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Spectroscopic and thermodynamic study of charge transfer interactions of retinol palmitate with [60]- and [70]fullerenes by absorption spectrometric method

Avijit Saha, Asok K. Mukherjee*

Department of Chemistry, The University of Burdwan, Golapbag, Burdwan 713104, India

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Abstract

Retinol palmitate (**1**), which is commonly called 'Vitamin A palmitate', has been shown to form charge transfer (CT) complexes with a series of electron acceptors including [60]- and [70]fullerenes, and from the trends in CT transition energies the vertical ionization potential of **1** has been estimated to be 7.73 eV. Stoichiometries of the fullerene complexes have been shown to be 1(Vitamin **1**): 1([70]fullerene) and 1(Vitamin **1**): 2([60]fullerene). The enthalpies and entropies of formation of these two complexes have been determined by estimating the formation constants spectrophotometrically at five different temperatures. The complexation phenomenon may be utilised to dissolve the fullerenes in the non-toxic Vitamin A oil and the solution may be used for testing the biological activity of the fullerenes in vivo.

Keywords: Retinol palmitate; Fullerenes; Vitamin A; CT complex; Ionization potential

1. Introduction

After the discovery of fullerenes [1] and, in particular, after their availability in pure form by utilizing host–guest complexation phenomena [2–4], [60]- and [70]fullerenes have become materials of current research activity in the fields of material science [5–7] on one hand and derivatisation [8–10] of the fullerenes on the other. In bio-molecular chemistry, fullerenes and carbon nanotubes are materials of current interest [11,12]. Some recent review articles [13–16] speak of such activities. In medicinal chemistry, the potential applications of [60]fullerene derivatives include inhibition of HIV-protease [17], antibacterial activity [18–20] and photocytotoxicity [21,22]. Being a good radical scavenger, this all-carbon molecule might also be used as an anti-apoptotic and/or anti aging agent [23–25]. Because of the insolubility of the fullerenes in water, all these potential applications can not be directly tested and derivatisation of the fullerenes is required [15]. However, the derivatives, particularly those involving electron repelling atoms and groups, may not have as much electron accepting power as the fullerenes themselves. So a better way out is to dissolve the fullerenes in a non-toxic solvent. Here also a problem is that the fullerenes form aggregates [26] in polar solvents, particularly in water [27]. The known solubility of fullerenes in aromatic solvents is due to charge transfer (CT) complex formation with the π-donor solvents [28]. A large variety of bio-molecules are known [29] to form CT complexes. The objective of the present work is to carry out a spectroscopic and thermodynamic study of complexation of [60]- and [70]fullerenes with the important bio-molecule, retinol palmitate (commonly known as 'Vitamin A palmitate', the structure of which is shown in Fig. 1), with the purpose that if such interaction is established the fullerenes may be solubilised in the non-toxic oil, Vitamin A palmitate.

2. Materials and methods

Retinol palmitate, menadione (i.e. 2-methyl 1,4-napthoquinone) and [60]fullerene were collected from Sigma and [70]fullerene from SES Research Inc., Houston, TX; they

* Corresponding author. Tel.: +91 34 22558545; fax: +91 34 22560810.
E-mail address: akm_13@rediffmail.com (A.K. Mukherjee).

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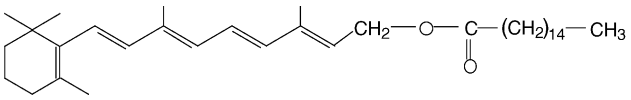

Fig. 1. Structure of retinol palmitate.

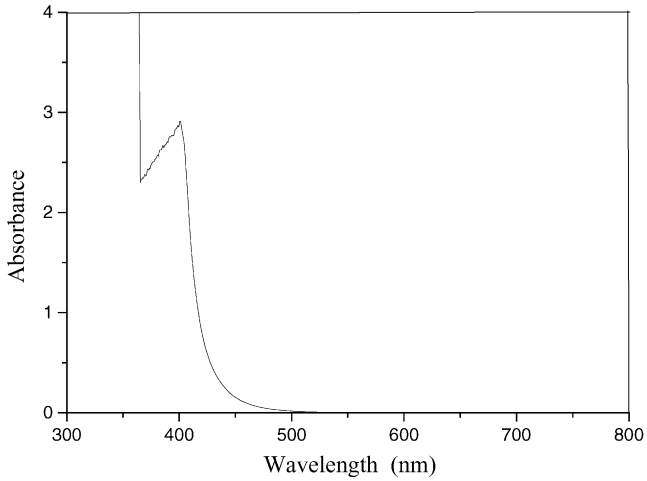

Fig. 2. Spectrum of compound **1** (2.111×10^{-2} mol dm^{-3}) against the solvent CCl_4 as reference.

