



Molecular Complexes of Crown Ethers: Part 8. Effect of Surfactant on the Charge Transfer Complexes of 18C6 with Picric Acid in the Presence of Alkali Metal Ions

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(Received: 19 May 2003; in final form: 5 January 2004)

Key words: charge transfer complex CTC, crown ether 18-crown-6, picric acid, alkali metal salts, triton X-100, critical micelle concentration CMC, dichloroethane solvent DCE, UV-Visible spectra

Abstract

The interaction of 18-crown-6 (CE) with picric acid (PA) was studied in the UV-Visible region in 1,2-dichloroethane (DCE) at 298.2 K. The effect of the surfactant Triton X-100 was studied, and it was found to have a pronounced effect on the interaction of 18-crown-6 with picric acid. The effect of the alkali metal cations, especially Na and K on the complex matrix donor–acceptor surfactant was studied. It is found that the extraction of the insoluble solid NaCl and KCl to the organic phase increased by more than 8-fold in the presence of the complex. The interaction of the alkali metals ions, i.e., Li, Na, K, Cs and Rb with the systems Donor–Acceptor and Donor–Acceptor–Triton were studied. It is found that the stability of the complexes formed between the system CE + Triton + Picric acid and the alkali metals ions depends on the ratio between the crown ether radius and the alkali metal radius.

Introduction

Crown ethers are known to be important extractants for metal ions due to their selectivity [1–4]. Molecular charge transfer complexes (CTC) of crown ethers with some acceptors have received increasing attention [5–17].

Picric acid is used to enhance the extraction of metal ions by crown ethers. Picric acid is known to form a wide range of charge transfer complexes [18] with a number of donors. Only one CT complex was reported between crown ethers and picric acid. Recently Salman *et al.* [11] reported the CT between picric acid and a number of crown ethers including 18C6. The results indicated the presence of a CT band at 379 nm and the complex formation constant K_c of this complex increases when NaCl or KCl is added. It was found that K_c for the CTC is higher when KCl is added, This was explained on the basis that 18C6 is selective for K^+ .

Surfactants have micelle properties, which are affected by the addition of small amount of electrolytes, nonpolar [19] and polar organic liquids [19–22]. The critical micelle concentration (CMC) [23] results from the hydrophobic interactions between the nonpolar part, which forms the core of the micelle, and a repulsion interaction between the polar head group.

The role of surfactants in molecular interaction is a new research area.

Surfactants consists of hydrophilic and hydrophobic parts. Recent studies indicate that ionic surfactants interact with macrocyclic compounds [24–29]. No data are available

concerning the interaction of macrocyclic molecules with electron acceptor in the presence of surfactants.

Recently Salman *et al.* [30] studied the interaction of dibenzo-18-crown-6 (DB18C6) with tetracyano ethylene (TCNE) with neutral surfactant Triton X-100. It is found that the surfactant increase the CT interaction between the donor and the acceptor, and that the charge transfer complex is encapsulated in the micelle structure.

The aim of this work is to study the interaction of picric acid and 18C6 in the presence of Triton X-100, and the effect of adding alkali metal cations on the complexes formed between different additives. Previous work [11] indicated that picric acid increase the extraction of the metal ion by the CE. This study tends to explore the effect of the micelle structure on the extraction of the metal ion by the complex PA + CE.

Experimental

18-crown-6 (CE) (Fluka) was of pure grade and used without further purification. Picric Acid (PA) (Aldrich) was of pure grade and was used without treatment but was kept dry using P_2O_5 . All other chemicals were of high-grade quality (BDH, Fluka). The UV/Vis spectra were recorded on a Perkin-Elmer lambda 2S spectrophotometer, using 1-cm fused silica cells. Dichloroethane (spectrosol, Fluka) was used as solvent. The significant figures are ± 0.005 .

