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Physico-Chemical Analyses on Polysaccharide-Surfactant Aggregates Hydrodynamic Behaviour

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Abstract - A mixture of surface-active substances is what is meant by the term "surfactant." Organic substances with amphiphilic properties often make up the surfactants. The terms "surfactant" and "amphiphile" are sometimes used interchangeably. "The expression alludes to the fact that all surfactant molecules contain two components, one of which is soluble in the fluid and the other of which is insoluble in the fluid" (the lyophobic part). The hydrophilic and hydrophobic portions are usually mentioned when the fluid is water. Surface tension, conductance, and spectrophotometric techniques were used to examine the interfacial adsorption and micellization of SDS in different chain lengths of aqueous liquid-vapor PEG. Both liquid and solid PEGs had comparable results, however there were slight variances. Additional precellization/preaggregation processes were seen in the case of solid PEGs.

Keywords - physico-chemical, polysaccharide-surfactant, hydrodynamic

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INTRODUCTION

Polymer-surfactant interactions is a fascinating and exciting subject of study because of its numerous potential uses. Such systems have gained a lot of interest because of their intrinsic scientific curiosity as well as their potential for use in commercial processes such increased oil recovery, pharmaceutical product preparation, packaged foods, cosmetic, & paints, to name a few. It's also similar to biologically structured themes. Rheological properties, phase behaviours, interfacial properties, and other features are controlled using polymer-surfactant aggregates.[1]

Different researchers have explored the interaction of polyions with opposite charges surfactants (both alone and in combination with nonionic surfactants). In these studies, surfactants interacted with synthetic polyanion or polycation and also natural polymers (from animals & plants). Dye probing, surface energy, viscous, turbid, fluorimetry, static & dynamic light scattering, conductance and e.m.f. measurements, and other techniques have been used in these research.

Whenever an opposite charges surfactant is applied to a polyelectrolyte, bigger aggregates form due to special bonding, resulting in the appearance of turbidity. Turbidimetric titration is an effective method for determining the degree of polymer- surfactant interaction. According to the literature review, the onset of turbidity with the integration of a fixed concentration of polymer is dependent on the CMC values of surfactants, the impact of charge density. and the structure of polymers. Cationic-nonionic mixed surfactants have also been shown to enhance turbidity more than nonionic mixed surfactants, owing to a lower CMC value due to a reduced charge density. The turbidity enhancement is lessened while the outcome of charge density overcomes the influence of CMC diminution.

One of the most imperative methods for distinguishing macromolecules & colloids s light scattering. In terms of biological interaction and technical application, the characteristics of polymer-surfactant complex solutions are imperative. In the literature, there are several investigations of light scattering on micellar & polyelectrolyte solutions. The system's behavior is determined by the interaction parameter that is the ratio of the molar concentrations of surfactant & polymer at equilibrium. As the polymer's binding sites become saturated with surfactant and at higher concentrations, unbound micelles coexist with complexes, as expected. These liberated micelles can advance resolubilize the polymer-surfactant complexes. The hydrodynamic radius of the complex is often less than or equal to that of the surfactant-free polymer coil. After the real repulsion between the polymer surfactant complexes reaches 1, there is a dramatic change. that primarily due to the screening consequence of the free micelles. This technique may readily attain the weight average molecular weight, gyration radius, and hydrodynamic radius of macromolecules & aggregating particles. Dynamic light scattering (DLS) can also be utilized to measure the aggregate's zeta potential and hydrodynamic radii for opposite charges polymer-surfactant aggregates. When an opposite-charged surfactant is supplementary to an aqueous polyelectrolyte solution, the medium's z.p. reverses as surfactant binding increases. A charge reversal phenomenon happens when surfactant is added after complete charge neutralisation, resulting in a drastic change in the nature & intensity of collaboration amongst oppositely charged polymer-surfactant aggregates in the presence of oppositely charged surfactants.[2]

