

Spectroscopic studies of the investigation of molecular interaction between Acid Red and cetyltrimethylammonium bromide

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Abstract : Interaction of an anionic textile dye namely Acid Red 266 (AR) with cationic surfactant like cetyltrimethylammonium bromide (CTAB) has been investigated by means of UV-visible spectroscopy in pre-micellar concentration range. The aggregation between surfactant and dye was found to be observed at surfactant concentration far below the critical micelle concentration of the surfactant. Aggregation is reflected by a significant change in λ_{\max} (bathochromic shift), with the appearance of two new bands in the spectrum of the pure dye. The binding constant (K_b) of complexation was determined from the Benesi-Hildebrand plot. The values of K_b for AR-CTAB complex increased with increase of dye concentrations. The values of binding constant for AR-CTAB system increased up to certain temperatures and then start to decrease with temperature. The effect of polyelectrolyte, sodium alginate (SA) on AR-CTAB interactions was studied and was observed that the binding constant (K_b) value in water-polyelectrolyte system was higher in magnitude than that in pure water system. The binding constant (K_b) gradually increases as the sodium alginate concentration increased up to 0.01% and then with further increase of

the sodium alginate concentration, precipitation occurs. The values of K_b for AR-CTAB system were found to be higher in magnitude in mixed solvent (water-alcohol) compared to that of pure water. With increasing alkyl chain length of alcohol, the binding constant (K_b) of AR-CTAB complex was found to be increased. The effect of pH on AR-CTAB interaction was found that there was a significant increase in K_b value with increasing pH. In all the cases, ΔG^0 values of the complexes were negative which indicated that the complex formation was thermodynamically spontaneous. The binding interaction between dye and CTAB was found to be hydrophobic in nature at lower temperature whereas both electrostatic and hydrophobic interactions exist at higher temperatures. Enthalpy-entropy compensation is observed from a linear relation between enthalpy and entropy changes in aqueous solution for AR-CTAB complex.

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Keywords : Acid red 266; Cetyltrimethylammonium bromide; Binding constant; Sodium alginate; Thermodynamic parameters.

INTRODUCTION

The interactions between dye and surfactant mol-

ecules are important in various dyeing processes such as textile dyeing, photography, luminescence, and lasers and printing ink, as well as in chemical research in

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fields such as biochemistry, analytical chemistry, and pharmaceutical applications^[1]. Application of dyes as auxiliary agents will probably continue to be important in the coloration of materials resulting from current and future developments in fiber science and technology. Knowledge of these interactions helps us to understand the chemical equilibrium, mechanisms, kinetics of surfactants, sensitized colors and fluorescence reactions^[2]. Knowledge of binding constant (K_b) has many applications in various fields of chemistry. Different synthetic chemical dyes are extensively used in many industrial processes for various purposes. Effluents coming out from these industries are highly coloured, resulting in major environmental problems. So these coloured wastes need to be treated before disposal^[3]. In addition, the change in environmental conditions such as temperature, pH, solvent properties etc. are known to affect the binding properties of dyes. A recent literature survey reveals that a detailed spectroscopic study on the interaction of AR with CTAB is rare. This is why; the study of interaction of AR as a model textile anionic dye with CTAB, a model cationic surfactant in water at different temperature, different water-organic mixed solvents and aqueous solution of electrolyte has been under taken in this study. To characterize the AR-CTAB interactions, values of K_b and thermodynamic parameters have been evaluated.

EXPERIMENTAL

Materials and methods

AR was obtained from China and CTAB was obtained from Aldrich, USA. Both AR and CTAB were used without any further purification. Dye solution (particular concentration) and surfactant solutions of varying concentrations were firstly prepared in distilled de-ionized water separately. 2.5mL of the dye and 2.5mL of each of the surfactant solutions were mixed properly. The resultant mixture were then kept in a shaking incubator (GFL 3031, USA) for about half an hour with constant stirring (80 rpm) to form dye-surfactant complexes. To observe the effect of polyelectrolyte (sodium alginate) on the interaction of dye with the surfactant, both the dye and surfactant solutions were prepared in the polyelectrolyte solu-

tion of a particular concentration. Similar procedure has been followed to observe the effect of alcohol and pH on dye-surfactant interaction. Absorption spectra over the range of 200-800 nm were recorded at desired temperature using a UV-visible spectrophotometer (UV-1601PC, Shimadzu, Japan). During the measurement of absorbance of dye-surfactant complexes solution, the temperature of the resultant mixture will be kept constant using the temperature controller unit (TCC-controller, Shimadzu) of UV visible spectrophotometer.