The critical micelle concentration (CMC) for Triton X-100 (Iso-octyl phenoxy polyethoxy ethanol) was determined

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in three solvents, Dichloromethane DCM, Dichloroethane DCE and Etanol. The critical micelle concentration CMC of Triton X-100 in different solvents was determined using the conductivity technique [30]. In dichloroethane the CMC was 2.0×10^{-2} M, in Dichloromethane it was 2.7×10^{-2} M, but in Ethanol no CMC was found in the concentration range applied for the previous two solvents. Surfactant solutions of variable concentrations were prepared and the conductivity was measured by a conductivity meter model Jenway 4020.

The fixed concentrations of CE used throughout this work is 1×10^{-2} M, PA concentration is 1×10^{-4} M, and Triton X-100 concentration is 2.0×10^{-3} M.

During this work the concentration of one of the species is changed while the concentration of other species is kept constant [1–4].

Results obtained in this study might be affected by the presence of water molecules in the matrix. PA was dried over P_2O_5 . Spectrosol solvents usually contain traces of water so is Triton. In this paper we did not try to investigate the effect of water molecules on our results. One can assume that the presence of water molecules in concentration comparable with that of the interacting species might play a comparative role with the interacting species. If water molecules are incorporated in Triton cavity then it will compete with the PA and CE molecules or it might be incorporated but form a hydrogen bond bridge between T cavity, which contain oxygen atoms, and PA. This effect might be important when the interacting species spectrum is measured in respect to time. This assumption needs to be proved experimentally and this will be achieved in future studies.

Results and discussion

The interaction of the donor, 18-crown-6, CE, and the acceptor, picric acid, PA, was studied under the following conditions:

- (1) PA + CE
- (2) PA + CE in the presence of the neutral micelle compound Triton X-100 (T).
- (3) PA + CE + Alkali metal chlorides
- (4) PA + CE + Alkali metal salt in the presence of Triton.

The data obtained (Tables 1–4) in this study using the UV-Visible spectrum of the individual and interacting species in DCE solvent are presented and discussed below:

(1) PA:

The spectrum of PA show one absorption at 338 nm.

(2) PA + CE system:

UV-Visible spectrum of mixture of fixed concentration of PA and CE was measured for the equilibrated solution. Then the same concentration of PA is replaced in the reference cell to omit any interference of the spectrum of PA with that of the mixture. A new band due to charge transfer, CT complex was observed at 379 nm with a shoulder at 420 nm. The absorbance of the CTC was 0.278 (Table 1).

Table 1. UV-Visible absorptions for the system CE, PA and T

No	System	R*	λ_{nm}	A	λ_{nm}
1	PA	S**	338		
2	PA + CE	PA	379	0.28	420(s) 0.12
3	PA + 2×10^{-3} T	PA	378	0.27	
4	CE	S	–	–	
5	PA + CE + T	PA	379	0.32	Day 1
6	PA + T	PA	375	0.14	Day 1
		PA	378	0.15	Day 2
		PA	378	0.20	Day 3
		PA	378	0.24	Day 4
		PA	378	0.29	Day 5
		PA	378	0.29	Day 6
7	PA + CE + T	PA	379	0.40	Day 2
			378	0.48	Day 3
			378	0.57	Day 4
			378	0.61	Day 5
			378	0.69	Day 6
			378	0.73	Day 7
8	PA + 1×10^{-2} T	PA	378	0.48	
	PA + 2×10^{-2} T	PA	378	1.28	
9	PA + CE + 1×10^{-2} T	PA	378	1.00	
	PA + CE + 2×10^{-2} T	PA	378	1.20	
10	CE + T + 10^{-5} PA	PA	377	0.18	
	CE + T + 10^{-4} PA	PA	379	0.32	
	CE + T + 10^{-3} PA	PA	379	>3.00	
11	PA + T + 2×10^{-2} CE	PA	377	0.59	
	PA + T + 5×10^{-2} CE	PA	378	0.79	

R* = Reference cell, S** = Solvent.

