

M. Prasad
R. Palepu
S. P. Moulik

Interaction between sodium dodecyl sulfate (SDS) and polyvinylpyrrolidone (PVP) investigated with forward and reverse component addition protocols employing tensiometric, conductometric, microcalorimetric, electrokinetic, and DLS techniques

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M. Prasad · S. P. Moulik (✉)
Centre for Surface Science,
Department of Chemistry
Jadavpur University,
Kolkata 700032, West Bengal, India
e-mail: spmcss@yahoo.com
Fax: +91-3324146266

R. Palepu (✉)
Department of Chemistry,
St. Francis Xavier University,
Nova Scotia, Canada
e-mail: rpalepu@stfx.ca
Fax: +10-9028672414

Abstract The interaction between polyvinylpyrrolidone (PVP) and sodium dodecyl sulfate (SDS) after the procedure of addition of the surfactant to polymer and the reverse procedure of addition of polymer to SDS micelles has been studied by tensiometric, conductometric, and microcalorimetric methods. The results have been analyzed and correlated with reference to SDS interfacial adsorption, association, and binding to PVP. Two aggregation states of SDS in presence of PVP have been found. The enthalpies of formation of SDS aggregates/micelles and their binding to the polymer have been evaluated. The interaction of PVP with SDS at concentrations below its critical micellar concentration (CMC) and above have evidenced distinctions. The for-

ward addition protocol (FAP, SDS addition to PVP) and reverse addition protocol (RAP, PVP addition to SDS) have shown similarities and differences. Electrokinetic measurements have evidenced the interacted (SDS–PVP) colloidal products to possess negative zeta potential in the range of –39 to –65 mV. The hydrodynamic diameters of the PVP–SDS dispersion obtained from DLS measurements have ranged between 60 and 160 nm. Both zeta potential and hydrodynamic diameter have depended on [SDS] showing a maximum for the former at twice the critical micellar concentration of SDS.

Keywords SDS–PVP interaction · Tensiometry · Conductometry · Calorimetry · DLS · Zeta potential

Introduction

Polymer–surfactant interaction is a fascinating and important topic of surface chemical research both for fundamental understanding and applications [1–6]. The topic has much relevance to enhance oil recovery process [7–9] wherein polymer and surfactant solutions are pushed into the underground rock capillaries to reduce capillary forces to effectively dislodge the trapped oil. The polymer–surfactant combines can form gels suitable for use as templates for the synthesis of nanomaterials [10, 11] and for other rheological purposes [12, 13]. Cationic surfactants are used for fiber conditioning and finishing to impart antistatic property to the fiber.

It is known that anionic surfactants favorably interact with water-soluble polymers, whereas cationic surfactants normally interact weakly with them and moderately under specified conditions [14–16]. In recent years, hydrophobically modified water-soluble polymers have been also used in such studies [16–21]. Lipid–protein interaction [22–25] and surfactant–biopolymer interaction [26–36] are known to have relevance to pharmacy, biochemistry, and biotechnology. Favorable interaction of cationic surfactants with DNA with a consequence of enhanced base-pair stability and condensation of the complex in globular form having a prospect for favorable transfer of genes in living cells (called transfection) has been reported [36–38].

Among the water-soluble polymers, polyvinylpyrrolidone (PVP) has been well studied in its interaction with anionic surfactants [9, 16, 37–43]. The polarizable pyrrolidone side group in the polymer can acquire positive charge on the ring nitrogen wherein an anionic group [like the surfactants sodium dodecyl sulfate (SDS), Aerosol OT, bile salts, etc.] [16, 41, 43] can interact. Like other nonionic polymers (polyvinyl alcohol, polyethylene oxide, ethyl hydroxy ethyl cellulose, etc.) [15–21], PVP has the ability to induce surfactant aggregation and binding of the aggregates to the polymer depending on the environmental conditions such as temperature and additives (salts and solvents) [16, 43, 44].

The methods tensiometry, conductometry, light scattering, fluorimetry, nmr chemical shift, calorimetry, etc. have been used for exploring the said interaction processes. Use of poly(styrene)-*b*-poly(2-vinyl pyrrolidone)-*b*-(ethylene oxide) for interaction with SDS has been recently studied: the polymer micelle has been reported to condense by the interaction of its PVP block with the surfactant [45]. Upon interaction with SDS, PVP has been also reported to become compact in solution [15]. The interaction of SDS with a star polymer has been also recently reported [46]. The micellar aggregates have been considered to bind in the polymeric arms of the star.

