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Solubility and thermodynamic micellization studies of the insecticide chlorpyrifos in aqueous medium

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- ✓ Micellar Solubility,
- ✓ Thermodynamic parameters.

Abstract

In this study, sodium dodecylsulphate (SDS) was used to solubilize chlorpyrifos (CPF) in water and monitored by the conductometric method. The critical micellar concentration (CMC) values as well as various thermodynamic parameters such as standard Gibbs energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) of micellization were determined in the temperature range of 304 to 332 K. On the other hand, CMC values and thermodynamic parameters of micellization were determined at various CPF concentrations. We noted a decrease in the SDS critical micellar concentration according to CPF concentration and temperature. The obtained thermodynamic parameters showed that $|T\Delta S^0|$ is higher than $|\Delta H^0|$ which suggests that the micellization process is entropy-controlled. The negative values of ΔG^0 showed that the interactions between CPF and SDS are spontaneous, i.e. thermodynamically favorable. The micellar solubilization of insecticide chlorpyrifos (CPF) with anionic surfactant improves its solubility in aqueous medium significantly.

1. Introduction

To obtain an optimal agricultural production, the plants must be protected from the devastating insects, bad grasses, fungicide diseases and other attackers. Thus, the farmers use pesticides to fight against the latter. Chlorpyrifos (CPF) or (O,O-diethyl O-(3,5, trichloro-2-pyridinyl) phosphorothioate), an organophosphorus insecticide-acaricide, is largely used for the control of the insects and parasites prone to affect harvests like cotton and cereals [1-2]. Moreover, it is one of the most used insecticides in residential medium, since it is contained in several products approved on the market [3].

Because of its potentially harmful effects on human health and some aquatic and terrestrial animals, an increased attention should be made during the applications [4-6]. CPF is an insecticide with broad spectrum i.e. concerning several species of insects, which has a moderate toxicity with a half-life duration ranging from 10 to 120 days, but can vary from 2 weeks to more than one year, according to the type of ground, the climate and other conditions [7-9]. It is a stable compound in neutral and acid media. It kills insects by direct contact or by ingestion, the normal operation of the nervous system is disturbed and he causes reproduction disorders [10-13]. It is effective against the sucker insects and machor and was largely developed to fight against various vegetables parasites [14]. It causes harmful effects on the not targeted vertebrate ones mainly by inhibiting the acetylcholinesterase activity, and an over-exposure can lead to an acute neurotoxicity, consequently to convulsion, paralysis and death [15].

Chlorpyrifos is an insecticide widely used in agricultural sector. For instance, in the United States, approximately 5 to 7 million kilograms are used each year [16]. Recent studies carried out in countries like China and the United States made it possible to detect traces of chlorpyrifos and these metabolites in the aquatic environment and the products of harvests, because of its massive use in agriculture. The contents were largely higher than the maximum limits of residues LMR (0.01-0.05 mg kg^{-1}) allowed by WHO and the European Union [17-20].

These high residues can cause for the man, the consumption of products contaminated with amounts higher than the acceptable daily dose (DJA) which is about 0.001 mg kg^{-1} day^{-1} [21-23].

In Senegal, the intensive agriculture practiced primarily in the Niayes area calls upon a strong use of pesticides to increase the outputs. Insecticide CPF is largely used in this zone which provides the majority of vegetables consumed in Dakar, to control different harmful insects [24, 25]. Consequently, these residues are present in the food matrices (water, vegetables) at traces level [26-29]. Insecticide is poorly soluble in water (2 mg L^{-1}) at 25°C [30-32]. This low solubility of the insecticide may result in low microbiological degradation in the environmental matrices, leading to the persistence of insecticide in surface and groundwater.

Because of the low solubility of chlorpyrifos in water, we undertook to make in the present work a study of micellar solubilization in aqueous medium in order to increase its solubility. Surfactant micellization is a thermodynamic phenomenon which can be studied using several techniques such as isothermal calorimetry and conductometry. The conductometric method is used in this work to study the solubility of insecticide CPF in aqueous micellar medium using sodium dodecylsulphate (SDS) which is an anionic surfactant. Conductometric methods are simple methods of analysis which are not difficult to realize. They have many advantages, in particular the low costs of equipment, the treatment of the samples, the speed, the sensitivity and the performance. They can thus be regarded as an alternative appropriate to the other analytical techniques like the spectrophotometric, spectrofluorimetric and chromatographic methods [33-37].