EXPERIMENTAL

The Klebsiella K28, K43, K51, & K20 test strains were generously donated by Dr. 8. Schlecht of the Max Plank Institute for Immunobiology in Freiburg, Germany. In nutritional agar medium, bacterial cells were grown, harvested, & dried. The capsular polysaccharides were isolated & purified using the phenol-water-cetavlon method. Catalytic surfactants BDHAC. CTAB.CPC, DPC. & nonionic surfactant polyoxyethylene sorbitan monolaurate (POESM) were among E Merck's products (Tween 20). They were claimed to be 99 percent pure, and they were used just as they were. At 298 K, newly obtained double distilled water with a specific conductance of 2.4 Scm-1 was used for all measurements. Utilizing a Milton Roy Spectronic -21D spectrophotometer, turbidimetry measurements were taken by adding 200 L (10 L) of surfactants were gradually added to a constant amount of SPS (10-4 M), and the medium's viscosity was measured with a DV III pro cone & plate type rotoviscometer (Brookfield. USA). Viscosity was measured at various shear speeds for various SPS- surfactant concentrations. To determine zero shear viscosity, the intersection of the plots of apparent viscosity vs. shear rate was employed. The temperature was maintained at 298 K utilizing a thermostatic water bath with a 0.1 K accuracy.[3]

Measurement of size & zeta potential

The measurements of DLS zeta potential were done with the Nano-ZS90 (Malvern, USA). The light source was a He-Ne laser with a wavelength of 632.8 nm. The DLS tests were conducted at a fixed scattering angle of 900 degrees. After filtration via a 0.45 m MilliporeTM membrane filter. SPS (2.5 mL) was transferred to a 4 mL quartz cuvette. The temperature was kept at 298 degrees Fahrenheit. 200 litres (5 litres in each phase) Using a Hamilton microsyringe (USA), 0.005 M surfactant was progressively added to the 2.5 mL SPS solution stored in quartz cuvette and the mixture was homogenised before data were obtained. The addition of surfactant had no effect on SPS dilution. We took the measurements with separately produced solutions. and the fluctuation was essentially identical to what we're seeing now. Made of polycarbonate with gold- plated beryllium/copper electrodes (U.K.). All of the tests were done at 303 degrees Fahrenheit.

RESULTS & ANALYSIS

All four SPS under investigation have had their main structures revealed previously. The following are the structures:

The basic structures of the 4 Klebsiella SPS described above demonstrated that they are made up of distinct repeating units that range from tetra- to hexa- saccharides. Additionally, each SPS contains glucuronic acid that acts as a possible anionic site for interactions with cationic dyes & surfactants causing them to behave as anionic polyelectrolytes. K20 SPS has a 2:1:1 molar ratio of D-galactose, D-mannose, and D-glucuronic acid (tetrasaccharide). whereas K-51 has a 1:2:1 molar ratio of D-glucose, D-galactose, & D-glucuronic acid (tetrasaccharide). The hexasaccharide K28 SPS, on the other hand, contains D-glucose, D-galactose, D-mannose. & D-glucuronic acid in the molar ratio 2:1:2:1, while the pentasaccharide K43 SPS has D-galactose, D- mannose & D-glucuronic acid in the molar ratio 1:3:1. Spectrophotometric and spectrofluorometric titrations have previously been used to estimate the equivalent weight of all SPS40. 41). The SPS equivalent weights were discovered to be K20 (646).

K28 (980), K43 (820), & 5K1 (594). Though these polysaccharides share some structural similarities, there are some notable differences in terms of the size of the repeating units, sugar components, linking patterns, and so on. These structural differences were reflected in later physico-chemical experiments on the polymer- surfactant interaction, as indicated in the sections below.[4]