The procedure that most of the cited studies has followed was the addition of surfactant in polymer solution and measurement of changes in physical properties to understand the nature of the interaction process. There are only preliminary tensiometric [16] and microcalorimetric [46] reports on the PVP–SDS interaction after the reverse procedure, i.e., addition of polymer to micellar solution of the surfactant. Sigmoidal type of dependence (increase) in surface tension (γ) and enthalpy change has been observed to occur. In the present work, we have made a detailed study on the interaction after forward and reverse procedures. In the latter, both monomeric and micellar solution of SDS were used. By this protocol, interaction of PVP with a constant state of aggregation of SDS could be followed. Elaborate isothermal titration microcalorimetry (ITC) experiments were performed to derive insight to the process, which was seldom done in the past [47–49]. The methods of tensiometry and conductometry were employed as well. Electrokinetic and DLS measurements were also taken to understand the dispersion characteristics of the interacted products. The results have been analyzed and correlated; new features of the interaction process have been realized.

Experimental section

Materials

The surfactant SDS used was a 99% pure product of Sigma (USA). The polymer PVP (molar mass 40K) was also obtained from Sigma (USA). They were used as received.

Doubly distilled water of specific conductance 2–4 $\mu\text{mho cm}^{-1}$ at 298 K was used for preparing solutions for the study. All experimental measurements were taken at 303 \pm 0.1 K.

Methods

Tensiometry The surface tension of SDS solution was measured with a calibrated Krüss (Germany) tensiometer by the platinum ring detachment method. PVP (0.5% w/v) or SDS (0.20 mM) solution depending upon the procedure followed was added successively in 10 ml water (or PVP solution) in steps using a microsyringe and measurements were taken after mixing and temperature equilibration. The accuracy of the measured γ was $\pm 0.1 \text{ dyne cm}^{-1}$.

Conductometry The conductivity measurements were performed with an EcoScan Conductivity meter series (Singapore). Ten milliliter of SDS or PVP solution of known concentration (depending upon the procedure followed) was placed in a thermostated container and PVP or SDS solution (depending again upon the procedure followed) of known concentration was progressively added using a microsyringe. The specific conductance was measured after each addition followed by thorough mixing and temperature equilibration. The critical micellar concentration (CMC) values were estimated from the break points in the conductance–concentration plots. The accuracy of conductance measurements was within $\pm 2\%$.

Microcalorimetry The ITC experiments were performed with an OMEGA Isothermal Titration Calorimeter (Microcal, USA). In an experiment, 1.325 and 1.8 ml of PVP (0.5%) or SDS (0.20 mM) solution was taken both in the reaction and reference cells, respectively. The injection syringe (350 μl) was filled with either SDS or PVP solution (as the case may be), which was injected at 3.5 min intervals in 32 steps (10 μl in each step) to the solution in the calorimeter cell under constant stirring (350 rpm) condition at 303 K. The heat flow in or out for each injection in the reaction cell depending on endothermicity or exothermicity of the dilution process was recorded in the calorimeter. The differential enthalpies of dilution per mole of the injectant were calculated with the help of MICROCAL ORIGIN 2.9 software, hence the critical aggregation concentration (CAC), CMC, and the enthalpy of interaction were obtained.

DLS and Zeta potential DLS measurements were taken in a Malvern Laser Particle Size analyzer—ZETASIZER 1000 HS (UK). Twice filtered samples through 0.45 μ membrane filters were taken in the capillary cell, interacted with a 633 nm He–Ne laser beam and the scattering intensity was measured at 90° angle. The processed data in the instrument provided the average hydrodynamic diameter (d_h) and the polydispersity index of the dispersion.

For the zeta potential measurement, a Malvern ZETA-SIZER 2000 (UK) with a He–Ne laser was used instead, after identical procedure for sample preparation and filtration. The electrophoretic mobility and zeta potential were measured in the capillary electrophoresis cell by injecting 3 ml solution.

