11]. The assemblies of surfactant molecules formed in water are called normal micelles. Their outside surface is hydrophilic, and the hydrocarbon radicals constituting the core of the micelle form a nonpolar medium. The micelles existing in nonaqueous solvents are called reversed micelles. In these micelles, the hydrophilic groups of the surfactant molecules and water are in the polar core, and the hydrocarbon radicals are in contact with the nonaqueous solvent.

Other types of microheterogeneous self-organizing assemblies of surfactant ions or molecules include microemulsions, which can be of the oil-in-water or water-in-oil type, depending on which solvent dominates [10, 12]. Microemulsions consist of 3–5 components and involve a surfactant, a so-called cosurfactant (a short-chain alcohol, amine, or ether), a nonpolar hydrocarbon (C_6–C_{12}), an electrolyte, and water. Microemulsion particles (5–50 nm in diameter) are much larger than micelles (<3–5 nm), and their interface is more heterogeneous. They are widely used in analysis [2, 3, 10, 13, 14].

Vesicles and liposomes are more rarely used in analysis [2]. Hydrophobic surfactant ions incorporated into them have, as a rule, two hydrocarbon radicals. These radicals arrange themselves towards each other and form a closed bilayer charged on the inside and on the outside. Vesicles and liposomes (50–150 nm) are even larger than micelles. In liposomes, amphiphilic lipid molecules act as surfactants. Another type of self-organizing systems formed on a solid support under contact with a surfactant monolayer on a liquid surface includes Langmuir–Blodgett films used in chemical sensors [15].

The solutions containing any of these types of surfactant assemblies are classified as liquid microheterogeneous organized media [2–7, 9, 10, 16]. These are transparent and optically isotropic media, in which supramolecular assemblies of surfactant molecules form an individual microscopic pseudophase in the sol-

1061-9348/00/5507-0608$25.00 © 2000 MAIK "Nauka/Interperiodica"

vent bulk. These media are single-phase and homogeneous on the macroscopic scale but microheterogeneous and two-phase at nanolevels.

One can point out some main features of microheterogeneous organized media that make them extremely efficient for analytical applications [2, 3, 6]:

(1) the ability to bring together and concentrate the components of the analytical reaction, even those with different hydrophobicity;

(2) multifunctional and multicenter interaction of the microphase with the solubilized substrate governed by hydrophobicity;

(3) pronounced oriented sorption governed by electrostatic, hydrophobic, and conformational factors, which, in their turn, determine the location and physicochemical properties of the substrate in the microphase of the organized medium;

(4) noticeable microscopic heterogeneity of the environment within the microscopic pseudophase in the direction from the pseudophase–solvent interface to the center of its core, which manifests itself as drastic changes in the dielectric constant, microscopic viscosity, polarity, acidity, and other properties of the environment.

Thus, in surfactant-based organized media, all changes in the solution properties occur locally near the solubilized particle rather than in the solvent bulk. That is, the unique properties of aqueous media necessary for the activation of polar (ionic) components of the reaction are combined with the hydrophobic and orienting microscopic environment of the microscopic pseudophase, in which less polar components of the reaction are dissolved. Polar components are usually localized at the outer surface of the micelle–water interface, and nonpolar components are localized nearby, on the inside. Nonaqueous solvents that came into play in the 1960s could provide neither this closeness nor this concentration of the reagents.

These properties of microheterogeneously organized media form a basis for their operation both in analytical reactions and in separation and preconcentration of analytes. These properties are in many ways similar to those of enzyme active centers, which allows one to draw the formal parallel between the reactions in organized and living systems and to call the former "bioid" [2, 10, 16]. Surfactants in organized media are used almost in every field of chemical analysis.

The effect of surfactant ions on the analytical processes and systems is based on different principles. As a rule, it is connected with the formation of hydrophobically hydrated neutral reagent (chelate)–surfactant ion pairs [1]. The fact that the mainly hydrophilic type of hydration of both the reagent and the metal ion changes to the hydrophobic type in formation of the chelate ion pair is responsible for the mechanism of the action of surfactant ions in photometric analytical reactions. Another result of this action is the change in the phase distribution of particles in the liquid–liquid extraction system and in the character of the exchange processes in the mobile phase–adsorbate–adsorbent system [1]. The latter takes place, say, in reversed-phase ion-pair liquid chromatography with hydrophobic interactions when surfactants are used as modifiers of mobile or stationary phases [5, 7, 9, 17].