RESULTS AND DISCUSSION

The UV-visible absorption spectra of dye solution in aqueous medium are changed due to the addition of CTAB solutions is as shown in Figure 1. AR may exist in anionic form in aqueous solution. The spectrum of AR in aqueous solution exhibits the absorption maximum (λ_{max}) at 498 nm. With addition of CTAB, spectra showed a significant change in λ_{max} (517 nm, bathochromic shift) with the appearance of additional two new bands, one at 547 nm (bathochromic shift) and other at 384 nm (hypsochromic shift). Such change in λ_{max} and appearance of two new bands indicated the presence of strong interaction between AR and CTAB. The formation of the dye-surfactant complex is a consequence of mutual influence of long range interaction (electrostatic attraction) and short range interaction (hydrophobic interaction). In aqueous solution both dye and surfactant molecules dissociate into ions and therefore electrostatic attractive interaction can appear between sulfonate group of dye and head group of surfactant. As the electrostatic attraction between the oppositely charged ions bring them into close proximity to form ion pair (Scheme 1), the hydrophobic interactions must align the hydrocarbon chain of the surfactant with the hydrophobic moiety of the dye^[4]. This may be the reason of the observed bathochromic shift in λ_{max} at 517 nm.

The new band may be attributed to dye dimerization in the presence of surfactant due to J-aggregation. According to Kasha exciton theory^[5], J- or H-aggregates can be formed depending on the angle (α) between the transition dipoles and the molecular axis of the aggregate. J-aggregates of dyes are characterized