Results and discussion

Basics of SDS–PVP interaction: The tensiometry has been an elegant method for the understanding of surfactant–polymer interaction. The results according to the forward addition protocol (FAP) on the SDS–PVP system in the absence and presence of polymer (0.5% w/v) are presented as γ vs $\log C$ plot in Fig. 1. The γ of water in presence of PVP was lower than its absence; the polymer was, thus, surface active. The decrease in γ was a cooperative process which started at $[\text{SDS}] \sim 0.02$ mM. In the absence of PVP, a break in the plot appeared at 8.1 mM which is the CMC of SDS at 303 K. In the presence of PVP, the first minimum in the plot at 1.91 mM was the critical aggregation concentration (CAC) of SDS. In this study, small aggregates started forming by the interaction of SDS with the polymer. Two processes, (1) binding of aggregates with PVP in the bulk and (2) binding of aggregates with PVP at the interface then occurred. The first process did not affect γ , whereas the second dislodged the polymer to sink into the bulk from the interface; consequently, the interface was stripped off both from PVP and SDS with an increase in γ until the binding process was complete at 12 mM of SDS. Upon completion of the process, there was monomer build-up at the interface associated with decline in γ until free micelles started to form in solution at 34.8 mM. It has been reported [15, 41, 42, 44] that the formation of CAC remains virtually independent on [PVP] but the polymer induced enhanced CMC increases with increasing [PVP].

In the main plot of Fig. 2a, γ vs $[\text{SDS}]$ profiles of the results depicted in Fig. 1 are illustrated with indications of normal CAC and normal and enhanced CMC points of SDS in presence of the polymer. In Fig. 2b, the conductometric pattern for the interaction of SDS with 0.5% PVP in aqueous medium according to FAP has been compared with the tensiometric pattern (Fig. 2a). Three distinct breaks in the specific conductance– $[\text{SDS}]$ profile were also realized at 1.9, 12, and 34.8 mM in presence of PVP, whereas in the absence of PVP, a single break at 8.1 mM was observed (Figs. 1 and 2a). Thus, the CAC and enhanced CMC points at 1.9 and 34.8 mM, respectively, were supported by the tensiometric and conductometric methods. The completion of transfer of SDS–PVP complex from the interface to the bulk at 12 mM was also evidenced from conductometric measurements. The binding of SDS with PVP reduced conductance, which was manifested with a break at 12 mM. The breaks in the conductance plot appeared with decreasing slopes. In overall consideration, the association process of

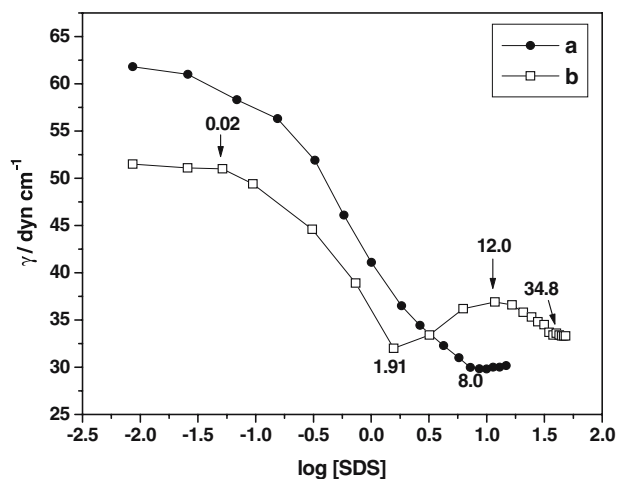


Fig. 1 Plot of γ vs $\ln[\text{SDS}]$ for **a** pure SDS system and **b** for SDS–PVP system at 303 K. [0.2 M SDS and 0.5% (w/v) PVP were used in the experiments]

SDS aggregates with PVP in solution occurred with increased counterion binding.

The ITC results on the SDS–PVP interaction are illustrated in Fig. 3b. The enthalpograms in the absence (curve a) and presence (curve b) of PVP have distinctions. The resultant enthalpogram (curve r) obtained by subtracting the heats of dilution of SDS in water from the heats of dilution in PVP solution has been considered for data analysis. The crests and troughs are marked against $[\text{SDS}]$ in which the crests marked as c_1 , c_2 , and c_3 have corresponded to 1.91, 12, and 34.8 mM, respectively, as in tensiometric (Fig. 3a) and conductometric (Fig. 2b) results discussed above. The above concentrations have corresponded to surfactant/polymer ratios (S/P) of 0.05, 0.3, and 1.0, re-