One should note that, though the mechanisms of the action of surfactant ions and surfactant-based organized media are different, the resulting effect on the properties of the analytical system components and on the analytical phenomena is much the same. Both in the formation of ion pairs by hydrophobic hydration of the reagent and in the solubilization of the reagents within the microphase of the organized medium, the properties of the microscopic environment of the particles change substantially [18], as well as the hydrophobicity, hydration, rigidity, and conformation of the particles themselves. In its turn, this changes the whole set of physicochemical properties of the components of the analytical process, namely, protolytic, tautomeric, complexing, redox properties, charge distribution in the molecule, and intra- and intermolecular energy and electron transfer; affects the interphase distribution of particles and their solubility; and influences the rate, direction, and equilibrium of analytical reactions [1, 2]. As a result, the intensity of the analytical signal increases substantially; spectroscopic, electrochemical, and chromatographic parameters are improved; and, as a result, the sensitivity and selectivity of analytical determinations increase.

APPLICATION OF SURFACTANTS IN ANALYSIS

Since the early 1920s, instances have been known when the color of the indicator changes in the presence of ionic or colloid forms of surfactants, and a so-called "colloid error" of colorimetric pH measurement arises [19]. However, attention to this fact was first drawn only in 1934 when Hartley published the paper [20]. According to the proposed "rule of signs," the most significant changes in the color and properties of dyes are observed when the charge of the surfactant ion is opposite to the indicator charge. This phenomenon was later used for the determination of ionic surfactants by titration with a standard solution of another surfactant counterion in the presence of an indicator [21] and for the determination of CMC [22]. The analysts paid attention to this fact only 20 years later when they studied the protolytic properties of indicators in the presence of surfactant ions and micelles [23]. The further chronology of the use of surfactants in analysis is the following:

1965, V. Svoboda and V. Chromy, titrimetry and photometric analysis [24];

1972, N. Ishibashi and K. Kina, fluorescence determination of metal ions [25];

1974, R.L. Venable and R.V. Ballad, atomic absorption analysis [26];

