



Mini-review

SURFACTANTS AND KINETIC DETERMINATIONS OF MICROELEMENTS

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ABSTRACT

The use of surfactant in kinetic-based determinations of trace metal ions is considered. Kinetic treatments of micellar catalysis are discussed. The effect of surfactant micellar media on catalysed and uncatalysed reactions for determination of metal ions is studied. Use of surfactants led to the improvement in sensitivity, detection limits, selectivity and matrix effects in a number of kinetic-based determinations, thus permitting their practical application.

Key words: kinetic analysis, micellar catalysis, metal ions

INTRODUCTION

For the determination of trace metal ions various methods, including UV-spectrometry, ETAAS, ICP-MS, NAA, FIA, ion chromatography and anodic stripping analysis, have been used. The advantages of instrumental methods are low detection limits, high sensitivity and selectivity, possibility for multicomponent analysis, nondestructive analysis, distance analysis and analysis "in vivo". Many of these methods require complicated and expensive instruments. These techniques are usually not available in most routine laboratories.

On the other hand the majority of easy available chemical methods suffer insufficient sensitivity. That is why one is considered that the possibilities of chemical reactions in trace analysis are exhausted. Exceptions to this are enzymatic catalytic methods. The high turnover numbers of enzymes allow one particle of catalyst to take part in a great number of elementary reactions. Moreover, the high selectivity of enzyme action ensures good selectivity of reactions. In most cases the reaction rate is monitored photometrically. The enzymatic catalytic methods combine low limits of detection, high selectivity and simple and available technique. That is why these methods compete successfully with the instrumental methods; moreover they are

irreplaceable for determination of enzyme activity in analytical practice (1).

Another catalytic means of analytical determination, much simpler than enzyme catalysis, is achieved using cations, anions and coordinative compounds. These types of kinetic catalytic methods have proved to be very appropriate for trace analysis. The best advantage of kinetic catalytic determinations (catalymetry) is the combination of very low determination limits (in some cases - in picogram range), with a simple and available experimental technique, especially with photometric monitoring of the reaction rate (2).

The relative cheapness of catalymetry and its reliability in instrumental analyses for trace determinations informed the reason for the intense studies of catalytic analytical reactions during the last century (1-6).

Catalytic kinetic methods are based on chemical reactions where the rate is influenced by the reaction conditions. That is why the development, optimisation and achievement of these methods rely mainly on application of modern theories on chemical kinetics, catalysis and coordination chemistry.

The theory and practice of catalytic analysis indicate that the use of activators is one of the most effective ways of improving the analytical features of catalytic reactions (2). The use of an activator in the catalysed reactions is usually intended to increase sensitivity and hence lower the detection limit for the catalyst, and to improve the selectivity and precision of the determination.

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Another way of improving the analytical features of kinetic methods is the use of organic microheterogeneous systems - surfactants. In the last two decades surfactant molecules and their aggregates have been used increasingly in analytical techniques in order to alter the properties, including the reactivity, of the analytes (7).

Surfactant aggregates often accelerate or “catalyse” chemical reactions, but they also inhibit reactions. The term, “micellar catalysis”, was first applied to the increases in rates of reactions produced by aqueous association colloids, in particular micelles (8). However, the term “micellar catalysis” is not entirely correct; it has become established and has useful currency.

Surfactant micelles can enhance the sensitivity and can bring about changes in solubility, pK_a , chemical equilibria, reaction rates and mechanisms, spectral distributions and intensities and the stereoselectivity of some chemical processes. There are a host of analytical methods involving micellar media. Most are equilibrium methods based on molecular absorption or emission spectroscopy; although micelle aggregates have also been utilised successfully with other techniques such as phosphorescence, atomic absorption and chemiluminescence (9, 10). Surfactants increase the absorptivity of the analytes and some of them also facilitate solubilisation of the analytical system (9, 11). Surfactants have been used increasingly in electroanalytical and chromatographic techniques (9).

Kinetic approaches in micellar catalysis

Numerous kinetic and catalytic kinetic methods involving micelles with the objective of determining trace metal ions have been investigated. Since a host of analytical kinetic methods are based on catalysed reactions, it is important to determine the effect of micelles on these processes in order to be able to assess the analytical potential of these media.

