# Effect of Solvent System on Critical Micelle Concentration Using Viscosity Equations for Anionic Surfactants at Various Temperatures

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Abstract: The critical micelle concentration (CMC) of Potassium Stearate (PS), Sodium Oleate (SO) and Sodium Dodecyl Sulphate (SDS) in alcohol- water solvent system (0%, 50%, 80%, 90%, and 100%) was driven from the density and viscosity measurements. The concentrations of PS, SO and SDS in different solvent systems used for the density and viscosity measurements were kept between 0.010 to 0.065g mol  $L^{-1}$  and measurements were taken at different temperatures. Experimental density values were seen to get decreased with the increase of the temperature. The viscosities are also represented in terms of Einstein, Vand, Moulik and Jones-Dole equations. We found that the viscosity of the salts in various solvent mixture decrease with increase in temperatures and all the values show positive trends.

Keywords: Density, Viscosity, PS, SO, SDS, Critical Micelle Concentration (CMC)

#### 1. Introduction

Potassium Stearate ( $C_{18}H_{35}KO_2$ ) is a fine, white powder that has a fatty odour. Potassium Stearate is used in Food, Beverage, Pharmaceuticals, Health & Personal care products, Agriculture/Animal Feed/Poultry etc. Potassium Stearate is used as an emulsifier from the Stearate salt family in cosmetics and beauty products to stabilize formulas and increasing the thickness, or add lubricating properties. It is used in a wide variety of skin care and hair care products, including eyeliner, eye shadow, mascara, lipsticks, blushers, face powders and foundations, and less often in perfumes, deodorants, and hair and skin care formulas.<sup>1</sup>

Sodium oleate ( $C_{18}H_{33}O_2Na$ ) is an unsaturated fatty acid. It is used for variety of commercial purposes, especially for the production of soap. It is often used in the production of insoluble metallic stearates. It is also used in industries as industrial lubricants and various oil-based cosmetics as a thickening or gelling agent.<sup>2</sup>

Sodium dodecyl sulphate (SDS) also known as sodium lauryl sulphate ( $CH_3(CH_2)_{11}SO_4Na$ ) is an important ingredient in industrial products such as car wash soaps, engine degreasers and floor cleaners.<sup>3</sup>The specific molecular structure of SDS, represented by long aliphatic chains with a sulphate ester group, confers amphiphilic properties and significant surface activity to the molecule.<sup>4</sup>It is widely used in cleansers because it is a cheap, highly effective cleansing and foaming agent. Like most detergents, it can irritate the skin<sup>5</sup>.

Many physical properties of surfactant solutions exhibit a characteristic transition over a narrow range of concentration. This transition is generally related to association of surfactant molecules arising from the intrinsic amphiphilic nature. The transition region could be used to determine the critical micelle concentration CMC above which multi-molecular aggregates are formed. CMC is a measure of surfactants efficiency.

Present investigation has been done with determination of densities and viscosities of Potassium Stearate, Sodium Oleate and Sodium Dodecyle Sulphate solutions of varying concentrations in ethanol-water solvent systems of varying percentage at various temperatures. An attempt has been made to determine intermolecular interactions in PS, SO and SDS in alcohol and water solvent systems. CMC values have been determined using densities and viscosities data which are further studied with the help of some well known equations.<sup>6</sup>

Measurement of viscosity in solution provides an excellent method of obtaining data on ion-ion and ion-solvent interactions. Hydrophobic and hydrophilic characters of the solute such as H-bonding formation and disruption are correlated to changes in the viscosity.<sup>7</sup>

Viscosity values were also calculated in terms of Einstein, Moulik, Jones-Dole and V and equations. These equations are -

Einstein equation:<sup>8</sup>  $\eta_{sp} = \eta_0 (1+2.5 \text{ V})C$  .....(1)

Moulik equation:  $(\eta/\eta_0)^2 = M + KC^2$  ......(2)

Jones-Dole equation:  ${}^{10}(\eta_{sp})/\sqrt{C} = A + B\sqrt{C}$  .....(3)

Vand equation: <sup>11</sup>  $1/C = (0.921/V) \ 1/ \log (\eta/\eta_0) + \phi V \ ....(1)$ 