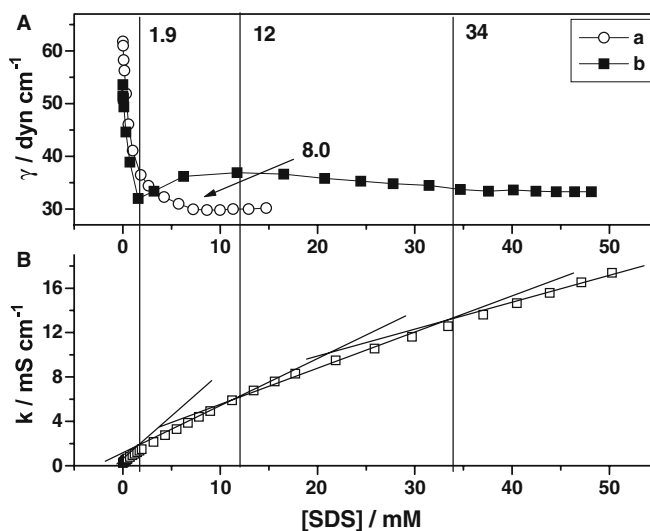


Fig. 2 Comparison of SDS–PVP interaction (normal protocol) by **panel A** tensiometry and **panel B** conductometry at 303 K. **Panel A** γ vs $[\text{SDS}]$ profiles (**a**, in absence of PVP; **b**, in presence of 0.5% w/v PVP **panel B** k vs $[\text{SDS}]$ profile)

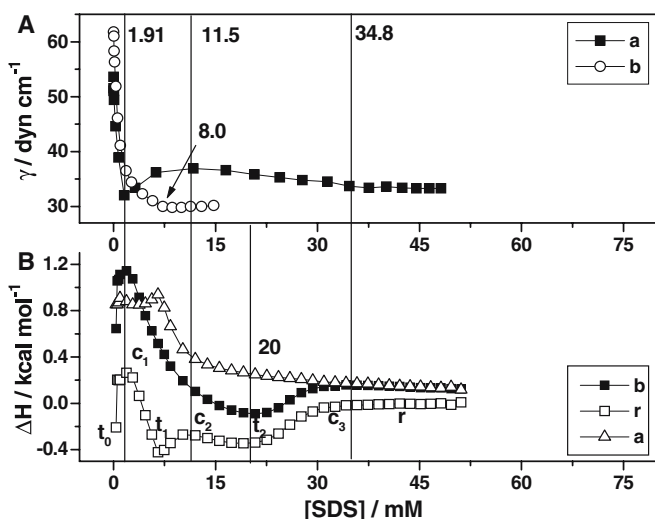


Fig. 3 Comparison of SDS–PVP interaction (FAP) by *panel A* tensiometry *panel B* calorimetry at 303 K. *Panel A* γ vs [SDS] profiles (**a**, with 0.5% (w/v) PVP; **b**, without PVP). *Panel B* ΔH vs [SDS] profiles (**a**, without PVP; **b**, with 0.5% (w/v) PVP; **r**, resultant profile obtained by subtracting the heats obtained in absence of PVP from that obtained in its presence)

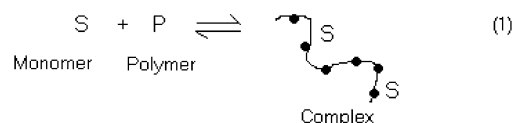
spectively. The troughs t_1 and t_3 have corresponded to S/P ratios of 0.20 and 0.50, respectively. The formation of CAC, SDS–PVP complex, and free micelles in solution were associated with identifiable enthalpy changes.

The information gathered from tensiometry, conductometry, and calorimetry on CAC, CMC_0 (in absence of PVP), and CMC_p (in presence of PVP) are presented in Table 1 in which results from other reports are also listed. The results obtained from the different methods and sources have shown good agreement. The CMC_p values have witnessed deviations. Griffiths et al. [44] have reported CAC and CMC_p of SDS at 2.0 and 23.0 mM, respectively, in 0.5% (w/v) PVP (molar mass 1,300K) by tensiometry, and 2.0 and 29.0 mM, respectively, by fluorimetry. By tensiometry, Chari et al. [41, 42] have reported CAC and CMC_p as 1.4 and 27 mM, respectively, in 0.5% PVP (molar mass 29K) in 1 mM NaCl at pH 6 at 298 K. Our results for CAC, have nicely agreed with that of Griffiths et al. [44] but that of Chari et al. [41, 42] was lower because of the presence of salt. The results on CAC have been found to be more or less independent of PVP molar masses which has also been the observation of Wang et al. [15]. Based on the reports from different workers, it can

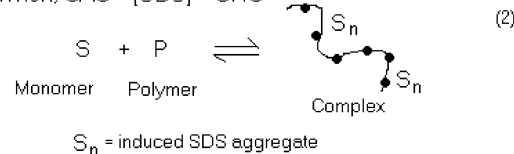
be concluded that while CAC values were close, the CMC_p values depended on the molar mass of PVP.