(3) PA + T system:

Fixed concentrations of PA and T were mixed and the spectrum was recorded for the equilibrated solution. The reference cell contains the same concentration of PA. A new band at 375 nm was observed with 0.14 absorbance (Table 1). This result indicated that there is a CTC between PA and T. Similar absorbance values were obtained for the systems PA + CE and PA + T indicating that PA form a similar complex with each of CE and T.

(4) CE + T system:

No absorption for the mixture in the range > 300 nm is observed.

(5) PA + CE + T system:

The three solutions were mixed and the spectrum was recorded for the equilibrated solution (Figure 1). The absorbance of the band at 379 nm is 0.32. This increase of the absorbance of PA + CE in the presence of T (0.278 for PA + CE and 0.14 for PA + T) (Table 1) indicates that Triton has a synergic effect. It increases the interaction between the donor and the acceptor. This result is similar to that obtained earlier for the interaction of DB18C6 + TCNE in the presence of Triton (30), PA was the reference.

(6) Effect of time on PA + T system:

A fixed concentration of PA and T are mixed together and

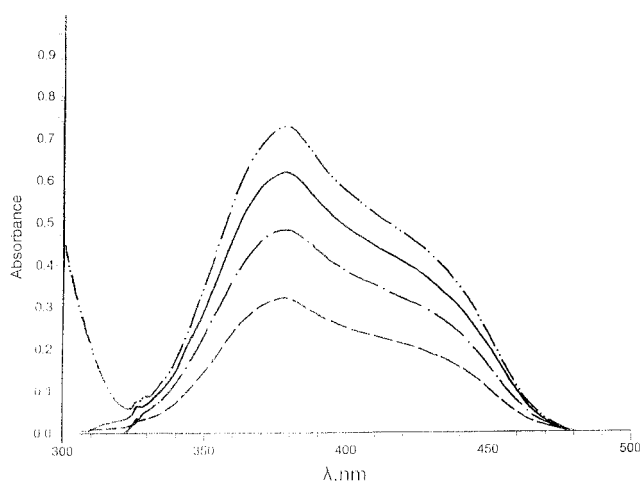


Figure 1. UV-Visible spectra for the PA (1×10^{-4} M) + CE (1×10^{-2} M) and T (2×10^{-3} M) as a function of time, First day ---, Third day -●-, Fifth day —, Seventh day -●●-.

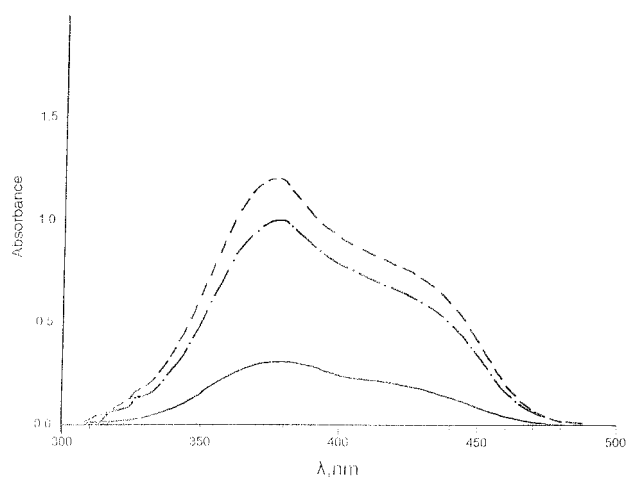


Figure 2. UV-Visible spectra for the PA (1×10^{-4} M) + CE (1×10^{-2} M) in the presence of variable concentration of T: (1) 2×10^{-2} M ---, (2) 1×10^{-2} M -●-, (3) 2×10^{-3} M —.

replaced in the sample cell while PA is kept in the reference cell. The absorbance of the CTC band was 0.14 in the first day compared to 0.32 for PA + CE + T. In the second day the absorbance of PA + T increased to 0.15. After six days the absorbance of this band increases to 0.29 compared to 0.69 for the system PA + CE + T (Table 1).