2. Material and Methods

2.1. Apparatus

Conductivity measurements were performed using a VWR CO 3100 L conductometer, with a cell constant of 0.84 cm^{-1} and one temperature gauge. The apparatus was calibrated with a KCl solution (0.01 mol L^{-1}). Its conductivities are 1278 and 1413 µs.cm^{-1} at 20 and 25°C. A VELP SCIENTIFICA magnetic stirrer (Heating Magnetic Stirrer) was also used to homogenize the solution. A STARTORIUS U3600S electronic balance (± 0.1 mg) made it possible to make the necessary weighing.

2.2. Chemicals

Chlorpyrifos (98% m/m), and sodium dodecyl sulphate (SDS, 98% m/m) were purchased from Sigma Aldrich. Distilled water, with a specific conductivity varying between 0.8 and 1.4 µs.cm^{-1} and with pH in beach 6.5-7, was supplied by the National Laboratory of Drugs Control (Dakar). The chemical structures of chlorpyrifos and SDS are presented in figure 1 and some physicochemical properties are listed in table 1 [38, 39].

2.3. Solutions preparation

Stock solutions of chlorpyrifos CPF (10^{-3} mol L^{-1}) and SDS (0.5 mol L^{-1}) were prepared in distilled water. All solutions were protected against light and stocked in the refrigerator in order to avoid possible photochemical transformations. The glassware consisted of oil-can, beakers, flasks and micropipettes. Glass bottles packed with aluminum foil were necessary to preserve the solutions in a refrigerator.

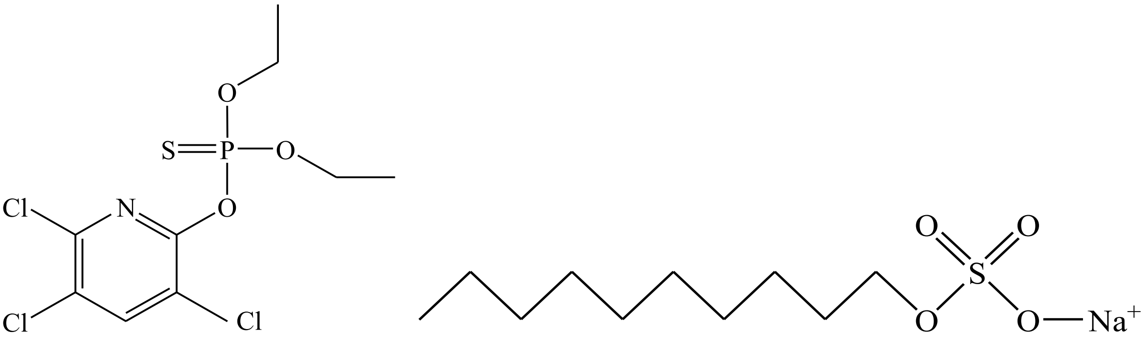

Figure 1: Chemical structures of chlorpyrifos (left) and SDS (right).

Table 1: Physicochemical properties of chlorpyrifos and SDS

Physicochemical properties	Chlorpyrifos	SDS
Chemical formula	$C_9H_{11}Cl_3NO_3PS$	$C_{12}H_{25}NaO_4S$
Molecular weight (g mol^{-1})	350.59	288.38
Water solubility (mg L^{-1})	2.0 at 25°C	100000
Chemical family	Organophosphorus	Anionic surfactant
Biological activity	Insecticide	-------
Melting point (°C)	43	204-207
Boiling Point (°C)	160	N/A
Relative density	1.398	1.01
CMC	-------	8.2 at 25°C
Lethal dose, LD50 (mg kg^{-1})	32 (oral, birds)	1288 (rat, oral)
Vapor pressure (Pa)	$2.49\ 10^{-3}$ at 25°C	1.05×10^{-10} at 25 °C

2.4. Conductivity measurement

All conductivity measurements were carried out in a glass beaker containing a known concentration of CPF in 80 mL of water necessary to soak all the significant part of the conductometric cell. A magnetic bar was put in the solution and the beaker was placed on a heating magnetic stirrer. A graduated burette was filled of the solution of surfactant, the temperature was fixed at a given value and a volume of 0.1 mL of CPF solution was added each time in the beaker. The solution was homogenized by agitation during 10 seconds before we noted the specific conductivity.