The SDS–PVP interaction can be grossly modelled as follows.

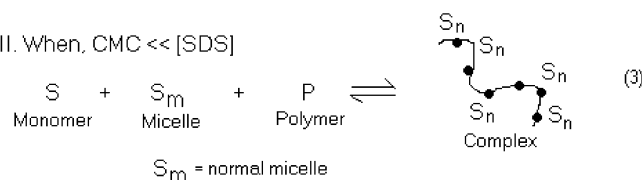
I. When, $0 < [SDS] < CAC$



II. When, $CAC < [SDS] < CMC$



III. When, $CMC \ll [SDS]$



In FAP, SDS was added in the solution to interact with PVP to produce the products. In the reverse addition protocol (RAP), PVP was expected to interact with S or S_m also to yield the same products. Thus, physicochemical measurements in FAP and RAP are expected to shed light on the nature of interactions involved.

Comparison of results of FAP and RAP

A comparison of the physicochemical features of FAP and RAP protocols on the interaction between SDS and PVP are discussed below. In such illustrations, the measured physical properties are profiled against surfactant/pyrrolidone mole ratio S/P. In RAP, the minimum concentration of SDS used was 4 mM, which was above CAC (1.91 mM) so that lower aggregates of SDS were always present in the system because, according to reports, CAC is independent of PVP concentration. Of course the extent of binding to the polymer depended on the S/P ratio, at S/P ~ 1.0 , PVP chain attained saturation with small SDS aggregates along with monomers

Table 1 The CAC, SDS–PVP interaction limit (SDS–PVP)_e, CMC_0 , and CMC_f found by different methods

Method	CAC/mM	(SDS–PVP) _e /mM	CMC_0 /mM	CMC_f /mM
Tensiometry	1.91, 2.0 [44]	12.0	8.16, 8.00 [44]	34.8, 23.0 [44]
Conductometry	1.9, 1.4 [41, 42]	12.0	8.00, 6.60 [41, 42]	34.0, 27.0 [41, 42]
Calorimetry	1.91	11.5	8.40	35.0, 35.0 [15, 16]
Fluorimetry	2.0 [44]	–	–, 8.00 [44]	–, 29.0 [44]

Our results are at 303 K; others' are at 298 K

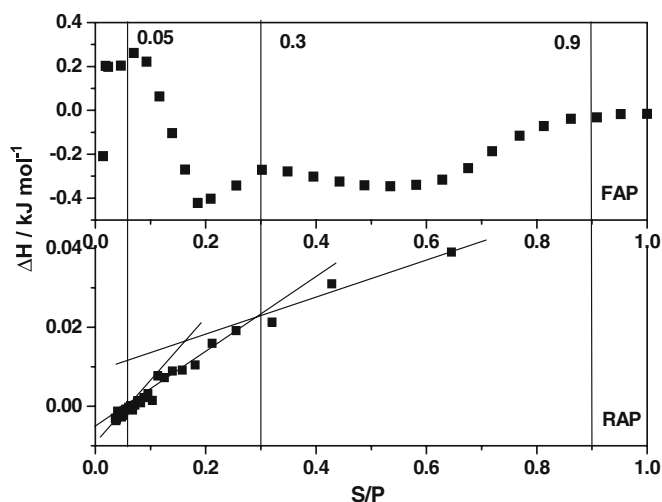


Fig. 4 Calorimetric results (ΔH against S/P) of FAP and RAP for 4 mM SDS at 303 K

to the formation of CMC (Fig. 3b). The S/P ratio was, thus, a measure of saturated/unsaturated states of the SDS/PVP combination. We have studied the RAP experiments at $[SDS]=4, 16, 24$, and 32 mM and graphical illustrations of the results are subsequently described.