Inasmuch as surfactants have been used for changing the kinetics of reactions, various kinetic models have been developed to describe micellar catalysis on chemical reactions (10-17). Kinetic treatments have been developed most extensively for reactions in the presence of aqueous micelles. In the pseudo-phase kinetic model proposed by Berezin (8) reactions are assumed to take place in the bulk aqueous and micellar pseudo-phases. The micellised surfactant is in equilibrium with solutes throughout the reaction, and observed rates can be treated as

the sum of rates of concurrent reactions in each pseudophase.

The pseudo-phase model in its various guises explains many features of micellar rate effects and it can be applied, at least qualitatively, to reactions in a variety of colloidal assemblies as reverse micelles and microemulsions. A large amount of kinetic data has been explained successfully in terms of the pseudo-phase model (14). However, this model fails to explain some of the kinetic data obtained in the presence of charged micelles and it is inappropriate for accounting electrolyte effects on the rates of micelle-catalysed reactions (7, 14). Ion distributions have been modelled in different ways. One, proposed by Romsted (12), includes counterion distributions in the micellar Stern layer in buffered solutions. Romsted et al. developed pseudophase ion exchange (PIE) model (13-15); in that micellar surfaces are treated as selective ion exchangers saturated with counterions. The number of assumptions and restrictive reaction conditions required is larger in the PIE model than in the pseudo-phase model (14).

In the Poisson-Boltzmann equation (PBE) model (16), reactions are assumed to occur in a surface region of defined thickness and solution of the PBE gives the concentration of ions in this region. In this model ions are regarded as point-charged ions and some of the calculated adjustable parameters are not very reliable (14).

The basic pseudo-phase model provided excellent qualitative and often good quantitative interpretation for many reactions (17). Analyses of various micelle-catalysed reactions on the bases of the pseudo-phase kinetic model led to the conclusion that two principal factors are responsible for the efficiency of micellar catalysis: *concentration effects in the micellar pseudo-phase* due to the hydrophobic, electrostatic and specific interactions of reactants with the micelles; and *changes in the reactivity* of reagents on transfer from water to the micellar pseudo-phase (10).

Study of the various micelle-catalysed reactions have shown that the major source of rate enhancements is the increased reactant concentration in the micellar pseudo-phase and that second factor contributes less significantly to the overall effect (10).

Concentration effects

Concentration through complex formation at the micellar surface

Micellar catalysis can occur in two modes: when all the reactants concentrate on the micellar surface (where the reaction takes place) and when only some of them approach micelles; so the reaction takes place in the micelle-bulk solution interface.

According to the pseudophase model, as the reactant concentrations in the micellar pseudophase determine the catalytic efficiency, the catalyst must also be concentrated at the micellar surface in order to combine the effects of micellar and chemical catalysis. Direct association between a catalyst and the micelles is often hindered by the fact that the reactant concentrations often are higher than that of the catalyst by several orders of magnitude (10).

The more promising alternative is no direct aggregate-catalyst interaction - the formation of a complex between the catalyst and one or more reactants, provided they readily bind to the micellar surface in order to allow the catalyst to be concentrated locally onto the micelles (7). This principle is used to increase the rate of the Pb(II)-catalysed reaction between Pyrogallol Red (PGR) and persulfate ion in the presence of dodecyltrimethylammonium bromide (DTAB) micelles (18). The "local concentration" of lead through formation of the PGR-Pb(II) complex at the micellar surface also results in substantially increased sensitivity and selectivity relative to the absence of surfactant.

Transient catalyst-substrate complexes are formed in many redox reactions where the catalyst reacts with a substrate to yield the product and its own activated form (7). When the substrate is an organic compound, interaction between this and the catalyst generally entails the prior formation of a charge-transfer complex between both species, which in turn requires that the

catalyst be temporarily concentrated at the micellar surface if the substrate is concentrated by a group other than that via which the catalyst forms the complex. Since this step will be the rate-determining step, the resulting "local concentration" of the catalyst can result in a more sensitive determination. We have used this approach for the determination of iron (III), with substantially improved sensitivity, based on the reaction of oxidation of sulfanilic acid (SA) by potassium periodate, activated by 1,10-phenanthroline (Phen) (19).