were used without further purification. The other two acceptors, viz. 2,3-dichloro 1,4-naphthoquinone from Sigma and *p*-chloranil from Fluka, Switzerland were purified by sublimation just before use. The solvent, carbon tetrachloride was of UV-Spectroscopic grade. This was further purified by keeping it in fused calcium chloride for 24 h and then distilling just before use. All optical measurements were done on a UV 1601 PC model Shimadzu spectrophotometer fitted with a Peltier controlled thermo bath.

3. Results and discussions

3.1. Observation of charge transfer bands

Vitamin **1** has orange colour in CCl_4 solution and its absorption spectrum is shown in Fig. 2. CT absorption bands of the complexes of **1** with the known electron acceptors, viz. (i) [60]fullerene (ii) [70]fullerene (iii) menadione (iv) *p*-chloranil, and (v) 2,3-dichloro 1,4-naphthoquine could be detected by recording the spectra of mixtures containing **1** and the individual acceptors in CCl_4 medium against the respective pristine acceptor solutions as reference and then subtracting from it the absorbance due to **1**. Four such spectra are shown in Fig. 3. In some cases multiple CT peaks were observed. In all the cases the wavelengths at the CT peaks are different from the known λ_{mas} values of the component acceptors. The vertical ionization potential of the compound **1** was determined from the trends in these CT transition energies as follows. For systems with multiple CT peaks, the longest wavelength peak was used for the following calculations.

The vertical electron affinities (E_A^v) of the first four acceptors mentioned above were collected from literature [30–33] and that of the fifth one has been recently determined [34]. These E_A^v values correlate well with the presently observed CT transition energies ($h\upsilon_{CT}$, Table 1) in accordance with the Mulliken [35] equation:

$$h\upsilon_{CT} = I_D^v - C_1 + \frac{C_2}{I_D^v - C_1} \quad (1)$$

where I_D^v is the vertical ionization potential of the donor (Vitamin **1**) and C_1 is given by the equation

$$C_1 = E_A^v + G_1 + G_0 \quad (2)$$

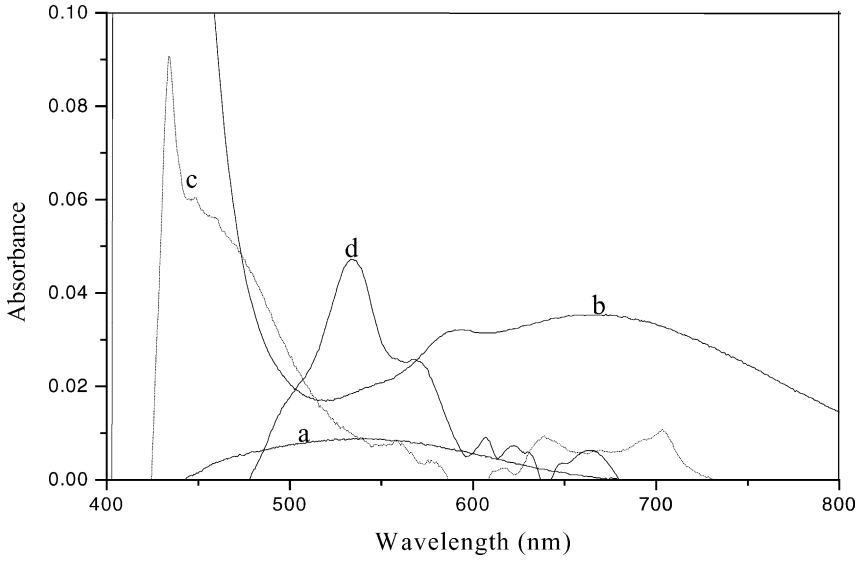

Fig. 3. CT absorption spectra of the complexes obtained by difference method from the actual spectra of mixtures containing vitamin **1** (10^{-2} mol dm^{-3}) and (a) 2,3 dichloro 1,4 napthoquinone (10^{-4}mol dm^{-3}) (b) *p*-chloranil (10^{-4} mol dm^{-3}) (c) [60]fullerene (10^{-5} mol dm^{-3}) (d) [70]fullerene(10^{-5}mol dm^{-3}) against the respective pristine acceptor solutions are reference.