The calorimetric results of FAP and RAP are compared in the illustrations of Fig. 4. All the three breaks observed in FAP at $S/P=0.05, 0.3$, and 0.91 , were not observed in RAP. The break at $S/P=0.9$ was not realized because the concentration of PVP used did not cover the range beyond $S/P=0.7$. Tensiometry and conductometry, on the other hand, evidenced three breaks (not illustrated).

Tensiometric and conductometric results of FAP and RAP experiments with $[SDS]=16$ mM are presented in Figs. 5 and 6, respectively. The break at $S/P=0.05$ was not observed in

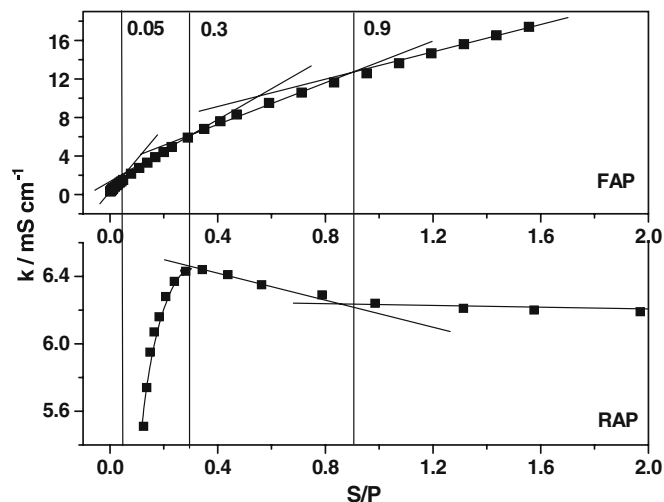


Fig. 6 Conductometric profiles (k against S/P) of FAP and RAP for 16 mM SDS at 303 K

RAP; those at $S/P 0.3$ and 0.9 were distinct. In conductometry, the initial course was a curvature. The directions of the two courses in both the figures were essentially not parallel, similar to that witnessed in Fig. 4.

In conductometric (Fig. 7) and tensiometric (not shown) profiles at 24 mM SDS, indication for CAC formation (at $S/P=0.05$) was again not observed in RAP. The initial curvilinear variation (as observed in Fig. 6) was much less in Fig. 7. In the ITC experiment, besides $S/P=0.3$ and 0.9 , a new inflection point at $S/P=0.60$ was observed in RAP which corresponded to the second minimum in the FAP profile (Fig. 8). Similar was the observations with $[SDS]=32$ mM in tensiometric, conductometric, and calorimetric experiments using RAP (not illustrated).

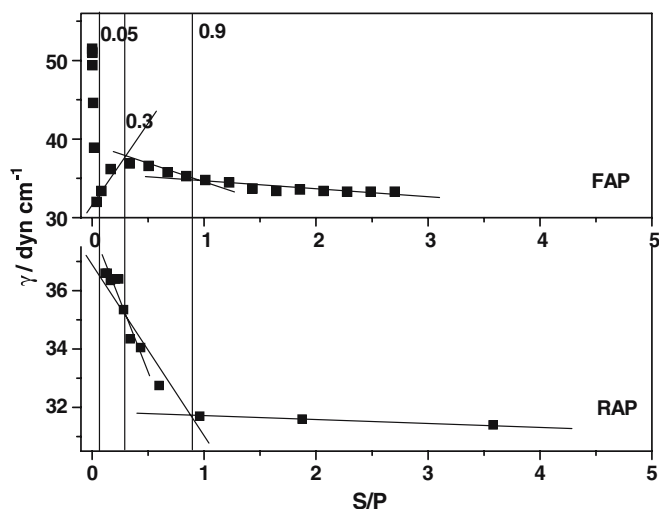


Fig. 5 Tensiometric profiles (γ against S/P) of FAP and RAP for 16 mM SDS at 303 K

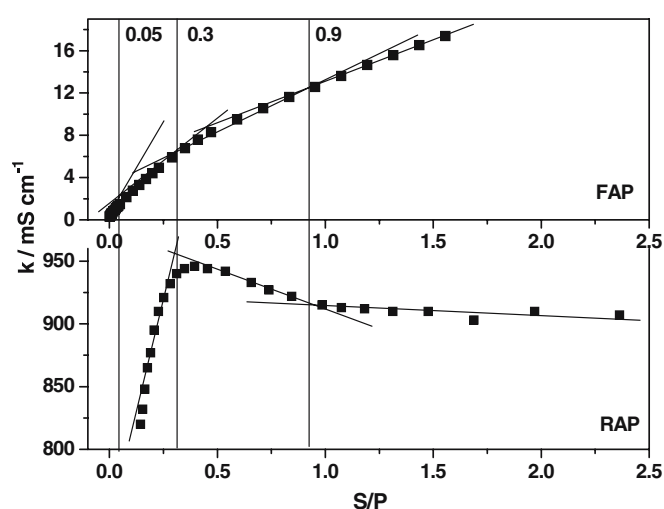


Fig. 7 Conductometric profiles (k against S/P) of FAP and RAP for 24 mM SDS at 303 K