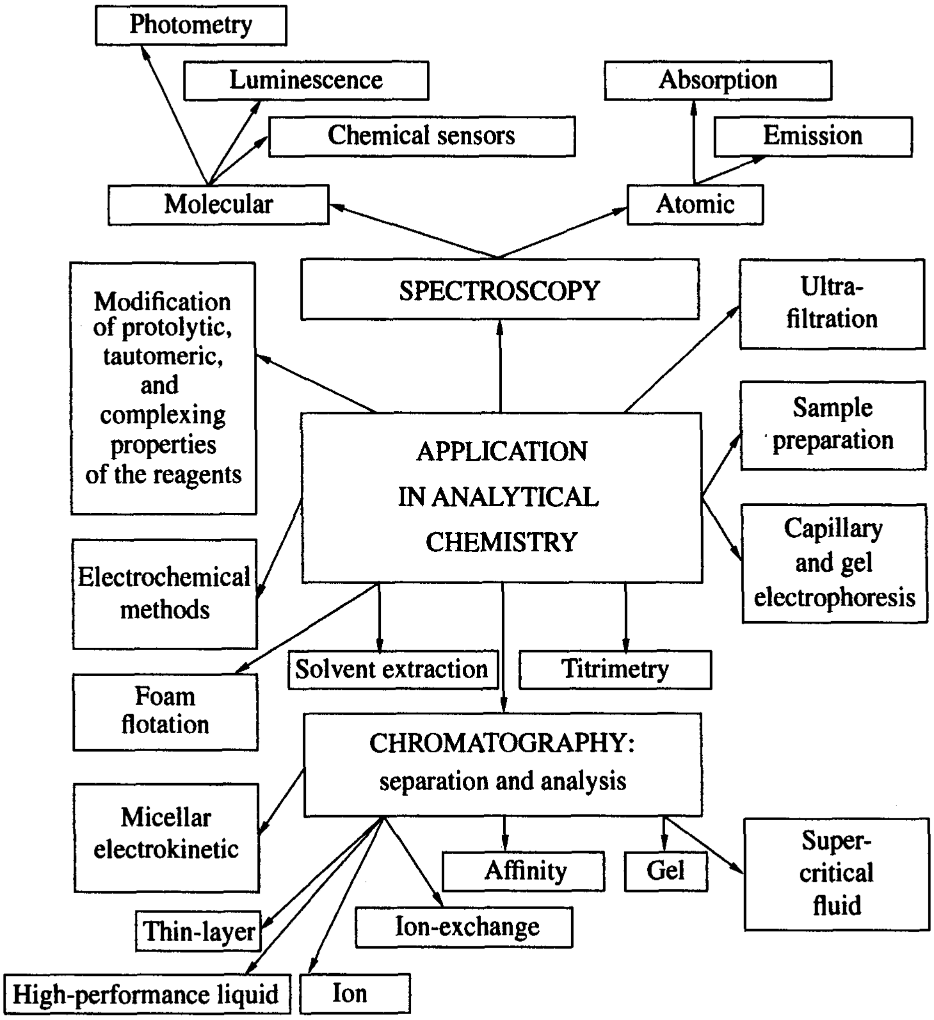

Fig. 1. Fields of application of surfactants in analytical chemistry.

1977, H. Ishii and H. Watanabe, micelle extraction [27];

1979, D.W. Armstrong and R.Q. Terrill, micellar thin-layer chromatography [28];

1980, D.W. Armstrong and S.J. Henry, micellar high-performance liquid chromatography [29];

1980, L.J. Cline Love, M. Scriles, and J.G. Habarta, micellar room-temperature phosphorescence [30];

1984, S. Terabe, K. Otsuka, K. Ichihara, *et al.*, micellar electrokinetic chromatography [31].

Figure 1 shows that, at present, surfactants are widely used in molecular and atomic absorption and emission (luminescence) spectroscopy, potentiometry, voltammetry, titrimetry, various versions of chromatography (thin-layer chromatography, high-performance liquid chromatography, ion chromatography, affinity chromatography, supercritical fluid chromatography, and gel chromatography), extraction, flotation, ultracentrifugation, capillary and gel electrophoresis, and other methods for determination and separation of organic and inorganic substances. In addition, surfactants are used for modifying the protolytic, tautomeric, and complexing properties of organic reagents and simplifying sample preparation for a number of samples [1, 2, 18, 32–34]. Summarizing almost 2000 publications shows that almost 60% papers are on spectrophotometry, and about 30% are on chromatographic analysis (Fig. 2) [2, 16]. The dynamics of publications on the use of organized media in some methods of analysis is shown in Fig. 3.

Application of surfactant ions. Ionic surfactants are used, in particular, for the modification of physicochemical properties and reactivity of organic reagents [1]. The modification is due to the formation of neutral reagent–surfactant ion pairs stabilized by both electrostatic and hydrophobic interactions [35]. It was shown [36] that the attachment of a hydrophobically hydrated surfactant cation to the reagent ion strengthens the structure of water in the vicinity of the particle and results in the hydrophobic rather than hydrophilic hydration of the ion [1, 37, 38]. The essence of the phenomenon is in the fact that the interaction between water molecules becomes stronger, and the interaction between water and the reagent becomes weaker. This lowers the polarity of the microscopic environment of the reagent. Consequently, this changes the protolytic, tautomeric, and complexing properties of the reagent and its electronic absorption and emission spectra, and weakens the hydration of the metal ion bound to the reagent [1, 18].

Ion pair formation between anionic forms of chelating organic reagents and cationic surfactants is widely used in the photometric determination of metal ions [1]. As a rule, the reagent–surfactant and metal–reagent–surfactant ion pairs are poorly soluble in water because of their hydrophobicity. To disperse them and obtain soluble forms for photometric determination, a small (three- to fivefold) excess of a cationic surfactant (to form mixed micelles) or micellar solutions of nonionic surfactants are added, or the chelate ion pairs are extracted by a nonaqueous solvent (extraction–spectrophotometric analysis). The latter technique is also used in extraction–fluorimetric and extraction–atomic absorption analysis [1]. Solvent extraction of surfactant-containing ion pairs is also used for the separation of mixture components [1].

Photometric reactions in the presence of surfactant ions and micelles were most extensively studied from the mid-1970s to the late 1980s (see Fig. 3) [1]. An examination of more than 1000 papers showed that the complexation of metals with organic reagents in the presence of surfactants can be followed by a two- to tenfold increase in the absorption and by an additional 20- to 100-nm bathochromic shift in the absorption spectra. These spectral changes, as well as the increasing sensitivity and selectivity of photometric determinations result from the changes in hydration of the particles in the solution and the following related processes [1, 38]: (1) increase in the number of ligands coordinated by the metal ion; (2) shift of the complex formation pH to the more acidic region; (3) increasing stability of chelates in solution; and (4) multicenter interaction in the metal–reagent–surfactant system.