(7) Effect of time on PA + CE + T system:

To study the stability of the CTC in the micelle structure a sample contains a fixed concentration of PA + CE + T was followed for one week. The reference cell contains the same concentration of PA. It was observed that the freshly prepared solution absorbance is 0.32. After one day the absorbance of the CT band increased to 0.40, then in the end of one week the absorbance was 0.73 (Table 1, Figure 1).

It is clear that the effect of T on the system PA + CE is more than its effect on PA. This might be due to the fact that T increases the interaction of PA with CE by encapsulating them into its cavity. This interaction increases further with elapsed time. This result might be explained on the basis that with elapsed time the number of PA + CE molecules encapsulated in the micelle structure increases.

(8) Effect of increasing concentration of T on PA:

In both the reference and the sample cell PA was fixed while the concentration of T is varied. In the first experiment T concentration was 2×10^{-3} M and the CT band observed at 378 nm has an absorbance = 0.27. The absorbance increased to 0.48 when the concentration of T increases to 1×10^{-2} M. The absorbance of the CT band increases further to 1.28 when the concentration of Triton increased to 2×10^{-2} M (Table 1).

In non-polar solvents like DCE it is expected that triton will form the reverse micelle structure where the polar part of triton forms the cavity and the non-polar hydrocarbon form the outer part. The increase in triton concentration will allow a higher number of micelle structure to form. Picric acid will most likely interact with the polar part of the triton

through hydrogen bonding allowing PA to be encapsulated inside the micelle structure as suggested below



(9) Effect of increasing T concentration on PA + CE system: The concentration of T was increase from 2×10^{-3} M to 1×10^{-2} M and 2×10^{-2} M with fixed concentration of PA and CE. The reference cell contains the same concentration of PA in the sample cell. The absorbance of the CTC changed from 0.32 when the triton concentration was 2×10^{-3} M, to 1.0 when the triton concentration changed to 1×10^{-2} M. The absorbance increased further to 1.20 when the triton concentration changed to 2×10^{-2} M (Figure 2, Table 1).

The results from experiments 8 and 9 suggest that the number of CTC molecules will be encapsulated in the micelle structure increases as the T concentration increase. This result suggests that the CMC will change with the addition of CE and PA allowing the formation of a higher number of micelle structures. This is an indication that triton encapsulates the CT complex between CE and PA, and that it is possible to differentiate between the interaction of PA with T, and between the complex and T. If we take the difference in the absorbance between PA + CE + T and PA + T we find that it increase as we increase the concentration of T especially at 2×10^{-3} M and 2×10^{-2} M. This is an indication that we have two types of interaction. The first is between PA and T and the second is between PA + CE and T. The first interaction is weaker than the second (compare the absorbance of PA + T with the difference in absorbance between the two interactions). At high concentration of T (2×10^{-2} M) the interaction between T and PA became comparable, or even, stronger than the interaction between PA + CE and T. The results suggest that inside the micelle cavity the polar terminal of T interacts with the hydroxyl group in PA, encapsulating PA as a first step, followed by PA interacting with the crown ether thus accommodate more CE molecules into the micelle cavity.

Table 2. Effect of NaCl salts on the system PA, CE and T

No	System	R	λ	A	Remark
12	PA + Na ⁺	S*	341	0.33	
13	PA + CE + Na ⁺	PA	375	1.39	
14	PA + CE + Na ⁺ + 2×10^{-3} T	PA	377	1.45	0.098 μ g
15	PA + CE + Na ⁺ + 1×10^{-2} T	PA	377	1.86	0.305 μ g
	PA + CE + Na ⁺ + 2×10^{-2} T	PA	377	1.96	0.752 μ g
16	PA + T + Na ⁺ + 1×10^{-2} CE	PA	377	1.23	Day 1
		PA	377	1.14	Day 2
		PA	377	1.47	Day 3
	PA + T + Na ⁺ + 2×10^{-2} CE	PA	377	1.32	Day 1
		PA	377	1.55	Day 2
		PA	377	1.61	Day 3
	PA + T + Na ⁺ + 5×10^{-2} CE	PA	377	1.55	Day 1
		PA	378	2.01	Day 2
		PA	379	2.02	Day 3
17	CE + T + Na ⁺ + 10^{-5} PA	PA	378	0.14	
	CE + T + Na ⁺ + 10^{-4} PA	PA	378	1.45	
	CE + T + Na ⁺ + 10^{-3} PA	PA	378	>3.00	