Table 1
Charge transfer absorption maxima (λ_{CT}), CT transition energy ($h\nu_{CT}$), electron affinity of the acceptors (E_A^v), vertical ionization potential (I_D^v) of Vitamin **1** and degrees of charge transfer (λ)

Acceptor	λ_{CT} (nm)	$h\nu_{CT}$ (eV)	E_A^v (eV)	$10^3 \times \lambda$	I_D^v (eV)
[70]Fullerene	665	1.866	2.59	3.30	7.73 ± 0.01
2,3-Dichloro-1,4 napthoquinone	545	2.277	2.38	3.18	
[60]Fullerene	703	1.765	2.31	3.14	
Menadione	490	2.533	2.18	3.08	
p-Chloranil	672	1.847	1.37	2.74	

In Eq. (2), G_0 is the sum of several energy terms (like dipole–dipole, van der Waals interaction, etc.) in the 'no-bond' state and G_1 involves several energy terms in the 'dative' state. In most cases G_0 is small and can be neglected while G_1 is mainly the electrostatic energy of attraction between D^+ and A^- in the dative state. The term C_2 in Eq. (1) is related to the resonance energy of interaction between the 'no-bond' and 'dative' states. A rearrangement of Eq. (1) yields

$$2C_1 + h\nu_{CT} = \frac{C_1(C_1 + h\nu_{CT})}{I_D^v} + \left(\frac{C_2}{I_D^v} + I_D^v\right) \quad (3)$$

Neglecting G_0 and taking the typical *D–A* distance in π-type EDA complexes to be 3.5 Å, the major part of G_1 is estimated to be $e^2/4\pi\varepsilon_0 r$ = 4.13 eV.

Using these values C_1 is obtained from Eq. (2) for each of the acceptors. A plot of $2C_1 + h\nu_{CT}$ against $C_1(C_1 + h\nu_{CT})$ for a given donor and various acceptors should yield a slope of $1/I_D^v$ from which the value of I_D^v of the donor can be obtained. In the present case, with the experimental CT transition energies shown in Table 1, the plot is fairly linear (Fig. 4) and the linear regression equation is

$$2C_1 + h\nu_{CT} = (0.1294 + 0.0039)(C_1 + h\nu_{CT}) + (7.871 \pm 0.208); r^2 = 0.99 \quad (4)$$

From the slope, I_D^v of Vitamin **1** is found to be 7.73 eV.

3.2. Degree of charge transfer (α)

In a Mulliken two state model [35], the ground (ψ_g) and excited (ψ_{ex}) state wave functions of the CT complexes are described by a linear combination of dative ψ (D°, A°) and ionic ψ (D^+, A^-) states,

$$\psi_g = \sqrt{1-\alpha}\psi(D^\circ, A^\circ) + \sqrt{\alpha}\psi(D^+, A^-) \quad (5)$$

$$\psi_{ex} = \sqrt{1-\alpha}\psi(D^+, A^-) - \sqrt{\alpha}\psi(D^\circ, A^\circ) \quad (6)$$

where α is the degree of charge transfer. The function ψ (D^+, A^-) differs from ψ (D°, A°) by the promotion of an electron from the donor to the acceptor and α is given [35,36] by

$$\alpha = \frac{C_2}{2(I_D^v - E_A^v + C_1)^2 + C_2} \quad (7)$$

The values of α, calculated by using Eq. (7) and shown in Table 1 are small and indicate that very little charge transfer occurs in the ground state. However, as expected with a fixed donor, α increases with increase in the electron affinity of the acceptors (Table 1).