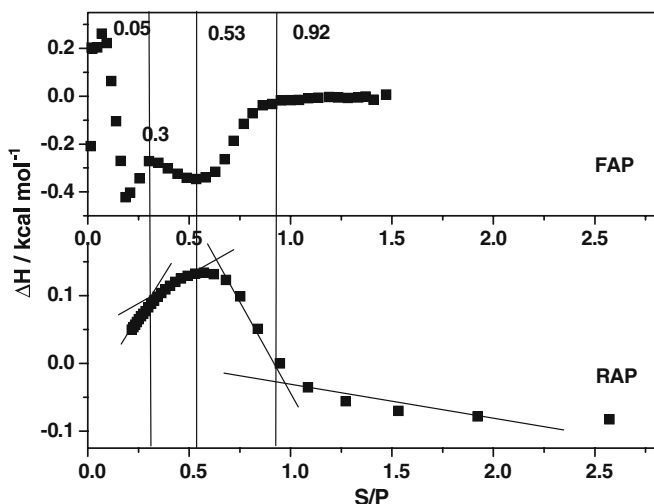


Fig. 8 Calorimetric profiles (ΔH against S/P) of FAP and RAP for 24 mM SDS at 303K

The findings of RAP differed from FAP in a number of ways.

1. The courses were hardly parallel (the ITC results in RAP on the whole followed an opposite course than FAP).
2. The S/P ratio of 0.05 that corresponded to CAC was not observed in RAP except in conductometry and calorimetry at $[\text{SDS}] = 4 \text{ mM}$.
3. In calorimetry (ITC), an inflection at $\text{S/P} = 0.60$ in RAP corresponding to the second minimum in FAP was observed.

The RAP was both less sensitive and informative than FAP. The way SDS interacted with PVP was not replicated when PVP was allowed to interact with monomeric and micellar solutions of SDS. In tensiometry, the region of $[\text{SDS}] = 12\text{--}34.8 \text{ mM}$ has been considered to be the region where monomers build up to the state of free micelle formation occurred. In the ITC experiments, this region in FAP has shown formation of a trough at $[\text{SDS}] = 20 \text{ mM}$ which in the RAP experiments has appeared as a crest. The ITC could, thus, differentiate monomer build up between c_2 and t_2 and self-aggregation between t_2 and c_3 (Fig. 3), which tensiometry and conductometry have failed to recognize.

Table 3 The electrophoretic mobility (μ), zeta potential (ζ)^a, and hydrodynamic diameter (d_h)^b of PVP–SDS dispersion at 303 K

[SDS]	S/P	$10^8 \mu / \text{m}^{-2} \text{ V}^{-1} \text{ s}^{-1}$	ζ / mV	d_h / nm
$1/2 \text{ cmc}$	0.083	−3.08	−39.1	—
	0.077	—	—	108
cmc	0.154	−5.11	−65.0	—
	0.250	—	—	112
2 cmc	0.303	−5.16	−65.6	—
3 cmc	0.250	—	—	158
4 cmc	0.625	−4.15	−52.8	—

^aThe errors in ζ and d_h were within $\pm 10\%$

^bThe dispersions were found to be fairly polydisperse with polydispersity index (PDI) ~ 0.5 . In respect of d_h and PDI, the results fairly agreed with our previous findings [43]