Rate enhancement in this reaction was observed at concentrations lower than the critical micellar concentration. Catalysis provided by premicellar aggregates can readily be rationalised in terms of the kinetic treatments derived for second-order reactions in aqueous micelles (8, 21). Based on such treatments, the reaction rate is determined by the reactant concentrations in the aggregates. Since small premicellar aggregates contain more reactant molecules per aggregate than micelles at the same reagent concentrations, a more efficient reagent concentration in the smaller aggregates often results in higher second-order rate constants for reactions in premicellar aggregates than for those observed in micelles (19).

To our knowledge, the reaction for determination of iron (III) based on its catalytic effect on the oxidation of sulfanilic acid by potassium periodate, in the presence of 1,10-phenanthroline, as activator, is the first application of catalysis by premicellar aggregates in kinetic analysis (19). The kinetic study carried out shows that the effect of this surfactant on the iron (III)-catalysed reaction could be entirely attributed to increased reactant concentrations in the surfactant micelle subunits.

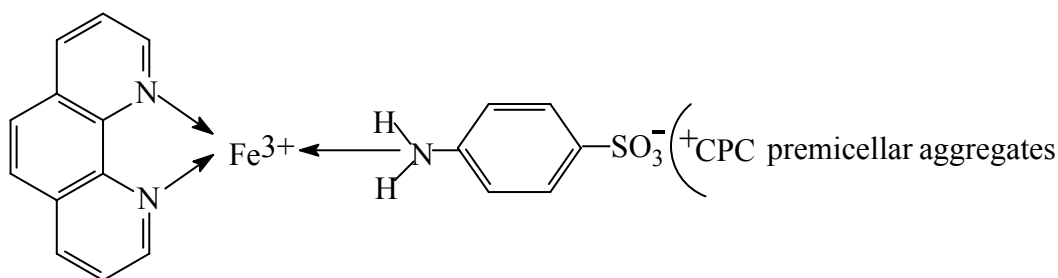


Figure 1. Incorporation of the phen-Fe (III)-SA transient complex into CPC premicellar aggregates

The value for binding constant of sulfanilic acid to the submicellar aggregates (K_{SA}) suggests a strong substrate-aggregate

interaction. Inasmuch as the other reactant in the determining rate step is the Fe (III)-phenanthroline catalyst, which bears positive

charge, a direct catalyst-micellar subunits association is impossible. This suggests indirect concentration of this catalyst on micellar subunits by formation of a transient phen-Fe (III)-SA complex, which probably concentrates in the surfactant aggregates through the sulfonic group of the sulfanilic acid. A likely structure of this complex is shown on **Figure 1**.

A similar approach can be applied to the catalytic effect of Mn (II) on the oxidation of sulfanilic acid by potassium periodate in the presence of cetyltrimethylammonium bromide (CTAB) (21). The surfactant did not modify the rate of the uncatalysed reaction in the whole concentration range tested. The absence of whatever influence on the almost zero background reaction from CTAB may be accepted as an experimental proof to eliminate the possibility that the surfactant accelerates reaction through concentration of the

substrates on the surface of surfactant aggregates or through sensitisation of the reaction product or modifications of its spectral characteristics. The last possibility could be excluded also because of the fact that the profile of the absorption spectra for the reaction products was identical in the presence and absence of CTAB. It may be supposed that the accelerating action of CTAB on the manganese catalysed reaction is due mainly to the formation of associates between surfactant aggregates and ternary complexes $\text{KIO}_4\text{-Mn(II)-SA}$. Taking into account the structure of the ternary complex $\text{KIO}_4\text{-Mn(II)-SA}$ in which the functional groups face the sulfonic group, it is reasonable to believe that there are electrostatic interactions between the negative sulfonic group and the positively charged head group of premicellar aggregates (**Figure 2**).