Where C is the concentration,  $\eta_{sp}$  is the specific viscosity,  $\eta$  is the viscosity of the solution,  $\eta_0$  is the viscosity of solvent,  $\phi$ is the interaction coefficient, and V is the molar volume. The solute-solute and solute-solvent interactions are representedby the constants A and B in Jones-Dole equation and M and K in Moulikequation respectively. In the present study viscometric properties of Potassium Stearate, Sodium Oleate and Sodium DodecyleSulphatehave been found out in alcoholic and aqueous solvents systems as well as in their mixtures of varying composition at 298.15K, 303.15K, 308.15K and 313.15K temperatures over the entire concentration range. The solute-solute and solute-solvent

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interactions as well as the effect of solvent systems on anionic surfactants have also been studied.<sup>12-15</sup>

# 2. Experimental Section

#### Material:

Potassium Stearate (PS, 98%CDH), Sodium Oleate (SO, 98%CDH) and Sodium Dodecyl Sulphate (SDS, 90%CDH) were used as purchased. All solutions have been prepared using absolute alcohol and conductivity water. Conductivity water was obtained by initially distilling distilled water with acidified KMnO<sub>4</sub> and later with tiny amount of NaOH pellets and resulting vapours were condensed and collected as conductivity water. Potassium Hydroxide was used to purify alcohol by keeping over it for a day and distilled. The distillate was refluxed with 1% of Calcium metal for about eight hours and then redistilled. Only analytical grade reagents were used.

#### **Density Measurement:**

The solutions were prepared by weight using Keroy digital balance with least count  $\pm 0.0001$ g in water or ethanol or in binary solutions of these as per requirement. Bi-capillary pyknometer calibrated with double distilled water at room temperature was used for finding densities of solutions.

#### Viscosity Measurement:

Ostwald Viscometer was initially calibrated using double distilled water and henceforth used for analysing viscosity. For ensuring precision in measurements, each solution was reckoned three times for finding time of flow of fluid in viscometer. The exactness of stopwatch was set at  $\pm 0.01$ s for estimation of liquid stream.

#### **Temperature Control**

All the measurements were carried out in a thermostatically controlled and well-stirred water bath with an accuracy of 0.1K. All the measurements of density and time of flow were made in a thermostatic water bath (Model: MD/ME-31A, JULABO, Germany) in order to maintain the desired uniform temperature. The sample was allowed to stand in the bath for about 30 minutes in order to maintain thermal equilibrium between the test samples and the bath liquids.

**Table 1:** Density and viscosity of pure solvents and solvent

 systems (water and ethanol) and comparison with literature

values										
Syste m	Temperatu	Densit (gm m		Viscosity(η) (centipoise)						
	re (K)	Experiment	Literatu	Experiment	Literatu					
	(K)	al	re	al	re					
00/	298.15	1.006	0.997	0.9000	0.8920					
0% alcoh	303.15	0.999	0.995	0.8002	0.7972					
ol	308.15	0.997	0.994	0.7211	0.7192					
01	313.15	0.993	0.992	0.6526	0.6527					
50%	298.15	0.938		0.8391						
alcoh	303.15	0.930		0.7449						
ol	308.15	0.924		0.6683						
01	313.15	0.919		0.6039						
80%	298.15	0.872		0.7801						
	303.15	0.865		0.6928						
alcoh ol	308.15	0.851		0.6155						
	313.15	0.844		0.5546						
90%	298.15	0.850		0.7604						

alcoh	303.15	0.844		0.6760	
ol	308.15	0.838		0.6061	
	313.15	0.831		0.5461	
100% alcoh	298.15	0.804	0.7852	1.0862	1.0606
	303.15	0.798	0.7809	0.9834	0.9613
ol	308.15	0.791	0.7767	0.8903	0.8735
01	313.15	0.789	0.7724	0.8132	0.7957

# 3. Results and Discussion

Jones-Dole, Moulik, Einstein and Vand equations are used to predict the nature and extent of solute-solute and solutesolvent interactions among surfactant molecules and solvent moleculesutilising viscosity data which are tested and verified by many workers earlier.