3.3. Molecular complex formation of vitamin *1* with [60]- and [70]fullerenes

3.3.1. Case 1: complexation with [60]fullerene

Spectra of mixtures containing a fixed concentration of [60]fullerene (6.944×10^{-5} mol dm^{-3}) and varying concentrations of the Vitamin **1** are given in Fig. 5. The two substances have absorption bands in the visible region and

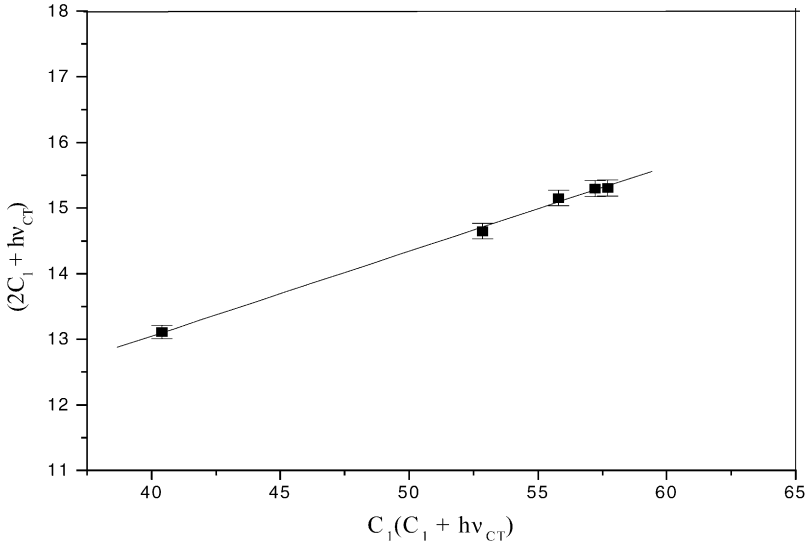

Fig. 4. Plot for determination of vertical ionization potential of vitamin **1** according to Eq. (3).

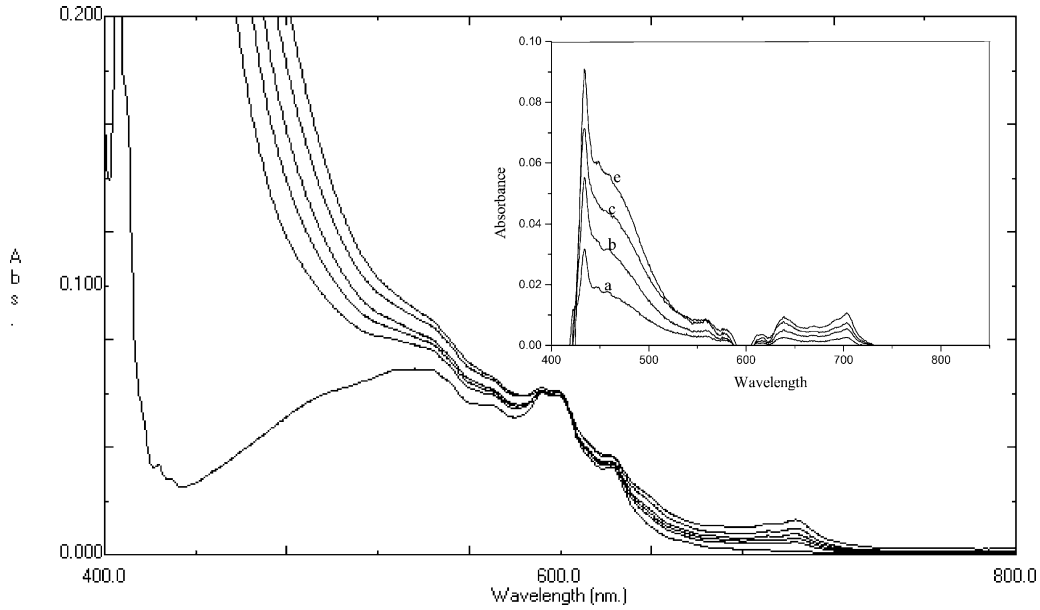

Fig. 5. Absorption spectra of [60]fullerene (6.944×10^{-5} mol dm^{-3}, lowermost curve) and of mixtures.containing [60]fullerene (6.944×10^{-5} mol dm^{-3}) and vitamin **1** (a) 2.917×10^{-3} (b)3.698×10^{-3} (c) 4.466×10^{-3} (d) 5.170×10^{-3} and (e) 6.475×10^{-3} mol dm^{-3} progressively upward, all taken against the solvent CCl_4 as reference. Inset: 400–850 nm range is the actual CT band of the complex at four different concentrations of **1** obtained by difference method.