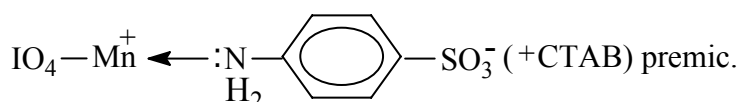


Figure 2. Formation of associates between complexes $\text{KIO}_4\text{-Mn(II)-SA}$ and micellar aggregates

Concentration of the reactants and multistep reactions

Micellar catalysis can also enhance the effect of chemical catalysis in multistep reactions even if the catalyst is not concentrated, whether directly or indirectly, at the micellar surface. If the indicator reaction takes place in two or more steps and the catalyst is only involved in one of them, its catalytic effect can be indirectly enhanced if the surfactant catalyses another different step (10). Thus, a sensitivity increase by roughly one order of magnitude was achieved in the kinetic determination of vanadium (V), which catalyses the two-step bromate oxidative coupling between catechol and p-phenetidine, in the presence of cetylpyridinium chloride (CPC) micelles (10, 22). Study of the mechanism accounts for the fact that no increase in selectivity resulted from the presence of CPC as this surfactant is not involved in the step where vanadium (V) exerts its catalytic activity. The enhanced overall reaction rate arising from the presence of the CPC micelles was the result of the combined effect of micellar catalysis (by concentration of the reactants at the micellar surface) and the increased molar absorptivity of the product formed.

Changes in the intrinsic reactivity

Changes in the reactivity and multicomponent

determinations

Concentration of substrates or products of a given analytical reaction in the micellar pseudo-phase can alter the physico-chemical properties of the concentrated species by changing molar absorptivities, causing wavelength shifts, etc.

Micelles can alter reaction mechanisms. When a given substrate can undergo two reactions and one of them is inhibited by micelles, the effect of micelles can be exploited for kinetic multicomponent determinations. Thus, Ni(II) and Co(II) were simultaneously determined by the complex-formation reaction between these ions and 5-octyloxymethyl-8-quinolinol in the non-ionic micellar medium provided by Triton X-100 (23). The non-ionic surfactant decreases the rate of formation of both complexes, however the formation of Co(II) complex is forty-four times faster than that of Ni(II), thus permitting the determination of the two ions by conventional spectrophotometry.

The effect of dodecyltrimethylammonium bromide (DTAB) micelles in the reaction between Pyrogallol Red (PGR) and Cr(VI), V(V) and Ti(IV) was exploited for the simultaneous determination of the three ions (24, 25). The oxidation reaction between PGR and Cr(VI) is accelerated by the presence of surfactant, while the reaction between PGR and V(V) is completely suppressed in a

DTAB micellar medium. In addition hyperchromic and bathochromic shifts were observed in the presence of surfactant.

Sensitization of the reaction product and modification of its spectral characteristics.

In the reaction between iodide and bromate ions, catalysed by Os(VIII) and accelerated by As(III) in the presence of DTAB micelles the concentration of the monitored species (triiodide) in the micellar pseudophase lead to enhanced analytical signals and increased reaction rate (26). Concentration of the monitored species within micelles can give rise to spectral shifts in addition to increased absorbance. The associate formed between triiodide ion and positively charged hexadecylpyridinium chloride (CPC) was reported to induce a bathochromic shift from 350 nm to 500 nm under given conditions (27). The spectral shift was accompanied by substantially increased absorptivity of the I_3^- complex. This was exploited for enhancing the sensitivity of Mo(VI)-catalysed reaction between iodide and H_2O_2 in the presence of the I_3^- - CPC associates (28).

Changes in acid-base equilibria

Concentration of reactants with acid/base properties on micelles may be used to induce changes in acid/base equilibria. Changes in the apparent pK_a values can result from the presence of micelles. Thus, anionic SDS micelles, which catalyse the reaction between hexacyanoferrate(II) and 1,10-phenanthroline (phen), accelerated by Hg(II), allow the ferriox complex to be formed under more acidic conditions (29). This results in an appreciably higher selectivity in the kinetic determination of Hg(II) relative to the reaction in a purely aqueous medium.

The accelerating effect due to concentration of the reactants in the micelles can be predicted and calculated theoretically. On the basis of the pseudo-phase model for a number of various micelle-catalysed reactions of second and higher orders the reaction rates in aqueous (k_w) and micellar (k_M) phases and the observed reaction velocity (k_{exp}) were calculated, in addition to determination of binding constants of solutes with surfactant aggregates (K_S) (7, 8, 10, 20, 21). The results obtained allowed to determine whether a given instance of micellar catalysis arises from purely extrinsic concentration of the reactants in the micellar pseudo-phase ($k_M = k_w$) or from changes in the intrinsic reactivity ($k_M > k_w$) and to confirm the validity of the

theoretical model used (10).