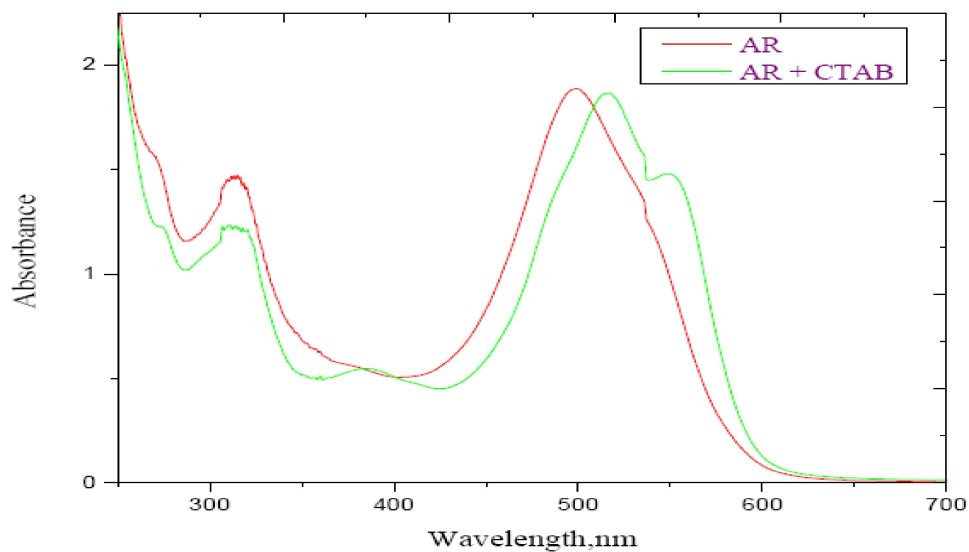
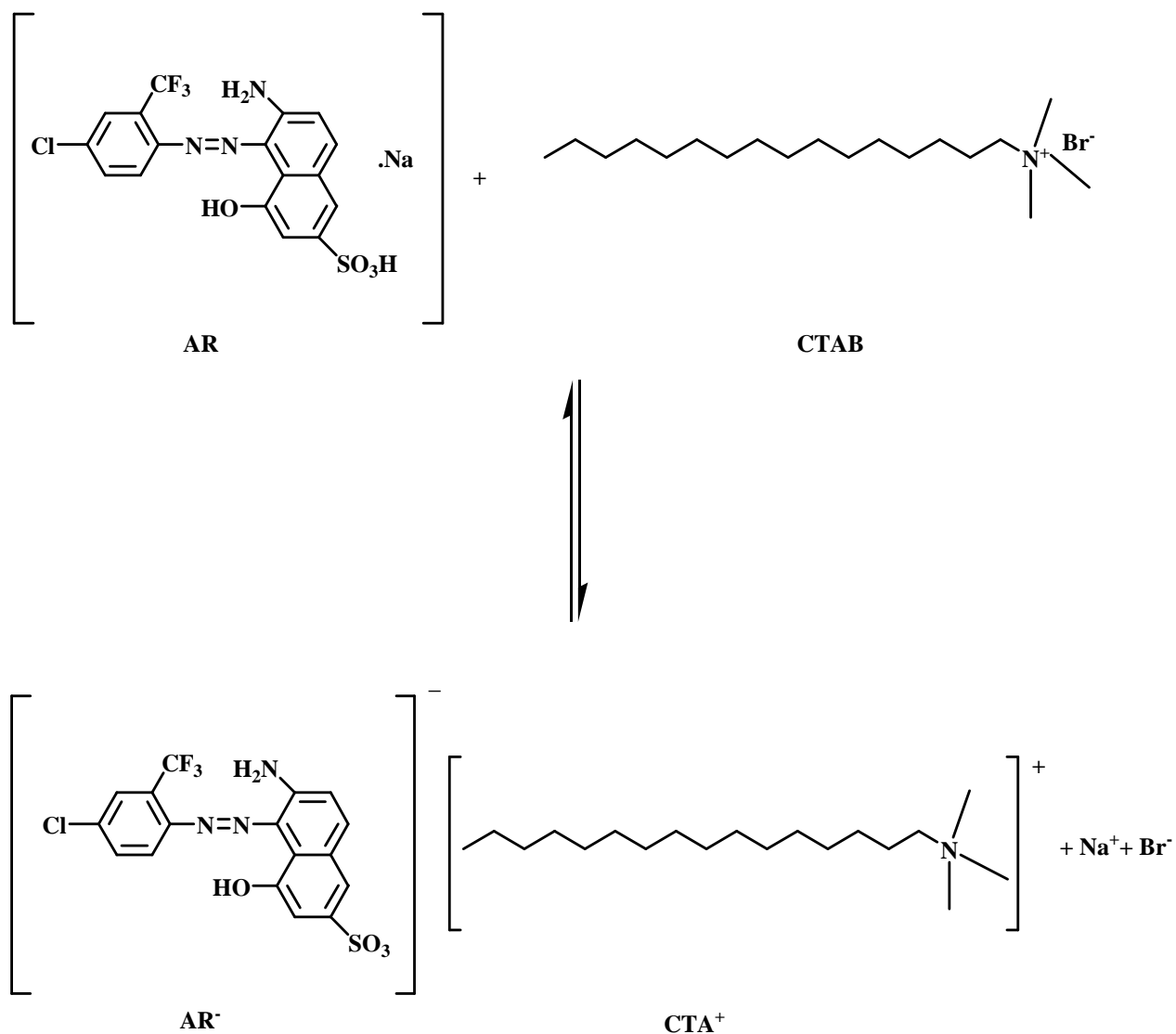


Figure 1 : The UV-visible spectra of aqueous solution of Acid Red in absence and presence of 0.6 mM CTAB



Scheme 1 : Ion pair formation between AR^- and CTA^+ ions.

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by an intense red shifted absorption band compared to the monomer's. The coupled monomers of J-aggregates would produce a side-by-side or a slipped face-to-face stacking geometry^[6]. Due to the formation of oppositely charged dye-surfactant complex, the repulsion forces are decreases and the hydrophobic interactions as well as van der Waals forces between the same charged dye particles are affected^[7]. Such associates may induct premicellar surfactant aggregation and enhances the solubilization of the dye^[8,9].

The binding constant, K_b for AR-CTAB system was determined by using the following Benesi-Hildebrand^[10] equation

$$[D]/A=1/K\epsilon[C]+1/\epsilon \quad (1)$$

Where [D] is the concentration of dye, 'A' is the absorbance of dye-surfactant band and [C] is the concentration of surfactant. The values of K_b for AR-CTAB systems having different concentrations of AR are presented in TABLE 1.

The K_b value was found to be increased with increasing concentration of AR. Such trend in increase in K_b value suggested that the anionic AR might interact electrostatically with the cationic CTAB head groups to reveal micellar properties^[11]. Moreover the formation of dye aggregates induced by surfactant is supported by the fact that the binding of AR to cationic surfactant in water is cooperative^[12]. An AR molecule that binds to the cationic surfactant creates a more hydrophobic binding site and facilitates the binding of another dye molecule. This implies that next to electrostatic interactions, hydrophobic stacking of the aromatic parts of the azo dyes is also important in the aggregation process.