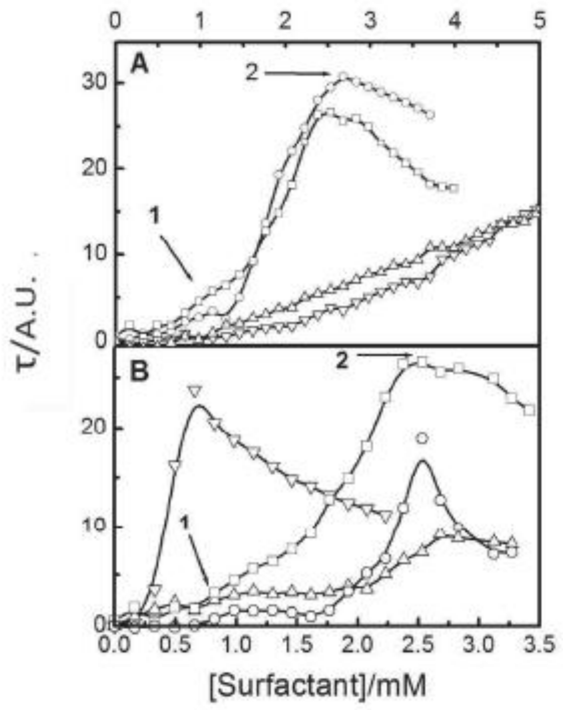
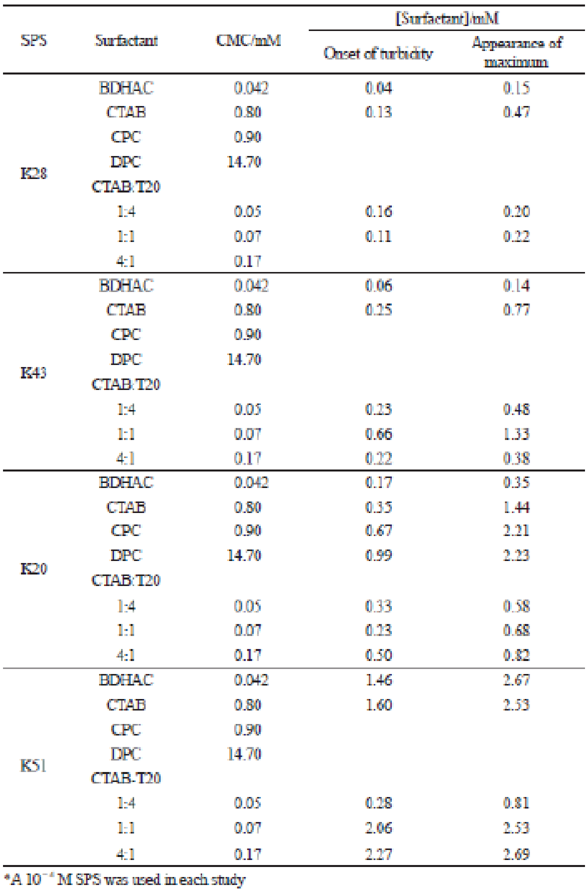


Fig. 1: Variation in the turbidity of Klebsiella K51 SPS with the addition of (A) cationic surfactants & (B) CTAB-Tween 20 mixed surfactants at 303 K. Cationic surfactants (A): O. BDHAC: o. CTAB: V7. CPC: a. DPC. Mole fraction of CTAB (B): 0. 1.0: a, 0.8; A, 0.5, VY . 0.2. [1: onset of turbidity; 2: maxima].A 10“ M SPS was utilized in each case

Figure 1 demonstrates the variation in turbidity with increasing surfactant concentration for various surfactants applied to Klebsilla K 51 SPS solution in water. Significant turbidity values were not achieved in the polymer solution until a certain amount of surfactant (marked as 1) was added. For pure surfactants, the beginning of turbidity varied in the following: BDHAC>CTAB, CPC>DPC. The surfactant CMC values were used to determine the order. At lower concentrations, a surfactant with a lower CMC should bind to the polymer matrix, & likewise. Table 1 summarises the results for all of the systems. The turbidity values grew dramatically with passing through maxim (shown as 2 inside the figure) once the threshold values were reached. This is a common occurrence in the literature. On the head groups, both CPC & DPC containing pyridinium cations exhibit reduced charge densities. When surfactants are coupled to opposite charges polyelectrolytes, charge neutralisation causes polymers to coil up, resulting in a reduction in overall size. However, in comparison to their hydrodynamic diameter, a reduction was minor. As a result, turbidity measurements failed to identify the size depletion of polyelectrolytes caused by surfactants. Further on, will be shown that such changes are untraceable utilizing DLS measurements. Turbidity increased as the polymer-surfactant aggregates phase separated. Phase separation occurs when the charge neutralised polymer-surfactant aggregates get dehydrated. Due to their less ionic character, these entities can be resolubilized in the existence of sufficient surfactants, resulting in a reduction in turbidity. On dispersion, the sequence of beginning of turbidity of the polymers was discovered to be K51K20K43K28. This could be owing to structural differences.[5]