S* = Solvent.

(10) Effect of increasing PA concentration on CE + T system:

The interaction in this system increases as we increase the concentration of PA. With the concentration of PA equal 10^{-5} M the absorbance of the CTC band is 0.18 while it exceeds the absorbance scale when the concentration of PA increases to 10^{-3} M.

(11) Effect of increasing CE concentration on the PA + T system:

The effect of increasing the concentration of CE is to increase of the interaction between CE and PA. This might be due to an increasing number of the complex molecules encapsulated into the micelle structure.

After that we studied the effect of the alkali metal ions on the systems PA, CE and Triton.

(12) The PA + Na + system:

A fixed concentration of PA was mixed with few crystals of NaCl. DCE was placed in the reference cell. The complex band appears at 341 nm with 0.33 absorbance (Table 2). This causes the formation of picric acid salt with absorbance similar to that of picric acid.

(13) The PA + CE + Na+ system:

The CT band appears at 375 nm with absorbance = 1.40 (Table 2). This increase in intensity compared to the value of 0.28 (Table 1) for the CTC is due to the formation of a strong complex between CE + PA and Na⁺.

(14) The PA + CE + T + Na⁺ system:

The spectrum of fixed concentration of PA + CE + T in the presence of Na⁺ was recorded. The reference cell contains the same concentration of PA and Na ions. This is done to eliminate any interaction between PA and Na⁺. The absorbance was 1.451 (Table 2). This indicates that the presence

of Na⁺ increases the stability and the intensity of the CTC. If the value of 1.57 for the absorbance of this complex is compared with that of PA + CE + T which is 0.32 then it is obvious that Na⁺ forms strong complexes with this matrix.

(15) The effect of increasing T concentration on PA + CE + Na⁺ system:

The absorbance of the CT band increases with increasing the concentration of the Triton thus the absorbance increases from 1.45 to 1.96 when the concentration of T increased from 2×10^{-3} M to 2×10^{-2} M (Table 2).

(16) The effect of increasing CE concentration on PA + T + Na⁺ system:

A fixed concentration of PA + T is mixed together and NaCl salt added to it, shaken and left to settle down then different concentrations of CE are added to it and the spectrum is recorded after the interacting species in the solution reached equilibrium. The solutions spectrum was recorded for different time intervals (Table 2). It is obvious that the interaction increases with increasing the concentration of the CE. Also leaving the solutions for three days increases the interaction.

(17) The effect of increasing PA concentration on the CE + T + Na⁺ system:

A fixed concentration of CE + T is mixed together and NaCl salt added to it, shaken and left to settle down then different concentrations of PA are added to it and the spectrum is recorded after the solution reached equilibrium (Table 2). The same concentration of PA is used in the sample and in the reference cell. It is obvious that the interaction increases with increasing the concentration of the PA.

(18) The PA + K+ system:

A fixed concentration of PA is mixed with KCl salt and the spectrum is recorded with DCE as a reference. A new band is observed at 341 nm and its absorbance is 0.364 (Table 3).

(19) The PA + CE + K+ system:

The spectrum of the interacting species PA + CE + K⁺ was recorded. The reference cell contains PA. The CT band absorbs at 374 nm and the absorbance is 2.0 (Table 3). The presence of K⁺ further increases the absorbance of the complex CE + PA. It is known that K⁺ is encapsulated well within CE. This result supported the assumption that the cation is encapsulated into the crown ether and this complex interact further with picric acid.