2.5. Determination Method of the Thermodynamic Parameters of Micelles

To quantify the effect of the additives in a mixture during a process of micellization, it is necessary to evaluate the various thermodynamic parameters which are: Gibbs energy of Gibbs, standard enthalpy and standard entropy of micellization. They are given starting from the variation of the CMC with the temperature. The standard Gibbs energy of micellization can be obtained from the following relation:

$$\Delta G^0 = (2-\alpha)RT\ln X_{CMC}$$ [40, 41] (I)

Where α is the micellar ionization degree of the counter-ions in the solution. It is obtained by conductometric measurements by using the method of Raoul Zana who proposes to calculate it by using the report/ratio of the conductometric slopes before and after the CMC [42]. T is the absolute temperature of the reactional medium, R perfect gases constant and X_{CMC}, the molar fraction at the CMC.

The standard enthalpy of micelle formation can be obtained from the Gibbs-Helmholtz equation:

$$\Delta H^0 = -T^2 \frac{\partial}{\partial T}\left(\frac{\Delta G^0}{T}\right) \qquad \text{(II)}$$

By replacing (I) in (II), the enthalpy of micellization can be written as follows:

$$\Delta H^0 = -RT^2(2-\alpha)\frac{d}{dT}(\ln X_{CMC}) \qquad \text{(III)}$$

The term $\frac{d}{dT}(lnX_{CMC})$ corresponds to the slope of the right-hand side $lnX_{CMC} = f(T)$.

The relation between the three thermodynamic functions: ΔG^0, ΔH^0 and ΔS^0 is:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad \text{(IV)}$$

Equation IV makes it possible to calculate the entropy change related to the process of micellization.

3. Results and discussion

3.1. Determination of the critical micellar concentration.

We carried out a direct dosage of a solution containing a fixed concentration of chlorpyrifos with active surface solution of concentration known at various temperatures. This experiment consists in following the evolution of the specific conductivity of an initial solution of chlorpyrifos of fixed concentration, according to the concentration of the added surfactant. Figure 2 present plots of the specific conductivity according to the SDS concentration in water in the absence (Figure 2A) and in the presence (Figure 2B and 2C) of CPF at different temperatures. The curves exhibit three parts: the small quantities of surfactant added (below the CMC) were not sufficient enough to form micelles. Then, the surfactant dissolves in the mixture to give free units (first part) [35]. When the concentration is close to the CMC, the monomers are gradually assembled in micellar aggregates with roughly spherical form. We then noticed a sharp increase in the specific conductivity of the solution. Above the CMC, the micelle formation continues and the presence of monomer also increases, leading to an increase of the conductivity, but in a less significant way (third part) [35].

3.2. Temperature and CPF concentration effects on the CMC

Figure 3 represents, the CMC variation curves of the surfactant according to the temperature at various CPF concentration. Increasing the temperature and the CPF concentration leads a notable reduction in the CMC which explains the CPF solubilization in anionic micellar medium. To well explain the decrease in the CMC according to the CPF concentration, we examined the chemical structure. CPF is a molecule with an aromatic nucleus (hydrophobic part) and several polar bonds (P=O, P=S, C-Cl) which shows that the molecule is characterized by a very high permanent dipole moment [43]. The molecule can thus strongly interact with the polar heads of the surfactants, which allows the hydrophobic molecule to favor the micellar solubilization [44]. Table 2 gives the values of the CMC, X_{CMC} and α according to the CPF concentration at various temperatures. With regard the additives effect like the pharmaceutical compounds [45-47] and the organophosphorus pesticides [35, 37] in particular, it was discovered that the presence of such compounds can affect the concentration to which the surfactant spontaneously forms structures at micellar bases with knowing the critical micellar concentration. The conductivity values for SDS solutions in the absence and the presence of CPF were studied in order to examine the CPF effect on the behavior of micellization of the anionic surfactant in these aqueous solutions.