CMC values fall with the addition of nonionic surfactant with the cationic surfactants, the commencement of turbidity in the instance of cationic-anionic mixed surfactants emerged at lower concentrations than the comparable pure cationic surfactants. In Fig. 1(Panel B), the variation in Klebsiella K51 after the addition of mixed surfactant is displayed. For combined surfactants, there was no systematic variance in the beginning of turbidity. The impact of the structure of SPS on turbidity formation is also accounted for by the variation that occurs with changes in polymer. The order of turbidity onset with varied SPS is K28>K43>K20>K51. The formation of turbidity is influenced by 2 parameters, namely charge density & CMC values, according to the literature. The CMC values of mixed surfactant systems are dramatically lowered when a nonionic surfactant is added. As a surfactants in each stage to a fixed amount of SPS (10-4 M) & measuring percent T at 420 nm, as turbidity was estimated as (100-percent T). The concentration of SPS employed for such measurements was found to be 10-4 M, which has been demonstrated to be the best value for turbidity monitoring. Variable amounts of result, the binding process should begin at a lower surfactant concentration. Interactions between polymers and surfactants are regulated by both electrostatic & hydrophobic forces. Hydrophobic interactions are expected to improve if CMC levels are reduced with nonionic surfactants. This was most likely the cause of increased turbidity in several systems that used blended surfactants. The addition of the nonionic surfactant resulted in another reduction in charge density, which resulted in a decrease in turbidity.

Table 1: At 303 K, the turbid metric titration of pure & mixed surfactants with 4 distinct SPS yielded the following results.



SPS	Surfactant	CMC/mM	[Surfactant]/mM	
			Onset of turbidity	Appearance of maximum
K28	BDHAC	0.042	0.04	0.15
	CTAB	0.80	0.13	0.47
	CPC	0.90		
	DPC	14.70		
	CTAB:T20			
	1:4	0.05	0.16	0.20
	1:1	0.07	0.11	0.22
	4:1	0.17		
K43	BDHAC	0.042	0.06	0.14
	CTAB	0.80	0.25	0.77
	CPC	0.90		
	DPC	14.70		
	CTAB:T20			
	1:4	0.05	0.23	0.48
	1:1	0.07	0.66	1.33
	4:1	0.17	0.22	0.38
K20	BDHAC	0.042	0.17	0.35
	CTAB	0.80	0.35	1.44
	CPC	0.90	0.67	2.21
	DPC	14.70	0.99	2.23
	CTAB:T20			
	1:4	0.05	0.33	0.58
	1:1	0.07	0.23	0.68
	4:1	0.17	0.50	0.82
K51	BDHAC	0.042	1.46	2.67
	CTAB	0.80	1.60	2.53
	CPC	0.90		
	DPC	14.70		
	CTAB-T20			
	1:4	0.05	0.28	0.81
	1:1	0.07	2.06	2.53
	4:1	0.17	2.27	2.69

*A 10^{-4} M SPS was used in each study

For a dilute polymer solution, intrinsic viscosity was calculated as a function of radius of gyration. The random arrangement of the polymer chain opens up at low concentrations due to ion-ion repulsion, resulting in an enlarged structure and increased viscosity. Charge neutralisation occurs when we continue to add surfactant, resulting in a reduction in electrostatic repulsion &, eventually, a drop in viscosity. Polymer—polymer interactions are less intense than polymer—surfactant interactions. The hydrodynamic volume occupied by the polymer mass is the intrinsic viscosity that could be determine using dilute solution viscosity measurements. In the literature on polymer physics, several theories link inherent viscosity to molecular properties. The inherent viscosity values can be used to calculate polymer solubility parameters in a variety of solvents. These solubility criteria were practical to drug-excipient interactions, transdermal patch advance, and drug absorption via the skin to discover the fundamental properties of materials. The degree of hydrophobic contacts. hydrolysis. & size of miceller clusters may all be detected via intrinsic viscosity measurement.[6] The relationship between intrinsic & relative viscosity could be determined using the subsequent equation:

$$[\eta] = \lim_{C\to 0} \frac{\eta_{sp}}{C}$$

The following equation can be utilized to calculate the specific viscosity:

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0}$$

Here. m9 is the viscosity of the polymer solution in the absence of surfactant, viscosity of the polymer solution when surfactant is present. To standardize the influence of the polymer. this value of the specific viscosity is divide by the polymer concentration & plotted against the surfactant concentration. 0.1 1 10

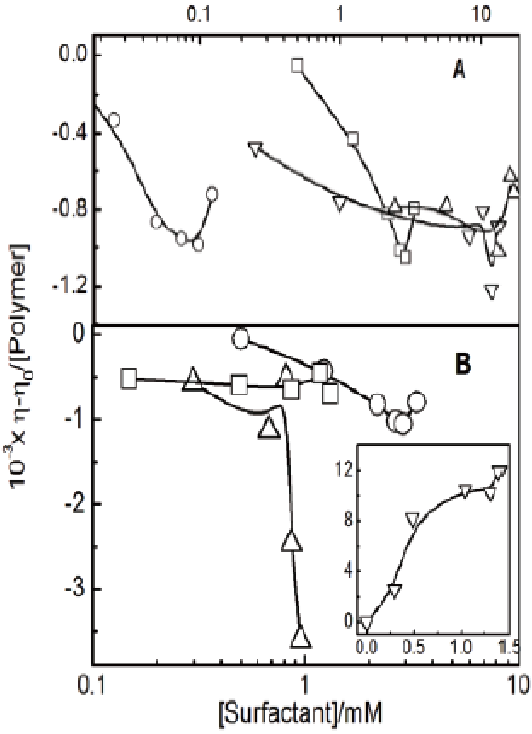
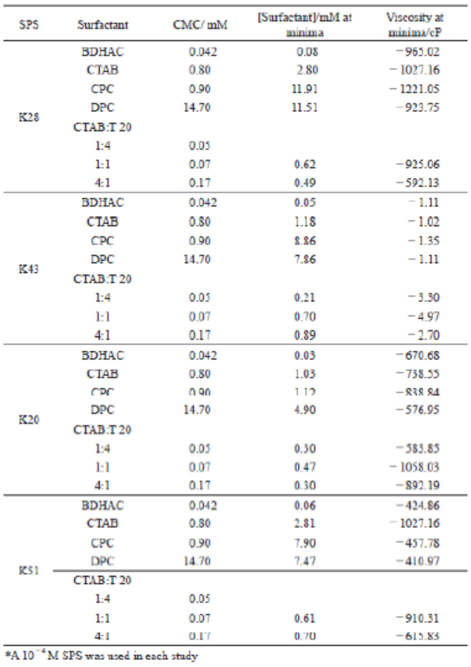


Fig. 2: Variation in viscosity of Klebsiella K28 in presence of (A) cationic surfactants (B) CTAB-Tween 20 mixed surfactants at 303 K. Cationic surfactants (A): 0, BDHAC: a. CTAB; V7. CPC: a, DPC. Mole fraction of CTAB: 0, 1.0: 5, 0.8; a, 0.5 inset V0.2. A 104 MSPS was utilized in all case.

The viscosity of the solution reduced until it reached the point of precipitation, after which it began to rise. The graph shows that the appearance of minima when pure cationic surfactants are added in the following: BDHAC>CTAB>CPC>DPC. Table 2 summarises the variation in the case of extra SPS. The interaction between the polymer and the surfactant causes the polymer to coil up, reducing viscosity. On interaction with the surfactant, the hydrodynamic radius of the SPS reduced then grew, subsequent in a decrease in intrinsic viscosity followed by an increase. The development of macroscopic aggregates causes an growth in viscosity beyond the point of precipitation. The surfactant CMC values are used to determine the order. The observed difference in viscosity was also differentiated as SPS varied. In the instance of K43 SPS, the variation appeared distinctive.[7]