In titrimetry, surfactant ions are used for two purposes: as titrants in the determination of counterions in aqueous or two-phase systems and as modifiers of metallochromic indicators in determination of metals [1]. In the former case, potentiometric or visual end-point detection is used, and in the latter case, visual end-point detection is used. The use of surfactant ions in complexometric titration somewhat enhanced the contrast of the color change of the metallochromic indicator and improved the selectivity of determinations because of the shift of the pH of complex formation and the difference in the stability of chelates in aqueous solutions [1].

In potentiometry with ion-selective electrodes and potentiometric titration, surfactant ions are used as main components of the electroactive substance of the ion-selective electrode membrane [1]. A counterion of another surfactant (cationic surfactant–anionic surfactant) or any organic or inorganic counterion can serve as another component of the membrane [39]. The membrane can contain nonionic surfactants as complex ion pairs with barium cation and tetraphenylborate anion [40]. The field of application of these surfactant-based electrodes grows steadily [41].

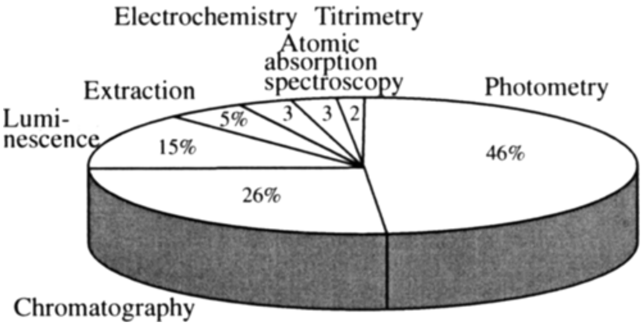

Fig. 2. Distribution of papers concerning application of surfactants in analysis by individual determination, separation, and preconcentration methods.

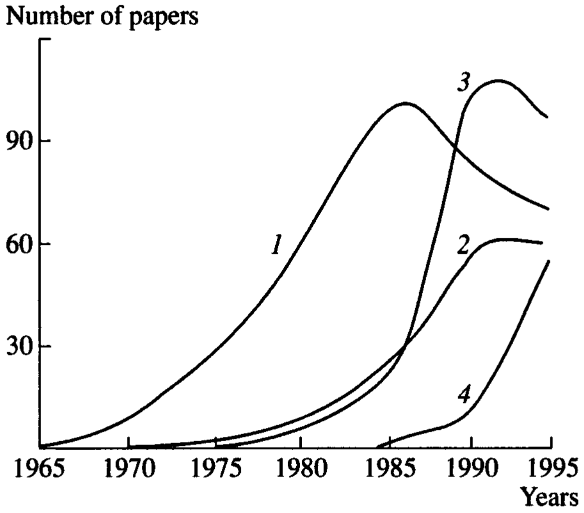

Fig. 3. The dynamics of publications concerning application of surfactants in (*1*) photometry, (*2*) luminescence analysis, (*3*) micellar liquid chromatography, and (*4*) micellar electrokinetic chromatography.

In reversed-phase ion-pair high-performance liquid chromatography and thin-layer chromatography, the use of surfactant ions makes it possible to control the eluting capacity of the water–organic mobile phase and the selectivity of separation of organic and inorganic ions [42]. The effect of surfactant ions is due to their adsorption on the stationary phase and the electrostatic interaction with the counterions to be separated in solution. An increase in the concentration of the surfactant ions in the mobile phase both increases the retention time of the counterions and extends the elution intervals, thus improving the selectivity of their separation. An increase in the concentration of the organic solvent in the mobile phase has the inverse effect. Theoretical models and application of ion-pair high-performance liquid chromatography and thin-layer chromatography are considered in [43, 44].

The formation of hydrophobic reagent–surfactant ion pairs is used in extraction–fluorimetric and extraction–atomic absorption analysis, for the extraction and flotation separation of organic and inorganic compounds, and in gravimetry [1].

Application of surfactant micelles. Surfactant micelles are more widely used in analysis than ions. This is due to greater opportunities for varying the properties of the microscopic environment of the reagents and their solubility, the protective action of the interface produced by the surfactant molecule (ion) assembly, the effects of bringing together and concentrating the particles, and other factors mentioned above. All these factors, as a rule, act simultaneously.

In titrimetry, surfactant micelles act as an environment for the reagents and modifiers of the reagent properties, such as in acid–base, redox, or complexometric titration [1, 45, 46]. This makes it possible to determine poorly soluble hydrophobic acids, bases, and other organic compounds by titrimetry and to enhance the range of the titrants used, indicator systems, methods for end-point detection, and ways of attaining an equilibrium of the analytical reaction.