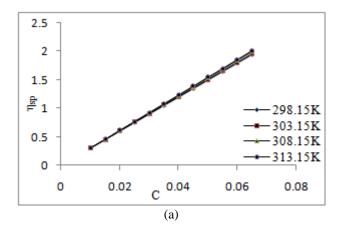
The critical micelle concentration (CMC) of Potassium Stearate, Sodium Oleate and Sodium Dodecyl Sulphate (SDS) in ethanolic and aqueous solutionsweredetermined from the density and viscosity measurement. The density and viscosities increase with increasing PS, SO and SDS concentration and decrease with increasing temperatures. The density and viscosity of the pure components are shown in Table 1. Table 2 shows CMC values (in gm/lit) of Potassium Stearate, Sodium Oleate and Sodium Dodecyl Sulphate (SDS) in alcohol-water solvent systems at different temperatures.

 Table 2: CMC values (in gmmol/lit) of Potassium Stearate,

 Sodium Oleate and Sodium Dodecyl Sulphate (SDS) in

 alcohol-water systems at different temperatures

alcohol-water systems at different temperatures.									
Temperature	0%	50%	80%	90%	100%				
alcohol alcohol alcohol alcohol alcohol									
Potassium Stearate									
298.15			0.025	0.020	0.025				
303.15			0.030	0.025	0.030				
308.15			0.035	0.025	0.035				
313.15			0.035	0.030	0.040				
Sodium Oleate									
298.15	0.030								
303.15	0.035								
308.15	0.040								
313.15	0.045								
	Sodium Dodecyl Sulphate								
298.15	0.020	0.030	0.025	0.020	0.025				
303.15	0.020	0.035	0.025	0.025	0.025				
308.15	0.030	0.035	0.030	0.030	0.030				
313.15	0.035	0.040	0.035	0.030	0.035				



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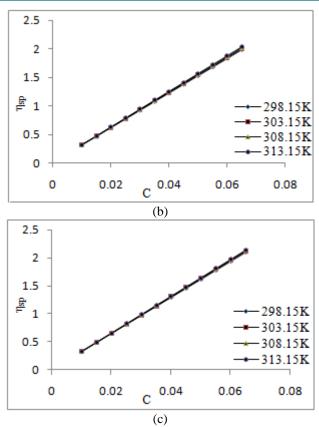
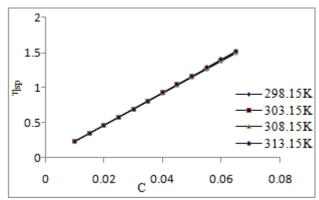
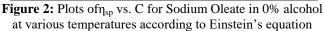
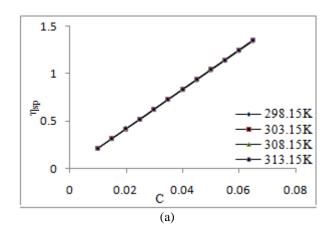
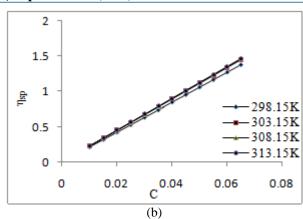


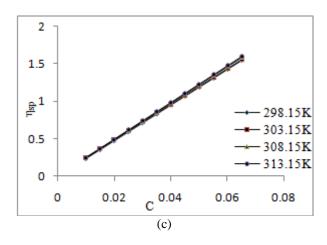
Figure1: Plots ofη<sub>sp</sub> vs. C for Potassium Stearate in alcohol water solvent system (a) 80% alcohol, (b) 90% alcohol and (c) 100% alcohol at various temperatures according to Einstein's equation

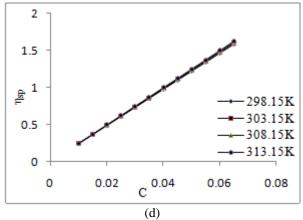












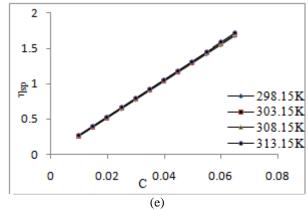
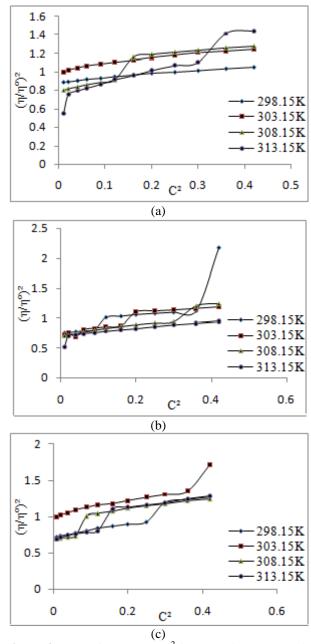