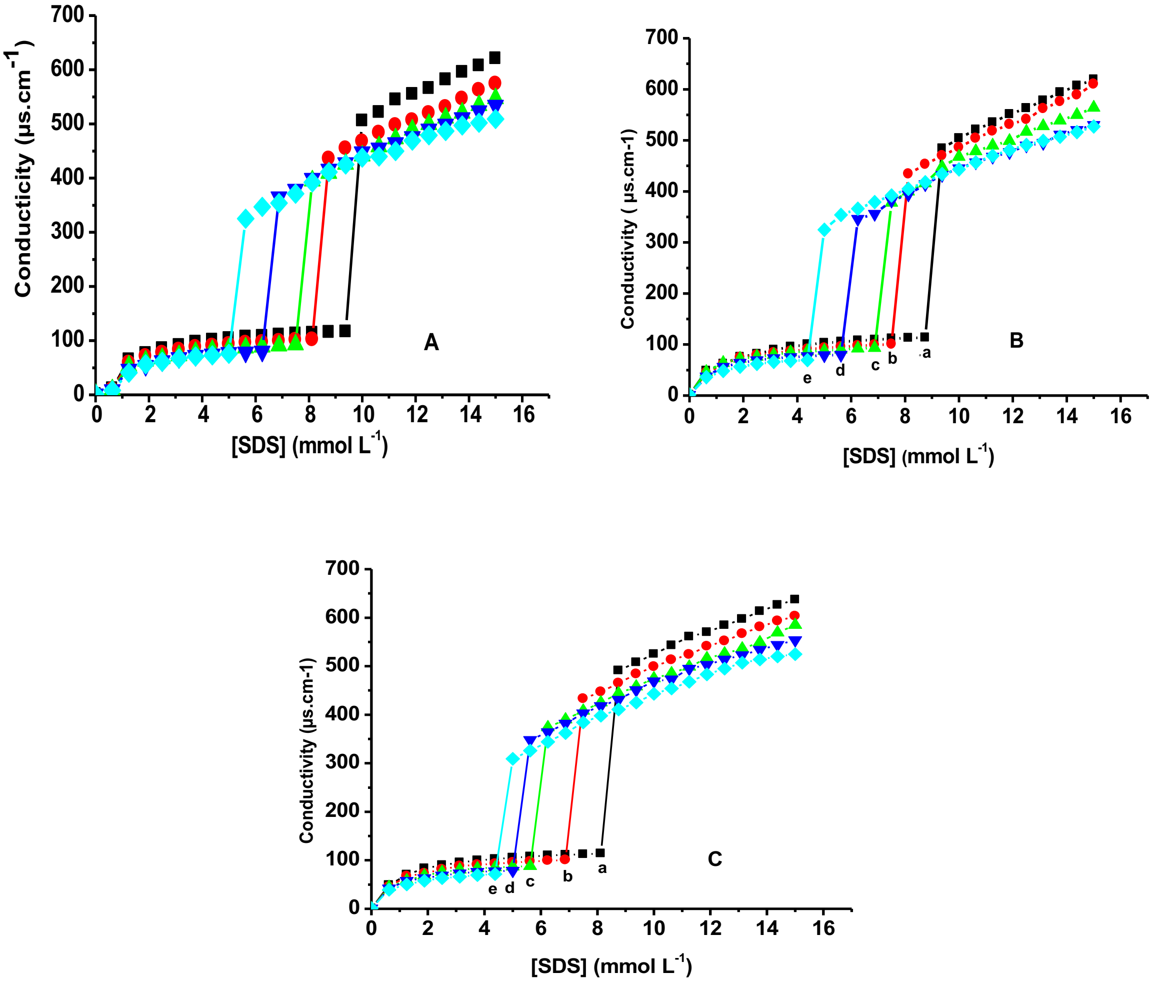

Figure 2: Variation of specific conductivity according to the concentration of SDS in the absence (A) and in the presence (B and C) of CPF concentrations (A: c = 0; B: c = $2x10^{-6}$ mol L^{-1}; C: c = $4x10^{-6}$mol L^{-1}) at various temperatures: (a:304 K, b: 311 K, c: 318 K, d: 325K and e : 332K).