In the determination of metals by micellar photometric analysis, the effects are similar to those observed with dispersed chelate ion pairs, but the analytical signal is more steady and reproducible. In addition, the use of micelles makes it possible to find the best spectral characteristics of the solubilized chelates and their analytical properties using, say, strong electrolytes or organic solvents [1, 47]. Another, more promising field of application of surfactant micelles in photometry is the determination of organic compounds [48, 49].

The luminescence of organic compounds and metal chelates in organized media has become the subject of study much later than their photometric properties. However, the researchers did not restrict themselves to normal micelles, as this was the case in photometry, but applied reversed micelles, microemulsions, and vesicles as well [3]. The observed spectral and analytical effects in fluorimetry, phosphorimetry, and chemiluminescence were more prominent than in photometry. The intensity of luminescence of many compounds increased 2–1000 times, which made it possible to lower the detection limits for 28 elements and more than 40 organic compounds by one or two orders of magnitude. One of the reasons for that large number of compounds determined by luminescence is the increasing solubility of hydrophobic luminophors solubilized in micelles or microemulsions.

The most interesting results were obtained and the most significant advance has been made in the application of organized media in phosphorimetry. The authors of [50] have first demonstrated that the phosphorescence signal due to micelles can be observed at room temperature rather than at 77 K. This effect was first used in analysis in [30]. Summarizing the data obtained showed that there are two necessary conditions for observing micelle-stabilized room-temperature phosphorescence [2, 3, 51]: (1) the presence of a heavy atom stimulating the intersystem crossing of the excitation energy from singlet to triplet state; and (2) removal of oxygen, which is the main quenching agent for the triplet state of molecules from the solution. In anionic surfactant micelles, thallium(I) salts are commonly used as heavy atoms [51, 52]. For a long time, deoxygenation of the solution was the most labor-consuming stage of the determination until the authors of [53] proposed sodium sulfite for the removal of oxygen in 1986.

A step forward was made after sensitized micelle-stabilized room-temperature phosphorescence based on the triplet–triplet excitation energy transfer was implemented in phosphorimetry. Originally, the substances were determined indirectly by the phosphorescence of biacetyl, which has the phosphorescence quantum yield close to unity [54]. Later, the method based on the more selective direct determination of analytes by their own phosphorescence was proposed [55–57].

The main achievements due to the use of micelles and microemulsions in flame and electrothermal atomic spectroscopy are the following [1, 2, 16]: (1) the intensity of the analytical signal increases 1.5–4 times; (2) the background intensity decreases, and the selectivity improves; (3) the sample preparation becomes simpler, and the analysis takes less time; (4) the analytical range for metal ions and operating pH range are extended. The first systematic investigations into this field were made in [58–60].

When surfactant micelles and microemulsions are used in electrochemical analysis, two processes should be taken into account: adsorption of surfactants on the electrode surface and solubilization of electroactive substances in the microscopic pseudophase of the organized media [1]. The phenomena observed in this case are thoroughly considered in reviews [1, 4, 6, 61]. The use of organized media made it possible to solve the following problems: (1) to determine redox potentials and study electrochemical behavior of organic substances insoluble in water; (2) to increase the electrochemical activity of a number of substances and stability of electrolytically generated radicals and intermediates; (3) to improve the sensitivity and selectivity of determination of organic and inorganic substances [62, 63]; and (4) in some cases, to make the use of organic solvents unnecessary, thus maintaining high conductivity of the solution.

Organized media, especially normal micelles, are widespread in various separation and preconcentration methods [1, 2, 5–7, 9, 10, 16]. More than 800 papers describe their use as modifiers of mobile and stationary phases in high-performance liquid, thin-layer, ion, gel, and supercritical fluid extraction, and micellar electrokinetic chromatography and capillary zone electrophoresis. First, surfactant-based micellar mobile phases were used in gel chromatography [64]. Later, it was shown that the retention time and selectivity of separation are governed by the following parameters: (1) surfactant nature and concentration, (2) solution pH and ionic strength, and (3) constants for organized medium–substrate binding.

The developed micellar liquid chromatography made it possible to simultaneously separate hydrophilic and hydrophobic substances, charged and neutral species, and optically active molecules; to make column regeneration unnecessary; to apply an electrochemical detector in gradient elution; and to directly inject body fluids into the column. Micellar mobile phases are especially efficient when a fluorescence or phosphorescence detector is used, because, in addition to the better separation, the intensity of the analytical signal also increases. One should note that the method is simple, efficient, and the necessity for using toxic organic solvents in micellar thin-layer chromatography can be eliminated [17, 28, 65–67].