The values of K_b for the dye-surfactant complex in water are changed due to the addition of the aqueous solution of a polyelectrolyte like sodium alginate (SA) at 303.15K and the corresponding values are presented in TABLE 2. It was found that the binding constant (K_b) value in water- polyelectrolyte system was higher in magnitude than pure water system. This proved that, stronger complexes are formed in the presence of sodium alginate^[13]. The binding constant gradually increases as the sodium alginate concentration increased up to 0.01% and then precipitation occurs on further increase of the sodium alginate concentration. This is

because, in the presence of higher concentration of polyelectrolyte, water insoluble dye-surfactant-polyelectrolyte complexes are formed and they remain insoluble in much broader concentration ranges of the components^[13]. Decrease of surfactant solubility with increasing salt concentration is known as salting out effect. This is because of an electrical attraction between the charged ion and the electric dipole moment of water molecules, which causes the so-called tying up of the water molecules. The net result is those water molecules are effectively removed from the solution which causes less availability of water molecules for solvating the surfactant. Hence the surfactant can more effectively bind the dye molecule and hence the K_b values are increased. A polyelectrolyte such as sodium alginate seems to break the hydrated shell around the surfactant molecule^[13]. The surface charges due to added polyelectrolyte allow the particles to settle to smaller volume. The effect is found to be increased with the increase of the concentrations of the polyelectrolyte and thus the dye has more accessibility to the surfactant molecule thereby forming stronger binding. So extent

TABLE 1 : Effect of concentration of AR on binding constant of AR-CTAB system

$c_{AR}/ (M \times 10^{-5})$	$K_b \times 10^4 / (\text{Litre mole}^{-1})$
5.00	1.17
10.0	1.83
25.0	1.99

TABLE 2 : Values of the binding constants (K_b) for the dye-surfactant complex in water and in aqueous solution of sodium alginate at 303.15K

System	$c_{SA}/ (\%, w/v)$	$K_b \times 10^3 / (\text{Liter mole}^{-1})$
Water	0.0000	3.81
Water-Na Alginate	0.0001	8.63
Water-Na Alginate	0.0010	10.50
Water-Na Alginate	0.0100	11.50

TABLE 3 : Effect of solvent composition on the values of binding constant (K_b) of dye-surfactant interaction at 303.15 K.

Solvent	$c_{alcohol}/ (\%, w/v)$	$K_b \times 10^3 / (\text{Liter mole}^{-1})$
Water	0.00	3.81
Water-methanol	10.00	3.99
Water-methanol	20.00	8.86
Water-Ethanol	10.00	10.50
Water-2-Propanol	10.00	16.80

of binding (K_b) increases with increasing concentrations of salt sodium alginate.

Effect of solvent composition on the values of binding constant (K_b) of AR-CTAB interaction at 303.15K are presented in TABLE 3. It has been found that the values of binding constants of the dye-surfactant complex at a fixed temperature are higher in magnitude in mixed solvent (water-alcohol) compared to that in pure water and the K_b values of AR-CTAB complex was increased with increasing alkyl chain length of alcohol.

The dielectric constant of water, methanol, ethanol and 2-propanol are 80, 33, 24.55 and 18 respectively^[14]. As water has a high dielectric constant^[15], so addition of methanol to water decreases the dielectric constant of solution resulting in a greater attractive force between water and methanol molecules. On the other hand, methanol is acting as a co-solvent and as a structure-breaking solute. The presence of structure breakers in the aqueous phase may disrupt the organization of the water produced by the dissolved hydrophobic group thereby water molecules are less available for solvating the CTAB. Thus CTAB can bind with AR more easily. At high alcohol content more and more

water and methanol molecules held together due to ion pair formation. Thus the binding constant of AR-CTAB complex increased with increase of methanol content. Among the homologous series of alcohols such as methanol, ethanol, 2-propanol at 303.15K, 2-propanol not only have the largest hydrophobic surface. 2-propanol also lowers the dielectric constant of water to a greater extent; ethanol falls in between 2-propanol and water whereas methanol has the smallest hydrophobic surface as well as the least effect in lowering the dielectric constant^[16].