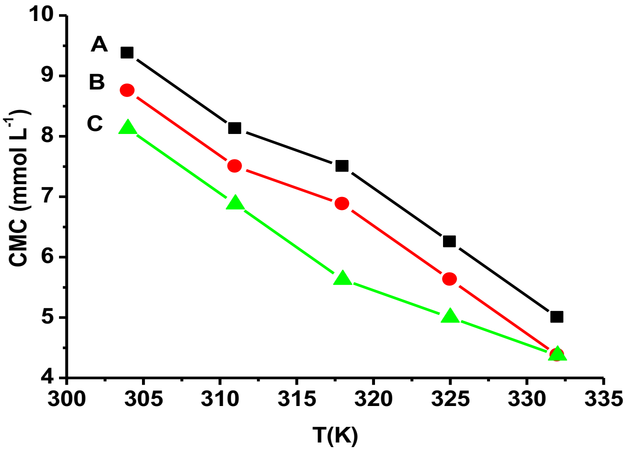

Figure 3: Temperature effect on the CMC of SDS at different CPF concentrations (A: 0, B: $2x10^{-6}$mol L^{-1} and C: $4x10^{-6}$mol L^{-1}).

Table 2: CMC, X_{CMC} and α values according to the CPF concentration at various temperatures.

$[CPF]x10^6$ ($mol\ L^{-1}$)	T (K)	CMC ($mmol\ L^{-1}$)	$X_{CMC}\ x10^3$	α (%)
0	304	9.375	2.228	15.073
	311	8.125	1.931	17.174
	318	7.500	1.783	21.442
	325	6.250	1.486	24.559
	332	5.000	1.189	29.040
2	304	8.750	2.080	15.353
	311	7.500	1.783	17.367
	318	6.875	1.635	18.621
	325	5.625	1.338	19.538
	332	4.375	1.041	35.193
4	304	8.125	1.932	17.760
	311	6.875	1.635	17.900
	318	5.625	1.338	21.309
	325	5.000	1.189	22.534
	332	4.375	1.041	25.046

SDS micelles formation is facilitated by the presence of CPF at higher temperatures and consequently a reduction of the CMC. This reduction of CMC value observed in the presence of CPF in this work seems to come from hydrophobic dehydrated state of CPF, which is likely to generate a more effective hydrophobic environment to facilitate the micellization [48-50].The influence of temperature on the CMC and α is explained by the head groups steric interactions and the deformation of the surfactant tails inside the micelles [47, 48]. This also leads to a decrease on the Gibbs energy of micellization [47, 48, 51]. The increase in the temperature involves firstly an increase in the dissociation degree of the free counter-ions in the solution and the hydration of the polar heads supporting the micellization and secondly, the rupture of the water molecules surrounding the hydrophobic groups which are favorable to micellization [47, 48, 51]. Micellar ionization degree increases with the CPF concentration, which results from the variation in the electronic charge density on the oxygen atoms of SDS. Further, the micellar ionization degree increases with the temperature due to electrostatic repulsion between the charged ions species [52]. Figure 4 shows a reduction in the critical micellar concentration when the CPF concentration increases. One observes an increase in the specific conductivity of active surface which can be explained by an increase of the free counter-ions (Na^+) number released in the solution with each addition of a quantity of surfactant.

3.3 Thermodynamic parameters of micelles formation

To thermodynamically characterize the occurrence of micellization in a mixture, it is necessary to examine the changes associated with the thermodynamic parameters such as the standard Gibbs energy, standard enthalpy and entropy. These various thermodynamic parameters were calculated by using equations (I) (II) and (III). ΔG^0, ΔH^0 and - $T\Delta S^0$ values obtained with different CPF concentrations at various temperatures are presented in the Table 3.