Analytical uses

Surfactants are used in kinetic analyses for developing new catalytic methods or for improving previously established catalytic methods. The use of micellar media in kinetic analysis has valuable effect on catalysed and uncatalysed reactions for determination of metal ions. **Table 1** lists some papers that focus on micellar catalysis in kinetic determinations.

Application of surfactants led to the gains in sensitivity, detection limits and selectivity in a number of kinetic-based determinations (19, 21, 23, 26, 28-30). Thus the enhanced sensitivity of the determination of Sb(III), which accelerates the reduction of 12-phosphomolybdate to a blue heteropoly compound, is due to its concentration on Triton-100 micelles. The detection limit of the reaction in micellar media was 7 times lower than that of the matching method involving an aqueous medium and the flow injection technique (30). Significantly improved selectivity was also obtained.

The catalytic activity of Mn(II) on the reaction between sulfanilic acid and potassium periodate in the presence of CTAB was increased by a factor of ca. 5 and the detection limit was 3 times lower than that of the corresponding method developed in an aqueous medium (21). The selectivity of the reaction was scarcely influenced by the presence of surfactant. On the other hand the catalytic activity of Mn(II) on the same reaction in the presence of the activator 1,10-phenanthroline was increased by factor more than 100 and detection limit was approximately 400 times lower. That is way, one may suggest that the simultaneous action of activator and surfactant on the catalytic

Table 1. Kinetic determinations of metal ions in the presence of surfactants

<i>N</i> <i>o</i>	Reaction	Metal ion	Surfactant	Method	Application	Ref.
1	PGR + S ₂ O ₈ ²⁻	Pb(II)	cationic DTAB	catalytic photometric	-	18
2	SA + KIO ₄ ; activator Phen	Fe(III)	cationic CPC	catalytic spectrophotometric	determination of serum iron	19
3	SA + KIO ₄	Mn(II)	cationic CTAB	catalytic spectrophotometric	-	21
4	Catechol + p-phenetidine	V(V), CPC	cationic CPC	catalytic spectrophotometric	-	22
5	Ni(II) + 5-octyloxymethyl-8-quinolinol Co(II) + 5-octyloxymethyl-8-quinolinol	Ni(II), Co(II)	Non-ionic Triton X-100	spectrophotometric	-	23
6	PGR + Cr(IV) PGR + V(V) PGR + Ti(IV)	Cr(IV) V(V) Ti(IV)	cationic DTAB	spectrophotometric	-	24, 25
7	I ⁻ + BrO ₃ ⁻ + 6H ⁺ → 3I ₂ + Br ⁻ + 3H ₂ O I ₂ + I ⁻ → [I ₃] ⁻ , [I ₃] ⁻ + H ₂ O ₂	As(III)	cationic DTAB	indirect, catalytic spectrophotometric	-	26
8	Hexacyanoferrate(II) + Phen	Mo(VI)	cationic CPC	catalytic spectrophotometric	determination of Mo in water soil extracts	28
9	12-posphomolybdate + ascorbic acid	Hg(II)	anionic SDS	catalytic photometric	-	29
0		Sb(III)	Non-ionic Triton-100	catalytic FIA	-	30
1	SA + KIO ₄ ; activator Phen	Mn(II)	cationic CTAB	catalytic spectrophotometric	-	31
1	Nuclear Fast Red + KIO ₄	Cu(II)	nonionic Tween-20	catalytic spectrophotometric	serum and urine	32
2	MBTH + DAOS; H ₂ O ₂ ; activator pyridine	Cu(II)	BDTAC	catalytic FIA	determination of Cu in pepperbush	33
3	Asure B + S ²⁻	Cu(II)	cationic CTAB	Catalytic FIA	water	34
4	o-Toluidine blue + KIO ₄	Rh(III)	cationic CTAB	catalytic spectrophotometric	water	35
5	PGR + IO ₄ ⁻	Pd(II)	anionic	catalytic spectrophotometric	three different hydrogenation catalysts	36
6	Au(III) + PDR Pd(II) + PDR	Au(III) Pd(II)	nonionic Brij-35	HPSAM	simultaneous determination of Au(III) and Pd(II) in jewellery and synthetic samples	37
7	1)Fe(III) + Co(II) → Fe(II) + Phen → 2)Fe(II) + Phen	Fe(III) Fe(II)	cationic CTAB	HPSAM	determination of Fe(II) and Fe(III) in synthetic mixtures	38
8	Chrome Azurol S + Be(II)	Be(II)	cationic CTAB	HPSAM	determination of Be(II) and Al(III) in	39
9,	Chrome Azurol S + Be(II)	Al(III)			environmental, geochemical and alloy samples	