Figure 3: Plots of specific viscosity  $(\eta_{sp})$  vs. Concentration for SDS in alcohol water solvent system (a) 0% alcohol, (b) 50% alcohol, (c) 80% alcohol, (d) 90% alcohol and (e) 100% alcohol at various temperatures according to Einstein's equation

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Figures 1, 2 & 3 (the plots of specific viscosity vs. Concentration for Potassium Stearate, Sodium Oleate and Sodium Dodecyl Sulphate) are characterized by an intersection of straight lines at a concentration which corresponds to the CMC of Potassium Stearate, Sodium Oleate and Sodium Dodecyl Sulphate. The curves blow the CMC are linear with intercept equalling zero indicating that Einstein's equation is applicable to dilute solutions of PS, SO and SDS below the CMC. The curves specific viscosity vs. Concentration for PS, SO and SDS salts at all temperatures almost overlap showing specific viscosity though viscosity changing in the same trend VS. concentration different plotsare well separatedat temperatures.



**Figure 4:** Plots of  $(\eta/\eta^{\circ})^2$  vs. C<sup>2</sup> for Potassium Stearate in alcohol water solvent system (a) 80% alcohol, (b) 90% alcohol and (c) 100% alcohol at various temperatures according to Moulik equation

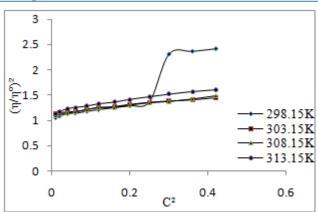
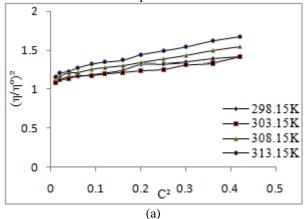
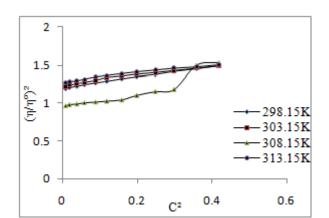
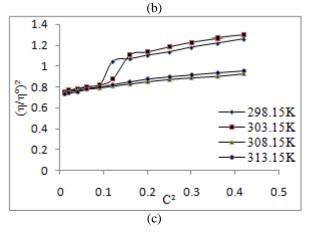


Figure 5: Plots of  $(\eta/\eta^{\circ})^2$  vs. C<sup>2</sup>for Sodium Oleate in 0% alcohol at various temperatures according to Moulik equation

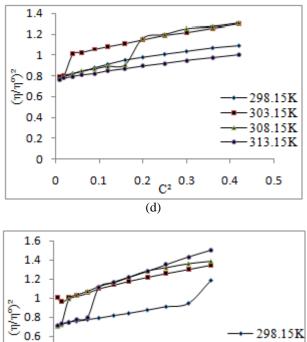


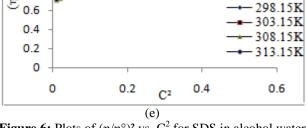




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**Figure 6:** Plots of  $(\eta/\eta^{\circ})^2$  vs. C<sup>2</sup> for SDS in alcohol water solvent system (a) 0% alcohol, (b) 50% alcohol, (c) 80% alcohol, (d) 90% alcohol and (e) 100% alcohol at various temperatures according to Moulik equation

The results show that the Moulik equation is in general applicable to PS solutions and SO solutions showing abrupt change in trend at CMC but in case of SDS it is applicable for dilute solutions. For all the cases ideal results are seen at higher temperatures i.e. at 308.15K and 313.15K. The values of Moulik constants M & K which give interactions between solute-solute and solute-solvent molecules have been calculated from the intercept and slope of the plots. The value of  $(\eta/\eta^{\circ})^2$  increases linearly for increasing concentrations.