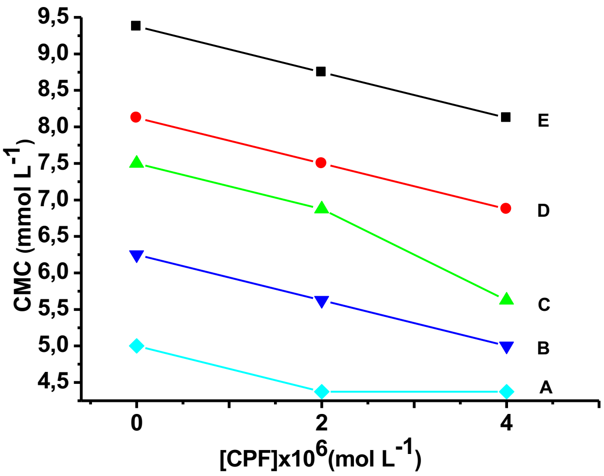

Figure 4: Variation of the CMC with the CPF concentration at various temperatures: A: T = 304 K, B: T = 311 K, C: T = 318 K, D: T = 325 K, E: T = 332 K.

Table 3: Thermodynamic parameters values at different temperatures.

[CPF]x10^{6} (mol L^{-1})	T (K)	ΔG^{0} (kj mol^{-1})	ΔH^{0} (kj mol^{-1})	-TΔS^{0} (kj mol^{-1})
0	304	- 25.374	34.514	- 59.888
	311	- 29.260	35.739	- 64.999
	318	- 29.570	36.256	- 65.826
	325	- 30.797	37.453	- 68.250
	332	- 31.196	38.496	- 69.692
2	304	- 28.780	36.276	- 65.056
	311	- 29.624	37.552	- 67.176
	318	- 30.265	38.977	- 69.242
	325	- 32.065	42.360	- 74.425
	332	- 31.102	38.618	- 69.720
4	304	- 29.394	31.085	- 60.479
	311	- 31.809	32.508	- 64.317
	318	- 31.233	33.321	- 64.554
	325	- 32.028	34.597	- 66.625
	332	- 33.132	35.592	- 68.724

We note a strong influence of the temperature on the micellization. Moreover, these results show an increase of the absolute value of ΔG^{0} and of ΔH^{0}. The negative values of ΔG^{0} presented in Table 2 show that the micellization process is spontaneous i.e. thermodynamically favorable [47, 48]. The substantial variations noted in the enthalpy change and the positive values obtained during the process of micellization show a compensation between the enthalpy and entropic factors (ΔH^{0} and TΔS^{0}) [48]. In Figure 5, we represent ΔG^{0}, ΔH^{0} and -TΔS^{0} vs. temperature and CMC for various CPF concentrations. These results show slight variations of the Gibbs energy and the enthalpy according to the temperature. However, these variations are more and more noted in the case of the evolution entropy according to the temperature. The enthalpy is an energetic characteristic, and the entropy is a measure of the disorder induced by the system during the process of micellization. According to equation (IV), for a spontaneous process, if the variation of enthalpy is positive a process, its entropy must also increase. These results show that the micellization process is partly controlled by the entropic term. This also reveals that the association reaction between the CPF and the surfactant (SDS) is entropic i.e. the increase in enthalpy during the micellization is compensated by the increase of system disorder.