To observe the pH effect on the binding constant of AR-CTAB complex, different concentrations of CTAB were mixed with aqueous solution of AR at three different pH values such as 2.85, 6.00 and 8.40. Hydrochloric acid and sodium hydroxide were used for the pH adjustment respectively to avoid interactions with buffer solutions. The K_b values of AR-CTAB complex at different pH values is shown in TABLE 4. The values of K_b were found to be increased with increase of pH values. In acidic solution, AR exists in protonated (HAR) form and shows red shift in UV spectra. When base is added, deprotonated (AR⁻) form of AR appears and in aqueous solution there is a possibility to exist as zwitterionic form and has a resonance structure between the two extreme forms. In acidic solutions, as the dye exist as protonated form therefore electrostatic attraction become less and hydrophobic interaction is predominant in this case. But in basic deprotonated

TABLE 4 : The values of K_b for AR-CTAB system at different pH values.

pH	$K_b \times 10^3 / (\text{Liter mole}^{-1})$
2.85	3.02
6.00	3.81
8.40	5.08

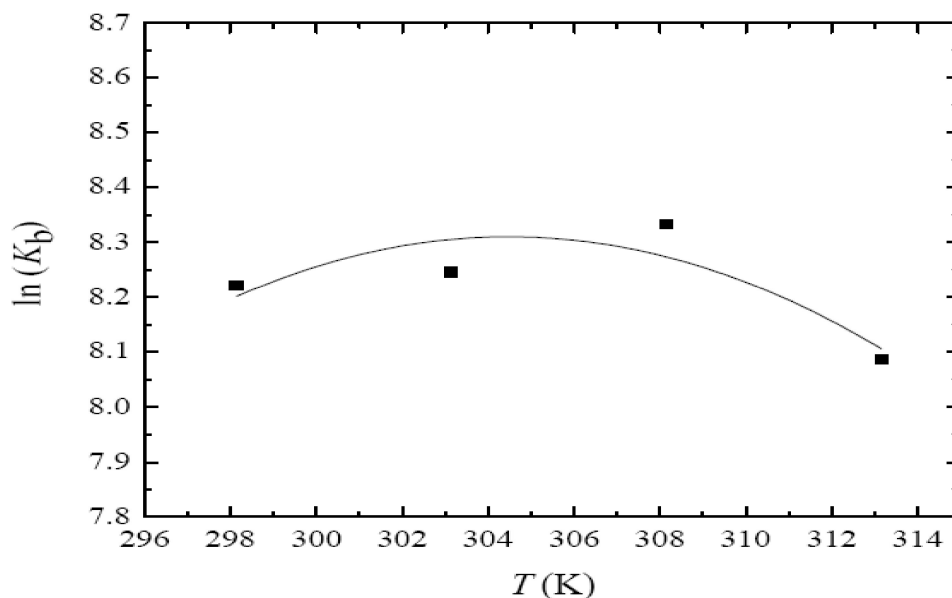


Figure 2 : Plot of $\ln(K_b)$ versus T to calculate ΔH° for AR-CTAB system in water.

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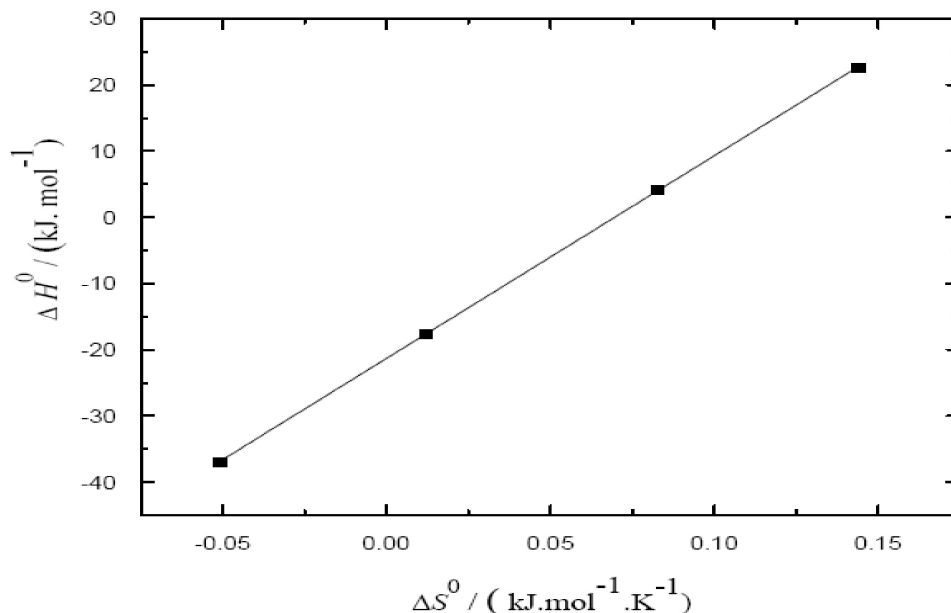


Figure 3 : Enthalpy –entropy compensation plot for AR-CTAB system in water.