Figure 2 depicts the variation in viscosity for cationic-nonionic mixed surfactan t systems with Klebsiella K28. Later, it was discovered that this matched the results of the dynamic light scattering measurement. In terms of SPS concentration, the order of variation can be summarised as 0.5>0.8>1.0. Except for BDHAC, mixed surfactant systems are more effective in changing viscosity than pure cationic surfactant systems. This is due to the fact that CMC values in blended surfactants were reduced. In the instance of blended surfactants, both CMC values & charge density impact the reduction in intrinsic viscosity. Because of the considerable fall in CMC value at lower mole fractions (X2 =0.8) of nonionic surfactant, the interaction in both the SPS & surfactant risen dramatically, causing a reduction in the medium's intrinsic viscosity.The effect of charge density is shown in the lowering of the cationic surfactant's mole fraction. The variation is distinct in the instance of K43. When SPS are altered, the variation changes as well.

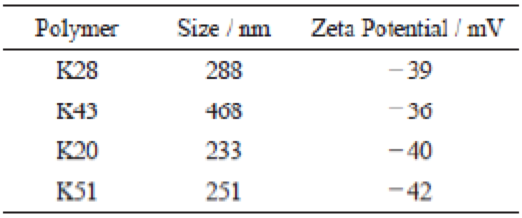
Table 2: At 303 K, the viscosity of pure & mixed surfactants was measured using four



SPS	Surfactant	CMC/ mM	[Surfactant]/mM at minima	Viscosity at minima/cP
K28	BDHAC	0.042	0.08	−965.02
	CTAB	0.80	2.80	−1027.16
	CPC	0.90	11.91	−1221.05
	DPC	14.70	11.51	−923.75
	CTAB:T 20			
	1:4	0.05		
	1:1	0.07	0.62	−925.06
	4:1	0.17	0.49	−592.13
K43	BDHAC	0.042	0.05	−1.11
	CTAB	0.80	1.18	−1.02
	CPC	0.90	8.86	−1.35
	DPC	14.70	7.86	−1.11
	CTAB:T 20			
	1:4	0.05	0.21	−3.30
	1:1	0.07	0.70	−4.97
	4:1	0.17	0.89	−2.70
K20	BDHAC	0.042	0.03	−670.68
	CTAB	0.80	1.03	−738.55
	CPC	0.90	1.12	−838.84
	DPC	14.70	4.90	−576.95
	CTAB:T 20			
	1:4	0.05	0.30	−583.85
	1:1	0.07	0.47	−1058.03
	4:1	0.17	0.30	−892.19
K51	BDHAC	0.042	0.06	−424.86
	CTAB	0.80	2.81	−1027.16
	CPC	0.90	7.90	−457.78
	DPC	14.70	7.47	−410.97
	CTAB:T 20			
	1:4	0.05		
	1:1	0.07	0.61	−910.31
	4:1	0.17	0.70	−615.83

*A 10^{-4} M SPS was used in each study

Table3: Size &Z.P values for 4 distinctSPS.



Polymer	Size / nm	Zeta Potential / mV
K28	288	−39
K43	468	−36
K20	233	−40
K51	251	−42

DYNAMICLIGHTSCATTERING（DLS）Analysis

Hydrodynamic diameter

The hydrodynamic light scattering experiments was carried out to confirm the SPS's hydrodynamic radius (Rh) in the presence of surfactants, as determined by viscosity measurements. For these research, we employed the Stokes-Einstein formalism, which is as follows:

$$\overline{D_z} = \frac{K_B T}{6\pi\eta R_h}$$

Here KB denotes Boltzmann's constant, I denotes solvent viscosity at absolute temperature T, Rh denotes hydrodynamic radius, & (D z) is the diffusion coefficient.[8]

Table 3 lists the sizes of the 4 main SPS. The change in surfactant binding with Klebiella K28, that influences size variation, is illustrated in Fig. 3, series is BDHAC=CTAB=CPC=DPC.

Size grows as the surfactant binds to the polymer & creates a polymer-surfactant aggregate. However, when neutralisation occurs, the size of the polymer may shrink due to the coiling up of the polymer. The amount of size increase is determined on the surfactant's type. The level of size increase differs depending on the SPS. Whenever DPC was gradually applied to K20, the size first fell and then increased, but when DPC was gradually introduced to the other three SPS, the size first enhanced &then reduced. This could be related to structural differences in SPS. The fluctuations were remarkably similar to those previously seen in viscosity measurements.