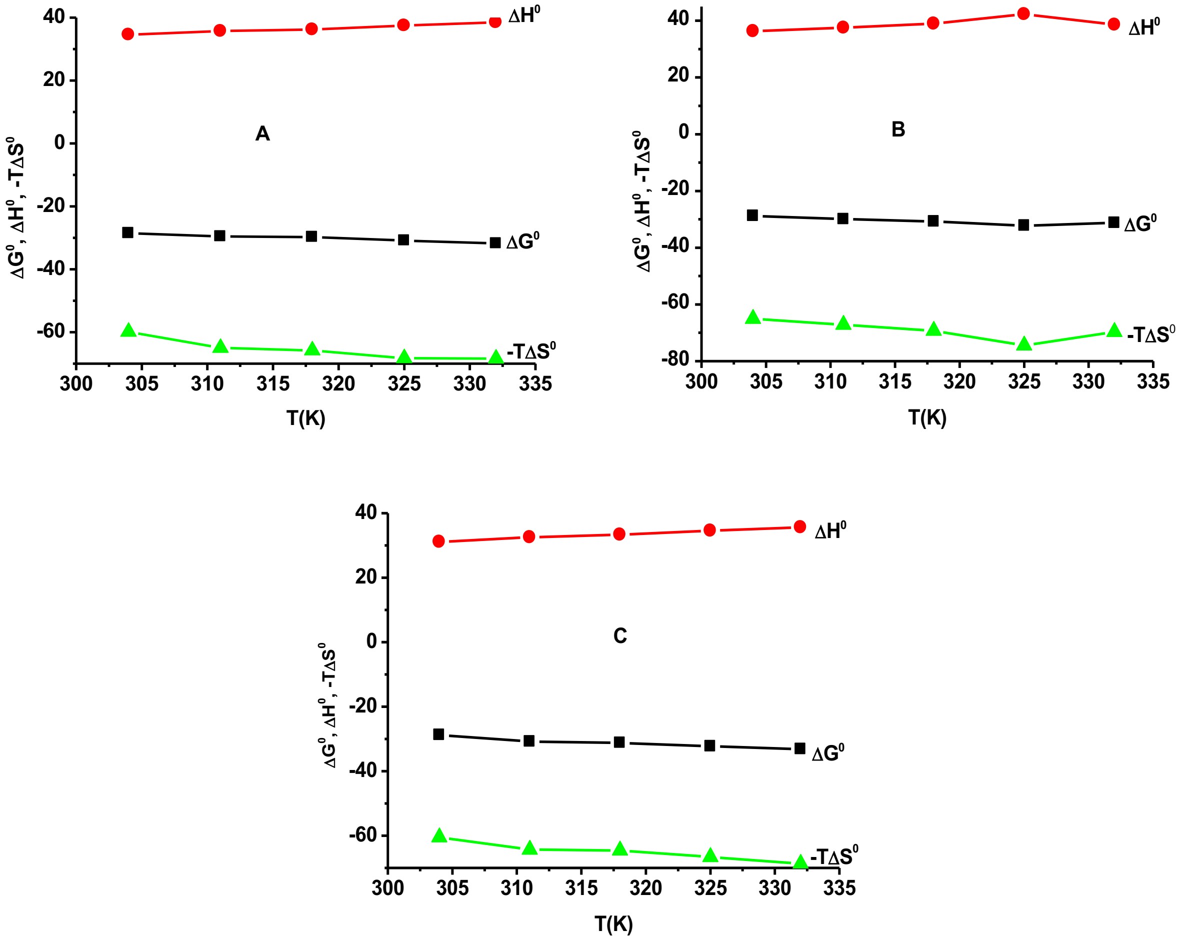

Figure 5: Variation of $-T\Delta S^0$, ΔG^0 and ΔH^0 in absence (A) and involved chlorpyrifos concentration: B ($2x10^{-6}$ mol L^{-1}) and C: ($4x10^{-6}$ mol L^{-1}) vs. temperature.

The results obtained in this work are similar to the results found in the literature [35, 42, 47, 48, 53, 54]. Thus, the method used in this work seems effective, reliable and allows an opening of windows for the analyses of pesticides slightly water soluble.

Conclusion

We studied the micellar solubilization of the insecticide CPF in aqueous micellar medium and the interactions between the insecticide CPF and SDS by the conductometric method. Various thermodynamic parameters like the standard Gibbs energy, standard enthalpy and the standard entropy were evaluated in this work. A reduction in the critical-micellar concentration of the surfactant (SDS) according to the CPF concentration and the temperature is also observed. The results of the study showed that the process of micellization is spontaneous i.e. thermodynamically favorable. The ΔG^0 values decreased sharply with increasing the CPF concentration and the temperature. This explains a strong association between CPF and the active surface, leading to a significant increase of the insecticide solubility in the heart of micelles.

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