The development of micellar electrokinetic chromatography in 1984 was the most important result of the application of micelles in capillary electrophoresis. This method combined the advantages of high-performance liquid chromatography and capillary zone electrophoresis [31]. High speed and efficiency of separation of both neutral and charged particles give rise to its extensive development at present (Fig. 3).

Micellar extraction is another example of successful application of micelles in separation and preconcentration [27]. Originally, only micellar solutions of nonionic surfactants were used, and phase separation of the solution was attained under heating to cloud point. Preconcentration factor was from 20 to 100. At present, the methods are found for stimulating the initiation of a new phase in the case of ionic surfactants as well [68]. Micellar extraction is successfully combined with determination, say, by photometry [27] or chromatography [69]. The possibility of using three-phase systems based on fluorine-containing surfactants with preconcentration factor of 10^4 was demonstrated [70]. The application of micelles and microemulsions in preconcentration and separation is described in more detail in the reviews mentioned above.

DEVELOPMENT TRENDS

The examination of papers makes it possible to recognize three avenues of research concerning further application of microheterogeneous organized media in analytical chemistry. The synthesis of functionalized surfactants whose molecules contain functional groups or macrocycles for selective binding of metal ions or organic molecules and their application in molecular spectroscopy, solvent extraction, and flotation can be placed in the first group. Synthesis and application of surfactants containing chiral atoms for analysis of enantiomers or surfactants containing supramolecular groups (cyclodextrins, calixarenes, etc.) for the chemistry of host–guest complexes seems promising.

Another group of papers involves widening the scope of application of microemulsions, vesicles, and Langmuir–Blodgett films in various methods of analysis. The third group deals with widening the scope of determination, separation, and preconcentration methods both by using the two former approaches and by using the reactions in excited state (triplet–triplet transfer, triplet–triplet annihilation, magnetic field-induced spin-selective reactions, etc.). Further development of micellar extraction, micellar electrokinetic chromatography, and micellar ultracentrifugation combined with various methods for determination of organic and inorganic compounds is necessary.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 97-03-33393a.

REFERENCES

1. Savvin, S.B., Chernova, R.K., and Shtykov, S.N., *Poverkhnostno-aktivnye veshchestva* (Surfactants), Moscow: Nauka, 1991.
2. Shtykov, S.N., *Proc. Int. Trace Anal. Symp.'98*, Tokyo, 1998, p. 173.
3. Shtykov, S.N. and Goryacheva, I.Yu., *Opt. Spektrosk.*, 1997, vol. 83, no. 4, p. 698.
4. Hinze, W.L., *Solution Chemistry of Surfactants*, Mittal, K.L., Ed., New York: Plenum, 1979, vol. 1, p. 79.
5. Hinze, W.L., *Ann. Chim. (Ital.)*, 1987, vol. 77, nos. 1–2, p. 167.
6. Pelizzetti, E. and Pramaouro, E., *Anal. Chim. Acta*, 1985, vol. 169, p. 1.
7. Pelitstsetti, E., Pramauro, E., and Minero, K., *Zh. Ross. Khim. O-va*, 1995, vol. 39, no. 1, p. 129.
8. Pilipenko, A.T., Volkova, A.I., Vasil'chuk, T.A., and Pshinko, G.N., *Zh. Anal. Khim.*, 1989, vol. 44, no. 7, p. 1157.
9. Berthod, A. and Dorsey, J.G., *Analysis*, 1988, vol. 16, no. 2, p. 75.
10. Watarai, H., *J. Chromatogr.*, 1997, vol. 780, p. 93.
11. Serdyuk, A.I. and Kucher, R.V., *Mitsellyarnye perekhody v rastvorakh poverkhnostno-aktivnykh veshchestv* (Micellar Transitions in Solutions of Surfactants), Kiev: Naukova Dumka, 1987.
12. *Micellization, Solubilization, and Microemulsions*, Mittall, K., Ed., New York: Plenum, 1977. Translated under the title *Mitselloobrazovanie, solyubilizatsiya i mikroemul'sii*, Moscow: Mir, 1980.
13. Ramos, R.G., Coque, A.G., and Berthod, A., *Anal. Chim. Acta*, 1988, vol. 208, no. 1, p. 1.
14. Shtykova, L.S., Mel'nikov, G.V., Shtykov, S.N., and Goryacheva, I.Yu., in *Problemy analiticheskoi khimii* (Problems of Analytical Chemistry), Saratov: Saratov Gos. Univ., 1999, p. 40.
15. Blinov, L.M., *Usp. Fiz. Nauk*, 1988, vol. 155, no. 3, p. 443.