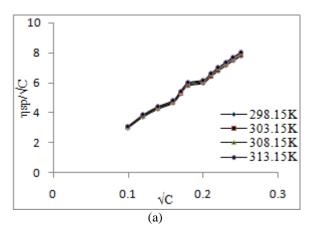
 Table 3: Physical constants M & K calculated from Moulik

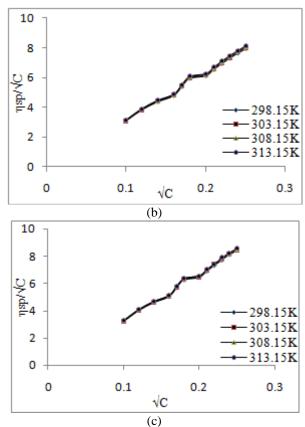
 equation for Potassium Stearate, Sodium Oleate and Sodium

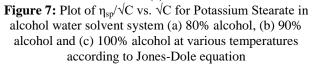
 dodogul Sulphate at various temperatures

dodecyl Sulphate at various temperatures								
Solvent	lvent 298.		15K 303.		308.	308.15K		15K
system	М	Κ	М	Κ	Μ	Κ	М	K
	Potassium Stearate							
80% alcohol	0.891	0.388	1.018	0.585	0.807	1.336	0.663	1.823
90% alcohol	0.654	2.3	0.716	1.289	0.678	1.218	0.665	0.735
100% alcohol	0.682	1.412	0.983	1.322	0.743	1.419	0.698	1.581
		S	odium	Oleate				
0%alcohol	0.878	3.572	1.132	0.789	1.114	0.914	1.168	1.11
		Sodiur	n dode	cyl Sul	phate			
0%alcohol	1.122	0.756	1.101	0.697	1.162	0.934	1.187	1.2
50% alcohol	1.189	0.73	1.233	0.655	0.893	1.325	1.276	0.593
80% alcohol	0.807	0.742	0.904	1.063	0.76	1.472	0.773	0.56
90% alcohol	0.767	1.338	0.74	1.547	0.751	0.444	0.746	0.547
100% alcohol	0.689	0.894	9.975	0.912	0.867	1.48	0.713	2.089

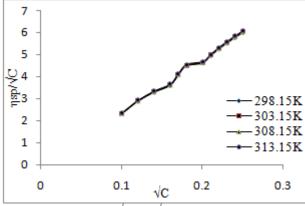
Observation of above table show that in general the solutesolute interactions are greater than solute-solvent interactions when the solvent is pure water or percentage of water is higher. With the increasing percent of ethanol the trend seems to get reversed. At higher percentage of alcohol solute-solvent interactions become greater. It can be explained on the basis of high dielectric constant of water therefore greater ionization in water and lesser solvation of molecules.



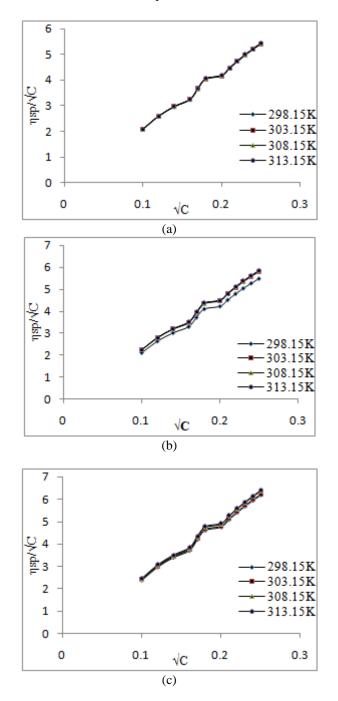


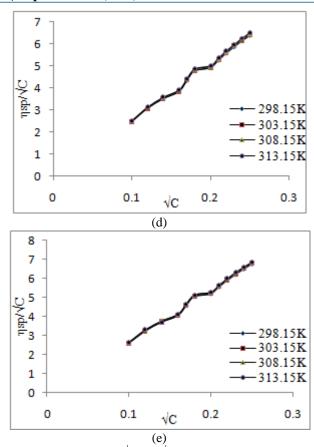


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**Figure 8:** Plots  $of\eta_{sp}/\sqrt{C}$  vs.  $\sqrt{C}$  for Sodium Oleate in 0% alcohol at various temperatures according to Jones-Dole equation