so in the inset the difference spectra (absorbance of mixture − the sum of the absorbances of **1** and [60]fullerene at concentrations present in the mixture over the wavelength range scanned) are shown. The calculation of the formation constant of the complex was done at the CT peak (703 nm). The inset of Fig. 5 is shown to clarify the CT spectra with different vitamin **1** concentrations. Absorbance data of the mixtures at four different temperatures are shown in Table 2. Formation constants of CT complexes with 1:1 (donor:acceptor) stoichiometry, are usually determined by using the Benesi–Hildebrand [37] (B–H) equation which, for cells with 1 cm optical path length, is:

$$\frac{[A]_0[D]_0}{d'} = \frac{[D]_0}{\varepsilon'} + \frac{1}{K\varepsilon'} \tag{8}$$

with

$$d' = d - d_A^0 - d_D^0 \tag{9}$$

Here $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor and donor respectively, d the absorbance of the donor–acceptor mixture at some suitable wavelength (λ) against the solvent as reference, d_A^0 and d_D^0 are the absorbances of the acceptor and donor solutions with same molar concentrations as in the mixture at the same wavelength (λ). The quantity $\varepsilon' = \varepsilon_c - \varepsilon_A - \varepsilon_D$ means the apparent molar absorptivity of the complex, ε_A and ε_D being those of the acceptor and the donor respectively at λ. K is the formation constant of the complex. Eq. (8) is valid under the condition $[D]_0\% \gg [A]_0$. If, however, the complex is of 2:1 (donor:acceptor) stoichiometry the B–H equation is to be modified to

$$\frac{[A]_0[D]_0^2}{d'} = \frac{[D]_0^2}{\varepsilon'} + \frac{1}{K\varepsilon'} \tag{10}$$

with

$$d' = d - d_A^0 - d_D^0 \tag{11}$$

The quantity ε' now means $\varepsilon_c - \varepsilon_A - 2\varepsilon_D$. Experimental data shown in Table 2 show a very wide scatter and bad correlation when Eq. (8) was tried. But an excellent linear plot according to Eq. (10) was obtained at each of the temperatures studied. One such plot is shown in Fig. 6a. From the slopes and

Table 2
Absorbance data for Vitamin **1**—[60]fullerene mixtures against the solvent CCl_4 as reference at five different temperatures

Acceptor	10^5 [Acceptor] (mol dm^{-3})	10^2 [Compound **1**] (mol dm^{-3})	Absorbance at 703 nm				
			293 K	298 K	303;K	308 K	313 K
[60]Fullerene	6.944	2.917	0.0046	0.0045	0.0045	0.0044	0.0043
		3.698	0.0062	0.0061	0.0061	0.0060	0.0059
		4.466	0.0078	0.0077	0.0074	0.0076	0.0082
		5.170	0.0098	0.0099	0.0096	0.0095	0.0098
		6.264	0.0129	0.0128	0.0128	0.0127	0.0132
		6.475	0.0134	0.0134	0.0133	0.0132	0.0128

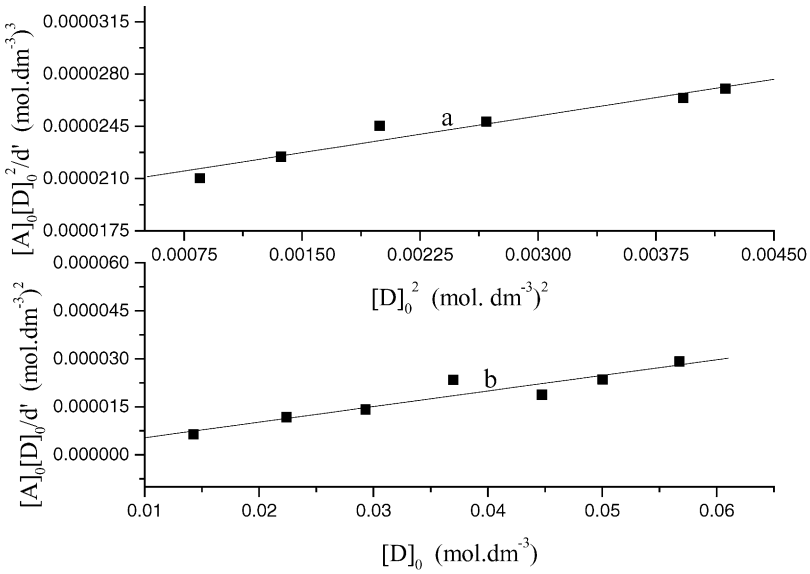

Fig. 6. Benesi–Hildebrand plot for mixtures of vitamin **1** with (a) [60]fullerene and (b) [70]fullerene at 293 K.

intercepts of such plots the formation constants were determined at five different temperatures. The stoichiometry of the complex is, therefore, 2:1 (vitamin **1**: [60]fullerene).