TABLE 5 : Values of the thermodynamic parameters for the AR-CTAB complex.

T/K	$\Delta G^0 / \text{kJ.mol}^{-1}$	$\Delta H^0 / \text{kJ.mol}^{-1}$	$\Delta S^0 / \text{J.mol}^{-1}.\text{K}^{-1}$	$\Delta H^{0,*} / \text{kJ.mol}^{-1}.\text{K}^{-1}$	T_c / K
298.15	-20.38	22.60	144.17	-21.32	306.07
303.15	-20.79	4.24	82.55		
308.15	-21.35	-17.64	12.04		
313.15	-21.06	-36.95	-50.75		

form, electrostatic interaction occurs between negative charge group of AR and positive head group of CTAB. As the electrostatic attraction between the oppositely charged ions bring them into close proximity, the hydrophobic interactions must align the hydrocarbon chain of the CTAB with the hydrophobic moiety of the AR^[4]. Therefore binding constant is increased in basic solution. In neutral solution, as AR may be a zwitterion form, electrostatic and hydrophobic interaction is in between acidic and basic form. So binding constant (K_b) of neutral solution of AR also falls in between acidic and basic form.

The thermodynamic parameters for AR-CTAB complexation were calculated from the following standard thermodynamic equations. The standard enthalpy change of the processes was calculated using the modified van't Hoff equation^[17-19]

$$\Delta H^0 = RT^2 \partial \ln(K_b) / \partial T \quad (2)$$

$\ln(K_b)$ vs. T plot was made to calculate ΔH^0 where values of K_b were taken in mole fraction units. The plot

was found to be non linear and shown in Figure 2.

The slope in the plot of $\ln(K_b)$ vs. T at each temperature was taken as $\partial \ln(K_b) / \partial T$ and was then used to calculate ΔH^0 ^[17-19]. The values of thermodynamic parameters for dye-surfactant solutions in pure water are presented in TABLE 5. The values of ΔG^0 for AR-CTAB complex were found to be negative which indicate that the binding process occurs spontaneously^[20]. The negative values of ΔG^0 increased with increase of temperature indicate that complexation process is thermodynamically spontaneous over range of temperatures studied. For AR-CTAB system in water, the ΔH^0 values were initially positive, the sign of ΔH^0 value changes from positive to negative and then the negative ΔH^0 value increases with further increase of temperature. The values of ΔS^0 were positive which decreased up to a certain temperature and the sign changed from positive to negative at $T=313.15\text{K}$. Thus the binding process is entropy controlled at lower temperature whereas that becomes both enthalpy and entropy controlled at higher temperature. The results reveal that the binding interactions between AR and CTAB are both electrostatic and hydrophobic in nature at higher temperature whereas only hydrophobic interaction plays the major role at lower temperatures.

A linear relationship (Figure 3) between ΔH^0 and ΔS^0 was observed in Figure 3 according to the following regression equation known as the enthalpy-entropy compensation^[21].

$$\Delta H^0 = \Delta H^{0,*} + T_c \Delta S^0 \quad (3)$$

Where the slope, T_c , the compensation temperature and the intercept $\Delta H^{0,*}$, is the intrinsic enthalpy gain. The values of $\Delta H^{0,*}$ and T_c for AR-CTAB complex in pure water are presented in TABLE 5. The intercept $\Delta H^{0,*}$ characterizes the solute-solute interaction and stands for an index of the effectiveness of the hydrophobic chain to participate in the micelle formation. The $\Delta H^{0,*}$ values stand for the enthalpy effect under the condition $\Delta S^0 = 0$. The higher negative $\Delta H^{0,*}$ value indicates that the micellization of CTAB is favoured even at $\Delta S^0 = 0$. For AR-CTAB system in pure water the value of T_c is 306.07 K which is comparable to that of the biological fluid^[22].

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