(20) The effect of K⁺ on PA + CE + T system:

The spectrum of fixed concentration of PA + CE + T in the presence of KCl salt was recorded. The reference cell contains the same concentration of PA. This is done to eliminate any effect of PA.

The absorbance was 2.056 and the CTC band blue shifted to 375 nm (Table 3). This indicates that the presence of K ion increases the stability and the intensity of the CTC.

When comparing the absorbance of the complex PA + CE + Na⁺ with that of PA + CE + K⁺ we observe a large

Table 3. Effect of KCl salts on the system PA, CE and T

No	System	R	λ	A	Remark
18	PA + K ⁺	S*	341	0.37	
19	PA + CE + K+	PA	374	2.00	
20	PA + CE + K+ + 2×10^{-3} T	PA	375	1.41	0.111 μ g
21	PA + CE + K+ + 1×10^{-2} T	PA	376	1.51	0.592 μ g
	PA + CE + K+ + 2×10^{-2} T	PA	376	1.61	0.81 μ g
22	PA + T + K+ + 1×10^{-2} CE	PA	377	1.82	Day 1
			377	2.12	Day 2
			377	2.08	Day 3
	PA + T + K+ + 2×10^{-2} CE	PA	377	2.19	Day 1
			377	2.43	Day 2
			377	2.38	Day 3
	PA + T + K+ + 5×10^{-2} CE	PA	377	1.99	Day 1
			377	2.29	Day 2
			377	2.17	Day 3
23	CE + T + K+ + 10^{-5} PA	PA	375	0.20	
	CE + T + K+ + 10^{-4} PA	PA	375	2.06	
	CE + T + K+ + 10^{-3} PA	PA	376	>3.00	
24	CE + K+ + PA + T	PA	373	2.23	
	CE + PA + K+ + T	PA	375	2.11	
	CE + PA + T + K+	PA	375	2.06	

enhancement of the CT in the case of K⁺ compared to that of Na⁺. But when triton and when comparing the absorbance of the system PA + CE + Na⁺ with that of CE + PA + K⁺ a small enhancement of the CT in the case of Na⁺ compared to that of K⁺ is observed. It seems that the interaction between CE + PA + K⁺ is much stronger than that of PA+CE+Na⁺. In general, triton has a small effect on the two systems but its effect is smaller for the system PA + CE + K⁺.

To study the effect of changing the concentration of PA, CE and T on the charge transfer complex and the cation the following experiments were performed:

(21) The effect of increasing T concentration on PA + CE + K⁺ system:

Table 2 shows the effect of increasing the concentration of Triton on the absorption of the system PA + CE + K⁺. The Absorbance increased from 1.451 to 1.613 when the concentration of Triton increased tenfolds. The extraction of the metal ion increased from 0.111 to 0.81 μ g.

(22) The effect of increasing CE concentration on PA + T + K⁺ system:

A fixed concentration of PA + T is mixed together and KCl salt added to it, shaken and left to settle down then different concentrations of CE is added to it, shaken and left to settle down and the spectrum is recorded after the solution reached equilibrium. The solutions spectrum was recorded for different time intervals (Table 3). It is obvious that the interaction increases with increasing the elapsed time. It is noticed with different concentration of CE that the absorbance increases when we change the concentration of CE from 1×10^{-2} M to 2×10^{-2} M but it surprisingly decreases when the concentration of CE increases to 5×10^{-2} M. The same res-

ults were obtained with increasing elapsed time thus it was observed that with the three concentrations the absorbance of the complex band at 377 nm decreased in the third day.

(23) The effect of increasing PA concentration on CE + T + K⁺ system:

PA has a tremendous effect on the system CE + T + K⁺. It increases the interaction and this causes the absorbance to increase from 0.14 to more than 3 when the PA concentration of PA increased by 100 fold (Table 2).