The variation in size of Klebsiella K28 after adding a mixed cationic-nonionic surfactant is illustrated in Fig. 3 as an example. Table 4 further shows that as mixed surfactants were applied, the onset of size augmentation began sooner, i.e. at lower surfactant concentrations. The extent of size augmentation with the addition of dissimilar mole fractions of CTAB altered as SPS changed. In the instance of K28, the commencement of size augmentation with surfactant containing 80 & 20 mole percent CTAB was substantially identical. The surfactant concentrations required for binding to begin are as follows: 0.2 0.50.81.0. DLS studies are more sensitive & thus more dependable than turbidity measures. As previously stated, the level of interaction between opposite charges polymer-surfactant systems is determined by the CMC as well as the surfactant's charge density (pure or mixed). Whereas the CMC was reduced when nonionic surfactants were added to ionic surfactants, the charge density was also diminished. This can be one of the reasons why the above surfactant interaction sequence was discovered. The CMC value of combined surfactants was lower than that of pure cationic surfactants, implying more interaction. The charge density was also shown to affect the fluctuation. The interactions of SPS with mixed surfactants was more broad, resulting in greater effective binding and effective size variation. The structural variation of the SPS was also a factor. The variances were likewise in goodagreement with the fluctuations found in combined surfactant viscosity measurement.[9]

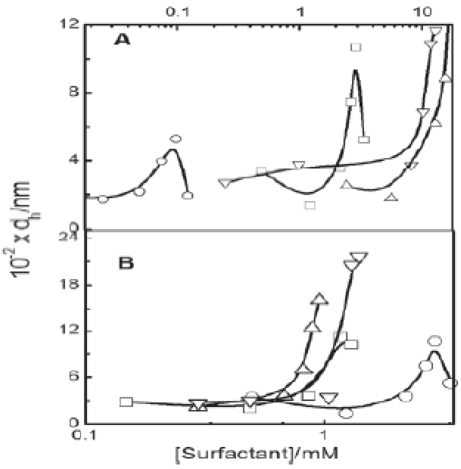


Fig. 3: Variation in hydrodynamic diameter (dn) of Klebsiella K28 in presence of (A) cationic surfactants (B) CTAB-Tween 20 mixedsurfactants at 303K. Cationic surfactants (A) : o, BDHAC: 5, CTAB: V7. CPC: a. DPC. Mole fraction of CTAB (B) : 0, 1.0; a, 0.8; VF. 0.2; A, 0.5. A 104M SPS was utilized in all case.

ZetaPotential

The DLS method was used to determine the zeta potential of the SPS solution. The Z.P values of the 4 SPS are listed on Table 3. In the absence of surfactants, all of the polymers had reasonably high negative Z.P values (about 40 mV), that are required for their stability in aqueous conditions. Though the hydrodynamic diameters of the polymers differed, the zeta potential values did not differ considerably (the values were in within analytical error limits). Figure 4 shows how the zeta potential values changed as the surfactants were added one at a time. The concentration of surfactant mandatory for charge reversal was discovered to be in the following order: BDHAC<CTAB<CPC.[10]

CONCLUSION

The data on the interactions of anionic SPS with cationic surfactants is scarce, while the current research group has conducted a few studies employing Klebsiella stains. Mixed surfactants have also been employed in a number of studies. These SPS-surfactant investigations had never been done before with the four test stains utilized in this study.

In the aqueous medium, show that the reported interaction parameters were largely consistent across the different methodologies. Utilizing turbidity, viscosity, & DLS measurements, the nature & dimensions of SPS-surfactant complexes formed. as well as their association or hydrodynamic sizes in the aqueous solution, were investigated. The complex of the SPS-surfactant interaction is revealed by the attachment of surfactant monomers to the binding domain of the anionic SPS, the prompted micelles bound to the polymer. or the association of the complexes formed & their configurationally modifications under the influence of enhanced surfactant concentration or the use of mixed surfactant.

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