16. Shtykov, S.N., in *Problemy analiticheskoi khimii* (Problems of Analytical Chemistry), Saratov: Saratov. Gos. Univ., 1999, p. 26.
17. Sumina, E.G., Shtykov, S.N., Parshina, E.V., *et al.*, in *Problemy analiticheskoi khimii* (Problems of Analytical Chemistry), Saratov: Saratov. Gos. Univ., 1999, p. 52.
18. Shtykov, S.N. and Parshina, E.V., *Zh. Anal. Khim.*, 1995, vol. 50, no. 7, p. 740.
19. Jarisch, A., *Biochem. Z.*, 1922, vol. 134, p. 177.
20. Hartley, G.S., *Trans. Faraday Soc.*, 1934, vol. 30, p. 444.
21. Samis, C.S. and Hartley, G.S., *Trans. Faraday Soc.*, 1938, vol. 34, p. 1288.
22. Corrin, M.L. and Harkins, W.D., *J. Am. Chem. Soc.*, 1947, vol. 69, p. 679.
23. Hiskey, C.F. and Downey, T.A., *J. Phys. Chem.*, 1954, vol. 58, no. 10, p. 835.
24. Chromy, V. and Svoboda, V., *Talanta*, 1965, vol. 12, p. 437.
25. Ishibashi, N. and Kina, K., *Anal. Lett.*, 1972, vol. 5, p. 637.
26. Venable, R.L. and Ballad, R.V., *Anal. Chem.*, 1974, vol. 46, no. 1, p. 131.
27. Ishii, H. and Watanabe, H., *Bunseki Kagaku*, 1977, vol. 26, no. 1, p. 86.
28. Armstrong, D.W. and Terrill, R.Q., *Anal. Chem.*, 1979, vol. 51, no. 13, p. 2160.
29. Armstrong, D.W. and Henry, S.J., *J. Liq. Chromatogr.*, 1980, vol. 3, p. 657.
30. Cline Love, L.J., Scriles, M., and Habarta, J.G., *Anal. Chem.*, 1980, vol. 52, no. 4, p. 754.
31. Terabe, S., Otsuka, K., Ichihara, K., *et al.*, *Anal. Chem.*, 1984, vol. 56, no. 1, p. 111.
32. Mchedlov-Petrossyan, N.O. and Kleshchevnikova, V.N., *J. Chem. Soc., Faraday Trans.*, 1994, vol. 90, no. 4, p. 629.
33. Shtykov, S.N. and Parshina, E.V., *Zh. Anal. Khim.*, 1994, vol. 49, no. 5, p. 469.
34. Shtykov, S.N., Malova, M.I., and Okunev, A.V., in *Problemy analiticheskoi khimii* (Problems of Analytical Chemistry), Saratov: Saratov. Gos. Univ., 1999, p. 62.
35. Savvin, S.B., Marov, I.N., Chernova, R.K., *et al.*, *Zh. Anal. Khim.*, 1981, vol. 36, no. 5, p. 850.
36. Chernova, R.K., Kartsev, V.N., Tsepulin, V.V., *et al.*, *Zh. Fiz. Khim.*, 1985, vol. 59, no. 11, p. 2740.
37. Kartsev, V.N., Tsepulin, V.V., Amelin, V.G., *et al.*, *Zh. Fiz. Khim.*, 1986, vol. 60, no. 1, p. 232.
38. Chernova, R.K. and Shtykov, S.N., *Fresenius' Z. Anal. Chem.*, 1989, vol. 335, p. 111.
39. Chernova, R.K., Kulapina, E.G., Barinova, O.V., and Materova, E.A., *Zh. Anal. Khim.*, 1995, vol. 50, no. 7, p. 705.
40. Chernova, R.K., Kulapina, E.G., Materova, E.A., *et al.*, *Zh. Anal. Khim.*, 1992, vol. 47, no. 8, p. 1464.
41. Kulapina, E.G. and Barinova, O.V., *Khim. Farm. Zh.*, 1997, no. 12, p. 40.
42. Kord, A.S. and Khaledi, M.G., *Anal. Chem.*, 1992, vol. 64, no. 17, p. 1901.
43. Hartwick, R.A. and Knox, J.H., *Anal. Proc.*, 1980, vol. 17, no. 12, p. 524.