(24) Changing the addition sequence of K⁺:

In previous study Salman *et al.* indicated (14, 15) that the sequence of addition of the cation might be an important factor affecting the stability of the CTC. In this work we change the sequence of adding K⁺ to the ternary system (Table 3) CE + K⁺ + PA + T the reference was PA. The absorbance was 2.23. CE + PA + K⁺ + T and the reference was PA the absorbance is 2.11 CE + PA + T + K⁺ and the reference was PA the absorbance is 2.06.

This result is in support of our conclusion that CE first encapsulates K⁺ then it will interact with PA. This complex is then encapsulated by the Micelle structure.

One can suggest the mechanism of interaction in the three cases as

(A) For the system CE + K⁺ + PA + T
 CE + M = Complex 1, CE.M + PA = Complex 2,
 (CE.M).PA + T = Complex 3, [(CE.M).PA] T [2]

(B) For the system CE + PA + K⁺ + T
 CE + PA = Complex 1, CE.PA + M = Complex 2,
 (CE.PA).M + T = Complex 3, [(CE.PA).M] T [3]

(C) For the system CE + PA + T + K⁺ CE + PA = Complex 1, CE.PA + T = Complex 2, (CE.PA). T + M = Complex 3, [(CE.PA). T] M [4]

It is obvious from Table 3 that the stability of the complex is in the following sequence

$$A [2] > B [3] > C [4].$$

In order to investigate the effect of the alkali metals size on the complex stability of the systems PA + CE and PA + CE + T the following experiments were performed.

(25) Interaction of alkali metals with PA + CE system:

The interaction of the system CE + PA with different alkali metal cations is given in Table 4.

CE + PA + Li⁺. The band appears at 357 nm with an absorbance of 1.25, with the band which was a shoulder appears as a separate band at 418 nm (with intensity of 1.05).

CE + PA + Na⁺. The band appears at 374.5 nm with an absorbance of 1.39.

CE + PA + K⁺. The band appears at 373.5 nm and absorbance of 2.0.

CE + PA + Rb⁺. The band appears at 376 nm with absorbance of 2.02.

CE + PA + Cs⁺. The band appears at 376 nm with absorbance of 1.92.

Table 4. The effect of the alkali metal salts on the interaction between CE + PA system and CE + PA + T system.

No	System	R	λ_{nm}	A	λ_{nm}	A	Atomic* Radius (pm)
25	PA + CE + Li ⁺	PA	357	1.25	418	1.05	152
	PA + CE + Na ⁺	PA	375	1.39			186
	PA + CE + K ⁺	PA	374	2.00			227
	PA + CE + Rb ⁺	PA	376	2.02			248
	PA + CE + Cs ⁺	PA	371	1.92			265
26	PA + CE + Li ⁺ + T	PA	368	1.38	418	1.10	
	PA + CE + Na ⁺ + T	PA	374	1.45			
	PA + CE + K ⁺ + T	PA	375	2.11			
	PA + CE + Rb ⁺ + T	PA	377	1.96			
	PA + CE + Cs ⁺ + T	PA	379	1.84			

* Reference [34].

(26) The interaction of the alkali metals with PA + CE + T system:

The interaction of the system PA + CE + T with different alkali metals is shown in Fig 3 and Table 4.

With Li⁺. The absorbance is 1.38 and the band appears at 368 nm. The shoulder appears as a separate band at 418 nm with band intensity = 1.05.

With Na⁺. The absorbance is 1.45.

With K⁺. The absorbance is 2.19.

With Rb⁺ the absorbance is 1.96.

With Cs⁺ the absorbance is 1.85.

It is known that the cavity diameter for DB18C6 and 18C6 range from 260 pm to 320 pm (31). It was suggested (32, 33) that K⁺ fits well inside the cavity and form a stable complexes with the above crown ethers, with the metal bound very tightly to the unshared pairs of electrons residing on the oxygen atom.