PGR – Pyrogallol Red; SA – sulfanilic acid; Phen – 1,10-phenanthroline; DTAB – dodecyltrimethylammonium bromide; CTAB – cetyltrimethylammonium bromide; BDTAC – benzyltrimethyltetradecylammonium chloride; CPC – cetylpyridinium chloride; SDS – sodium dodecyl sulfate; MBTH – 3-methyl-2-benzothiazolinone hydrazone ; DAOS – n-ethyl-n-(2-hydroxy-3-sulfopropyl)-3,5-dimethoxyaniline; PDR – 5(p-dimethylaminobenzylidene)rhodanine; HPSAM – H-point standard addition method

activity of Mn(II) in this reaction would be more efficient.

The results obtained did not entirely confirm the above suggestions. The catalytic activity of Mn(II) on the oxidation of sulfanilic acid by potassium periodate, activated by 1,10-phenanthroline in the presence of cetylpyridinium chloride (CPC) was increased less than 2 times compared to the same reaction developed without surfactant (31). However, the simultaneous action of activator and surfactant in this case led to the increase of the catalytic activity of Mn(II) by factor of approximately 200. Using of surfactant in these reactions was to a significant extent less effective than that of activator.

Some additional advantages of micelles include their ability to shorten analysis times, which in turn translates to the increased outputs and more convenient assays. Thus, cetylpyridinium chloride (CPC) had strong positive effect on the Fe(III)-catalysed reaction of oxidation of sulfanilic acid by potassium periodate (19). The time needed to obtain the final absorbance was considerably shortened by the presence of CPC (ca. 1 h) relative to an aqueous medium (ca. 48 h), the final absorbance value being identical for both media. The catalytic activity of Fe(III) was apparently increased by a factor of ca. 5 in the presence of cetylpyridinium chloride (CPC) according to the sensitivity obtained in the micellar subunits and the aqueous medium. The detection limit was improved about 7-fold in the presence of CPC based on the same measurement method. The accelerated reaction was applied to the determination of Fe(III) in blood serum. Probably the successful application of the reaction for serum iron determination is due not only to the improved detectability and selectivity, but also to the minimised interfering action of serum matrix in the presence of surfactant.

The enhancing effects of surfactants have been exploited in the application of a number of analytical kinetic methods (28, 32-36). Thus, triiodide-hexadecylpyridinium chloride micellar system was applied to the determination of Mo in aqueous extracts of soil samples with no prior separation (28). The Cu(II)-catalysed reaction between Nuclear Fast Red and potassium periodate in Tween-20 microemulsion medium has been applied to many real samples such as urine and serum (32).

The oxidative coupling of 3-methyl-2-benzothiazolinone hydrazone with *n*-ethyl-*n*-(2-hydroxy-3-sulfopropyl)-3,5-dimetho-

xylaniline in a micellar medium was successfully applied to the determination of copper in pepperbush (33).

Cationic micellar medium in the reduction of azure B by sulphide was applied to the determination of copper in water samples (34).

Trace concentrations of Rh (III) were determined in water samples by the reaction of oxidation of o-Toluidine blue with periodate in micellar medium (35).

The reaction of oxidation of Pyrogallol Red in anionic micellar medium was applied to the determination of Pd (II) in three different hydrogenation catalysts (36).

Some H-point standard addition methods performed in micellar media have been applied to the simultaneous determination of Au(III) and Pd(II) in jewellery and synthetic samples (37); Fe (II) and Fe (III) – in several synthetic mixtures (38) and Be(II) and Al (III) – in environmental, geochemical and alloy samples (39).

CONCLUSIONS

Micellar surfactant systems can modify reaction rates and have been recognised as very useful alternatives for improving analytical methodologies. Much research has been devoted to the kinetics and mechanisms of reactions taking place in the presence of micellar systems. However they have not been used in conventional kinetic determinations, in spite of the numerous reports demonstrating that micelles have great analytical potential.

Micellar systems in kinetic determinations of metal ions are still unexplored field. Future progress in this area will broaden their applications.

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