**Figure 9:** Plot of  $\eta_{sp}/\sqrt{C}$  vs.  $\sqrt{C}$  for SDS in alcohol water solvent system (a) 0% alcohol, (b) 50% alcohol, (c) 80% alcohol, (d) 90% alcohol and (e) 100% alcohol at various temperatures according to Jones-Dole equation

Shown in figures7, 8 and 9 plots of  $\eta_{sp}/\sqrt{C}$  vs.  $\sqrt{C}$  for PS, SO and SDS respectively and these are characterized by a break at points which correspond to the CMC. The values of Jones-Dole constants A & B calculated from the intercept & slope of linear portions blow the CMC for the salts under experimentation are represented in table 4. The results show that the solute-solute interaction is lower than the solute-solvent interaction which is partially in agreement with the information obtained from Einstein's equation.

 Table 4: Physical constants A & B calculated from Jones 

 Dole equation for Potassium Stearate, Sodium Oleate and

 Sedium dedecul Sulphate at accurate former and forme

Sodium dodecyl Sulphate at various temperatures									
Solvent	298.15K		303.15K		308.15K		313.15K		
system	Α	В	Α	В	Α	В	Α	В	
		Pota	assium	Steara	ate				
80%alcohol	0.157	31.52	0.153	31.73	0.161	32.29	0.153	32.53	
90%alcohol	0.148	32.29	0.149	32.50	0.160	32.77	0.158	33.05	
100% alcohol	0.159	34.13	0.169	34.41	0.169	34.72	0.167	34.79	
	Sodium Oleate								
0%alcohol	0.121	24.32	0.124	24.49	0.117	24.51	0.124	24.65	
	S	odium	n dode	cyl Su	lphate				
0%alcohol	0.116	22.13	0.097	21.92	0.112	22.04	0.116	22.13	
50%alcohol	0.104	22.30	0.111	23.57	0.111	23.73	0.115	23.87	
80%alcohol	0.123	25.16	0.122	25.36	0.122	25.77	0.127	26.01	
90%alcohol	0.125	25.82	0.127	26.01	0.121	26.17	0.125	26.40	
100% alcohol	0.137	27.32	0.134	27.51	0.131	27.72	0.156	27.91	

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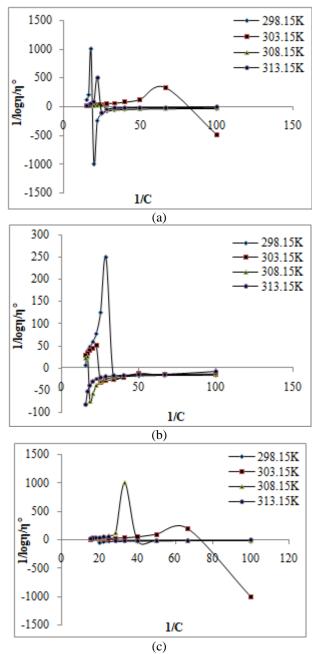
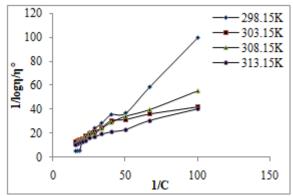
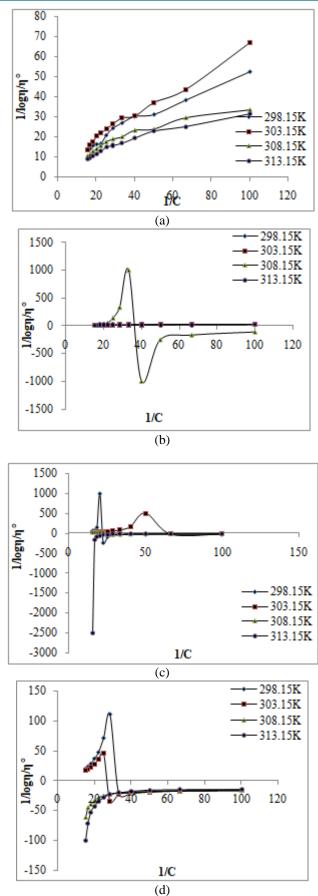


Figure 10: Plot of 1/C vs.  $1/\log\eta_{/} \eta^{\circ}$  for Potassium Stearate in alcohol water solvent system (a) 80% alcohol, (b) 90% alcohol and (c) 100% alcohol at various temperatures according to Vand equation.