44. Stahlberg, J., *J. Chromatogr.*, 1986, vol. 356, no. 2, p. 231.
45. Underwood, A.L., *Anal. Chim. Acta*, 1977, vol. 93, p. 276.
46. Okawa, Sh., *Bunseki Kagaku*, 1987, vol. 36, no. 8, p. 484.
47. Shtykov, S.N., Sumina, E.G., and Malova, M.I., *Zh. Anal. Khim.*, 1997, vol. 52, no. 7, p. 702.
48. Chernova, R.K., Doronin, S.Yu., Pankratov, A.N., and Gusakova, N.N., in *Problemy analiticheskoi khimii* (Problems of Analytical Chemistry), Saratov: Saratov. Gos. Univ., 1999, p. 37.
49. Esteve-Romero, J.S. and Monferrer Pons, L., *Anal. Lett.*, 1994, vol. 27, no. 8, p. 1557.
50. Kalyanasundaram, K., Grieser, F., and Thomas, J.K., *Chem. Phys. Lett.*, 1977, vol. 51, p. 501.
51. Cline Love, L.J. and Scrilec, M., *Int. Lab.*, 1981, vol. 11, no. 3, p. 50.
52. Levshin, L.V., Shtykov, S.N., Goryacheva, I.Yu., and Mel'nikov, G.V., *Zh. Prikl. Spektrosk.*, 1999, vol. 66, no. 2, p. 201.
53. Diax-Garcia, M.A. and Sanz-Medel, A., *Anal. Chem.*, 1986, vol. 58, no. 7, p. 1436.
54. DeLuccia, F.J. and Cline Love, L.J., *Anal. Chem.*, 1984, vol. 56, no. 14, p. 2811.
55. Mel'nikov, G.V., Goryacheva I.Yu., and Shtykov S.N., *Dokl. Akad. Nauk*, 1998, vol. 361, no. 1, p. 72.
56. Shtykov, S.N., Melnikov, G.V., and Goryacheva, I.Yu., *Proc. Int. Trace Anal. Symp.'98*, Tokyo, 1998, p. 43.
57. Shtykov, S.N., Melnikov, G.V., and Goryacheva, I.Yu., *J. Mol. Struct.*, 1999, vol. 482/483, p. 679.
58. Kodama, M., Shimizu, S., Sato, M., and Tominaga, T., *Anal. Lett.*, 1977, vol. 54, no. 8, p. 1325.
59. Kodama, M. and Miyagawa, S., *Anal. Chem.*, 1980, vol. 52, no. 14, p. 2358.
60. Kornahrens, H., Cook, K.D., and Armstrong, D.W., *Anal. Chem.*, 1982, vol. 54, no. 8, p. 1325.
61. Cline Love, L.J., Habarta, J.G., and Dorsey, J.G., *Anal. Chem.*, 1984, vol. 56, no. 11, p. 1132.
62. Zhang, Y. and Yue, G., *Anal. Chim. Acta*, 1995, vol. 309, nos. 1–3, p. 63.
63. Dalangin, R.R. and Gunasinfham, H., *Analyst* (Cambridge, U.K.), 1994, vol. 119, no. 7, p. 1603.
64. Armstrong, D.W. and Fendler, J.H., *Biochim. Biophys. Acta*, 1977, vol. 478, p. 75.
65. Shtykov, S.N., Sumina, E.G., Parshina, E.V., and Lopukhova, S.S., *Zh. Anal. Khim.*, 1995, vol. 50, no. 7, p. 747.
66. Shtykov, S.N. and Sumina, E.G., *Zh. Anal. Khim.*, 1998, vol. 53, no. 5, p. 508.
67. Shtykov, S.N., Sumina, E.G., Smushkina, E.V., and Tyurina, N.V., *J. Planar Chromatogr.*, 1999, vol. 12, no. 2, p. 129.
68. Casero, I., Sicilia, D., Rubio, S., and Perez-Bendito, D., *Chimia*, 1998, vol. 52, no. 718, p. 418.
69. Fröschl, B., Stangl, G., and Niessner, R., *Fresenius' J. Anal. Chem.*, 1997, vol. 357, p. 743.
70. Igarashi, Sh., Kuywa, T., Matsuura, M., and Yotsuyanagi, T., *Chem. Lett.*, 1994, p. 1189.