There are two remarks when observing Table 4. The first is that in all complexes the CT band appears in the range 370–380 nm with a shoulder at 420 nm. With Li⁺ it is observed that the shoulder separates from the main band and we obtained two bands (Table 4, Figure 3). The first band appears at 368 nm and the second at 418 nm. This might suggest that those two bands are due to the formation of two complexes. The size of the alkali metal ions is primary responsible for their complexing characteristics. Smaller ions like Li are so strongly solvated that considerably more energy must be expended in the solution formation step. This suggests that the solvation energy for the two complexes formed with Li⁺ is different, thus allowing the absorption of two bands. More work is needed to prove this assumption and that we have more than one complex absorbing in the region 360–420 nm and this work is in progress.

The second note is that the absorbance of the complex PA + CE or PA + CE + T with different alkali metal ions show a large increase in going from Li, Na to K, Cs and Rb ions suggesting that the complex formed in the case of K⁺ is much stronger than that formed with Li or Na ions. In the case of K, Cs and Rb ions the absorbance decreases gradually with increasing the size of Rb and Cs ions (34)

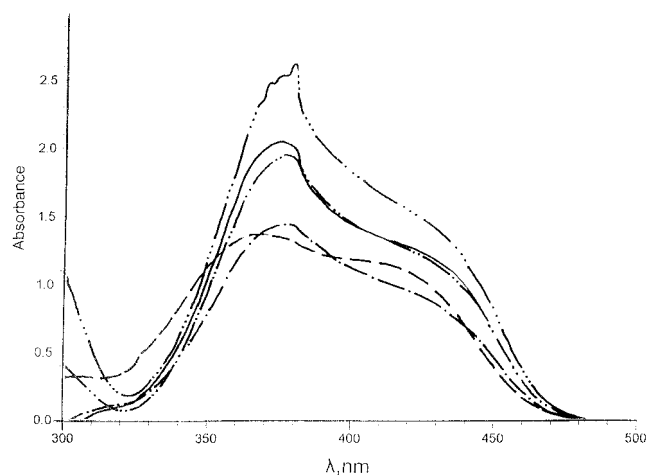


Figure 3. UV-Visible spectra showing the effect of different alkali metals ions on the interacting species for the PA (1×10^{-4} M) + CE (1×10^{-2} M) and T (2×10^{-3} M): (1) Li⁺ - - - -, (2) Na⁺ - ● -, (3) K⁺ - ●●● -, (4) Rb⁺ —, (5) Cs⁺ - ●● -.

suggesting that those two ions form a strong complex with CE because their atomic radius are still comparable with the size of the CE cavity, while Li and Na ions are much smaller than the minimum cavity size of CE.

It is interesting to note that the complex PA + CE is encapsulated into the micelle structure and this structure increase the extraction of the cations from the solid phase into the organic phase. This is proved by carrying the atomic absorption, AA, analysis for the two systems PA + CE + different concentrations of T + NaCl and KCl salts (Tables 2 and 3).

It is interesting to note that the concentration of Na⁺ in the organic phase increased from 0.098 μg with 2×10^{-3} M Triton to 0.752 μg with 2×10^{-2} M Triton (Table 2). With K⁺ the extraction increased from 0.111 μg with 2×10^{-2} M Triton to 0.818 μg of K⁺ in 2×10^{-2} M Triton solution (Table 3). This result represents more than 8 times the increase of the cation concentration which is extracted to the organic phase due to its inclusion into the CT complex PA + CE + T.

The above results might suggest the possibility of the following mechanism. In the first step PA will interact with the polar cavity of Triton and will be encapsulated by it. Then PA will attract the complex formed between CE and the alkali metal and encapsulate them into the micelle structure.

The results obtained in this work support the previous work [11] that PA increases the interaction of CE with the metal ion and thus increases its extraction to the organic phase. Also Triton, through its encapsulation of the complex PA + CE + M⁺ increases dramatically the extraction of the metal ion into the organic phase.

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