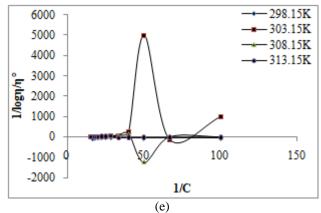


**Figure 11:** Plot of 1/C vs. 1/logη/ η° for Sodium Oleate in 0% alcohol at various temperatures according to Vand equation



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**Figure12:** Plot of 1/C vs.  $1/\log\eta/\eta^{\circ}$  for SDS in alcohol water solvent system (a) 0% alcohol, (b) 50% alcohol, (c) 80% alcohol, (d) 90% alcohol and (e) 100% alcohol at various temperatures according to Vand equation

Vand equation is showing abnormal behaviour in alcohol water dissolvable system (50%, 80%, 90% and 100% alcohol), yet 0% alcohol tends to normal behaviour. Behaviour also tends to normal at higher temperatures. Alcohol's hydroxyl group can take an interest in H- bonding, leaving it more viscous and less polar natural compound. The dielectric consistent of ethanol is lesser than that of water therefore in alcohol ionization of surfactant is similarly less. Ionization of surfactant continues increasing with the increasing percentage of water in the solvent system. Further H-bonding may likewise affect the ionization of salt and viscosity of the solution Mobility of ions should increase with increasing temperatures due to which again tendency turning towards ideal nature. The estimations of the molar volume V for Potassium Stearate, Sodium Oleate and Sodium Dodecyl Sulfate as got from the slopes of the plots (figure 10, 11 and 12) are shown in table 5. The estimations of the interaction coefficients  $\phi$  calculated from the intercept of the plots are presented in table5.

**Table 5:** Physical constants molar volume (V) & interaction coefficient ( $\phi$ ) calculated from Vand equation for Potassium Stearate, Sodium Oleate and Sodium Dodecyl Sulphate at

various temperatures										
Solvent	298.15K		303.15K		308.15K		313.15K			
system	V	ø	V	ø	V	ø	V	ø		
	Potassium Stearate									
80% alcohol	0.003	-36.19	0.059	-37.87	0.434	-34.87	0.035	-37.46		
90%alcohol	0.125	-41.63	0.383	-37.54	0.112	-38.77	0.725	-56.75		
100%alcohol	0.083	-34.99	0.055	-34.15	0.01	-37.38	0.557	-40.39		
		( )	Sodiun	n Oleat	e					
0%alcohol	0.92	9.113	2.51	21.8	1.904	10.69	2.779	15.13		
		Sodiu	m dod	ecyl Su	ılphate	•				
0%alcohol	2.113	16.73	1.695	12.58	3.371	28.5	3.582	23.00		
50%alcohol	4.390	-45.11	5.770	-60.01	0.012	-36.39	7.616	-79.00		
80%alcohol	0.017	-37.38	0.010	-35.50	0.342	-33.36	0.010	-38.90		
90%alcohol	0.313	-42.66	0.506	-37.88	1.148	-69.39	0.590	-58.05		
100% alcohol	0.254	-42.47	0.005	-33.32	0.013	-35.29	-0.670	-40.63		

# 4. Conclusion

An extensive and near investigation of anionic surfactants Potassium Stearate, Sodium Oleate and Sodium Dodecyl Sulfate in alcoholic and watery dissolvable system (0%, 50%, 80%, 90%, and 100% alcohol) has been completed. The density and viscosity of PS, SO and SDS solutions increases with increases concentration. The viscosity results of the salts in binary solvent systems have been agreeably clarified as far as Einstein, Vand, Moulik, and Jones-Dole equations. The outcomes obtained from different conditions demonstrate almost similar trend, yet results got from Vand equation indicate abnormal behaviour in solvent systems of changing composition. The values of different constants got from these known equations show that there is a significant interaction between PS, SO and SDS molecules themselves and with those with dissolvable particles.

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