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ORIGINAL CONTRIBUTION

Test of Hofmeister-like series of anionic headgroups: clouding and micellar growth

Sanjeev Kumar · Harsha Patel · Sandeep R. Patil

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Abstract Phenomenon of clouding in charged micellar solutions is a fairly recent addition to conventional phenomenon shown by aqueous nonionic micelles. In this paper, we have tested a Hofmeister-like ordering of charged headgroups in the context of cloud point (CP) and micellar growth. For this purpose, we have used various combinations of surfactant (sodium dodecyl sulfate, SDS; sodium dodecylbenzene sulfonate, SDBS; sodium salts of α-sulfonato myristic acid methyl ester, MES; and α-sulfonato palmitic acid methyl ester, PES) and tetra-*n*-butylammonium bromide (TBAB). Different surfactant concentrations and TBAB concentrations are used and CP measurements have been performed. CP values were found in the order SDBS<SDS<PES<MES for the same concentration of surfactant and TBAB. This order has been discussed in the light of water affinities of interacting ionic species (i.e., surfactant headgroup and TBA^+ counterion). The ordering was found similar for the case of micellar growth studied by dynamic light scattering (DLS). A bimodal distribution of aggregate size was found that transforms to giant aggregates at CP. The micelles of roughly 10-nm size convert to aggregates of 1 μm. The study has a few novelties: (1) headgroup dependence of CP, (2) micellar growth on heating, and (3) confirmation of Hofmeister-like series of headgroup.

Keywords Surfactant · Cloud point · Hofmeister series · Micelle · Dynamic light scattering

S. Kumar (✉) · H. Patel · S. R. Patil
Soft Material Research Laboratory, Department of Chemistry,
The Maharaja Sayajirao University of Baroda,
Vadodara 390002 Gujarat, India
e-mail: drksanjeev@gmail.com

H. Patel
e-mail: harsha_smile12@yahoo.com

S. R. Patil
School of Engineering and Technology, Navrachana University,
Vadodara, India
e-mail: srpatil14@gmail.com

Introduction

Surfactants form a unique class of chemical compounds due to their amphiphilic nature. Unusual properties of surfactants continue to attract the interest of scientists/technologists and have inspired them to design new surfactants with intriguing solution behavior [1–3]. Amphiphilicity of surfactants has extensively been exploited in the preconcentration of metal ions, solvent extraction, mobility of drugs in aqueous media, probing of biological systems, templating of nanomaterials, etc. The relation between solution behavior and heating observed in ionic surfactants is found different than their nonionic counterparts. Most nonionic surfactant solutions have propensity to show clouding on heating, followed by formation of two isotropic phases (surfactant-rich and surfactant-lean phases) [1]. This separation is reversible when the system is cooled. The threshold temperature, at which clouding first appears in surfactant solution, is known as cloud point (CP) or lower consolute temperature (LCT). However, the phenomenon that occurs in ionic surfactant solutions is not common, which may be due to the presence of coulombic repulsions between ionic micelles. Recently, research activities have been directed towards studying the relatively uncommon clouding phenomenon with ionic surfactant solutions [4–9]. Most of the work on clouding in aqueous anionic surfactant systems were made when tetra-*n*-alkylammonium counter ion (TAA^+) was added or was a counter ion of the surface-active species [6,7,9–12].

Various phenomena in surface and colloid science that involve counterions show pronounced ion specificity. More than a century back, Franz Hofmeister concluded that the effectiveness of the salts in denaturing proteins increases with their water structuring ability [13]. Since the report of Hofmeister, it is now common to discuss about ion series instead of series of salts. In a recent report [14], a comprehensive attempt has been made to establish a Hofmeister-like series for surfactant headgroups. The proposed series