The resultant enthalpogram (r) presented in Fig. 3 has helped to reveal different states of interaction process clearly [43]. The enthalpogram has produced two peaks at 1.91 and 12.0 mM, and enhanced CMC (CMC_e) at zero resultant enthalpy at $[\text{SDS}] = 34.8 \text{ mM}$. Levelling the crests as c_1 , c_2 , and c_3 and troughs as t_0 , t_1 , and t_2 (Fig. 3) in the resultant enthalpogram, the sections t_0c_1 , c_1t_1 , t_1c_2 , c_2t_2 , and t_2c_3 have been considered as regions of PVP induced formation of CAC of SDS at c_1 ; binding of the aggregates to PVP up to t_1 ; interaction of SDS with interfacial PVP resulting in its delivery in bulk up to c_2 ; dilution of SDS to build monomer up to t_2 , and self-aggregation of SDS monomer in PVP solution with enhanced CMC at c_3 . An approximate measure of enthalpies for the aforesaid processes can be obtained from the differences between the pair of points as described above in the resultant enthalpogram [48, 49]. In the studied SDS–PVP system, different kinds of processes were operative, therefore, treatment of ITC data for thermodynamic analysis based on site binding interaction model usually done for small molecule polymer system [53] could not be followed (Table 2).

Zeta potential and size of PVP–SDS combines The SDS-bound PVP complex was expected to form condensed products as evidenced for DNA-cationic surfactant [50–52] and ethylhydroxyethyl cellulose and SDS complexes [16]. The products in this study should possess a negative charge with negative zeta potential. The electrophoretic mobility

Table 2 Enthalpy of different kinds of processes in the SDS–PVP system found from ITC experiments

System (PVP–SDS)	Enthalpy change ^{a,b} / kJ mol^{-1}				
PVP (w/v), %	ΔH_{cac}	$\Delta H_{\text{b(agg)}}$	$\Delta H_{\text{b(int)}}$	ΔH_{ma}	$\Delta H_{\text{(cmce)}}$
0.5	1.93	−2.75	0.627	−0.288	1.228

^a ΔH_{cac} =enthalpy of formation of small aggregates; $\Delta H_{\text{b(agg)}}$ =enthalpy of binding of aggregate with polymer; $\Delta H_{\text{b(int)}}$ =enthalpy of binding with PVP at the interface; ΔH_{ma} =enthalpy of monomer accumulation; and $\Delta H_{\text{(cmce)}}$ =enthalpy of free micelle formation in solution

^bThe enthalpy of overall binding of SDS with PVP (estimated by subtracting the integral heat of dilution of SDS in water from that in PVP solution) was found to be $-429 \text{ (J mol}^{-1} \text{ (cf. 15b))}$

and the zeta potential (ζ) of the PVP–SDS complexed products have been measured. The results are presented in Table 3. The compositions of the studied products were PVP–SDS (1/2 cmc) at S/P=0.083, PVP–SDS (1 cmc) at S/P=0.154, PVP–SDS (2 cmc) at S/P=0.308, and PVP–SDS (4 cmc) at S/P=0.625. The results were average of 50 measurements taken on each sample. The potentials were all negative and their magnitudes were higher for [SDS]=1 cmc and 2 cmc; the magnitude declined at [SDS]=4 cmc. The increased magnitude of ζ suggested increased charge (and hence potential) of the complex with increasing SDS concentration. The lowering of ζ in the fifth system was due to shrinking of the electrical double layer by enhanced counterion condensation on the complex. The values at 1 cmc and 2 cmc were very close suggesting charge maximization before its decline at higher [SDS]. For a better understanding, further studies are warranted.

The PVP–SDS complexes at different [SDS] and specified S/P ratios have evidenced sizes falling in the range of 63–158 nm (Table 3). Although at [SDS] = $\frac{1}{2}$ cmc, the d_h was 108 nm, it increased at [SDS]=1 cmc and 3 cmc to 112 and 158 nm, respectively. The rise in magnitude of ζ potential at [SDS]=1 cmc and 2 cmc to –65.0 and –65.6 mV, respectively, and its reduction at [SDS]=4 cmc to –52.8 mV have not shown a parallelism with the size variations of the complexed products. More studies in this direction are wanted.

Conclusions

The following conclusions can be drawn from the experimental findings:

PVP induced self-aggregation of SDS at a concentration much lower than its aqueous CMC. The system has evidenced different kinds of interacting features which have produced distinctions at S/P ratios of 0.05, 0.3, 0.6, and 0.91 that corresponded to CAC formation, SDS aggregate–PVP binding in bulk, SDS–PVP binding at the interface, and free micelle formation in solution. Among the methods used, ITC has been found to be a better method for probing the system. The complex has been found to acquire negative charge with fairly large ζ potential. The hydrodynamic radius of the SDS–PVP complex increased with increasing presence of SDS in solution.

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