3.3.2. *Case 2: complexation with [70]fullerene*

In this case, the spectra of mixtures containing **1** in varying concentrations and [70]fullerene at a fixed concentration (2.381×10^{-5} mol dm^{-3}) are very complex but the difference spectra are simple as shown in Fig. 7. Although the longest wavelength CT peak is at 665 nm, the intensity of absorption is small at this wavelength; hence for calculation of the formation constant of the [70]fullerene complex we selected the 532 nm peak which is one of multiple CT peaks; at this wavelength, variation of absorption intensity with change in concentration of **1** is appreciable (Fig. 7). Absorbance data (Table 3) in this case fit excellently into the Eq. (8) thereby showing that the stoichiometry of the [70]fullerene–Vitamin **1** complex is 1:1. One typical B–H plot is shown in Fig. 6b.

3.3.3. *Formation constants, enthalpies and entropies of formation of the fullerene complexes of **1***

Formation constant (K) of the fullerene complexes, as determined from the slopes and intercepts of the B–H plots at a number of temperatures are shown in Table 4. Complexes of both the fullerenes have low values of K compared to their inclusion complexes (which are of the order of 10^3

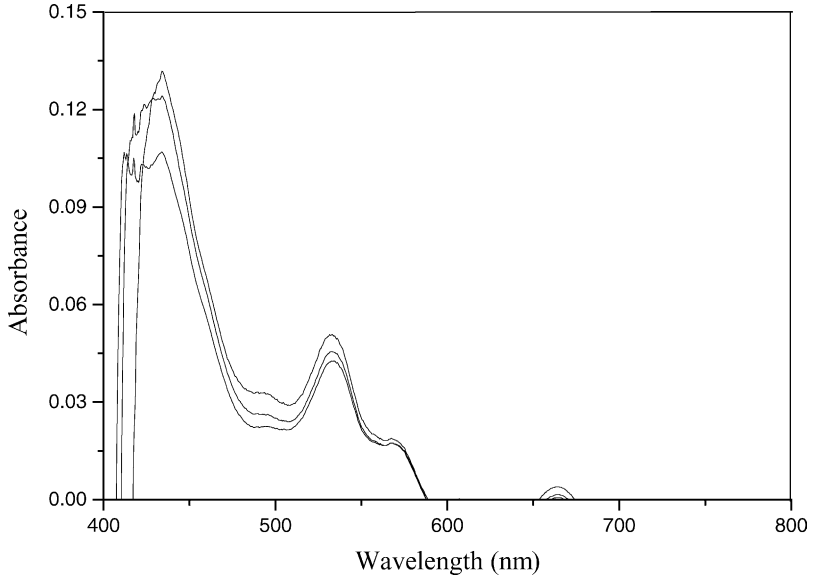

Fig. 7. Variation of CT absorption spectra of mixtures containing [70]fullerene (2.381×10^{-5} mol.dm^{-3}) and three different concentrations (2.240×10^{-2}, 2.930×10^{-2} and 4.472×10^{-2} mol dm^{-3}) of **1**, progressively upward, obtained by the difference method.

Table 3
Absorbance data for Vitamin **1**—[70]fullerene mixtures against the pristine [70]fullerene solution as reference at five different temperatures

Acceptor	10^5 [Acceptor] (mol dm^{-3})	10^2 [Compound **1**] (mol dm^{-3})	Absorbance at 532 nm				
			293 K	298 K	303 K	308 K	313 K
[70]Fullerene	2.381	1.427	0.0543	0.0537	0.053	0.05	0.0488
		2.240	0.0472	0.0459	0.0444	0.0438	0.0426
		2.930	0.0518	0.0515	0.0503	0.0499	0.0491
		3.698	0.0406	0.0370	0.0373	0.0363	0.0349
		4.472	0.0603.	0.0580	0.0573	0.0566	0.0558
		5.003	0.0546	0.0531	0.0526	0.0516	0.0509
		5.675	0.0509	0.0500	0.0493	0.0486	0.0477

Table 4
Formation constants, enthalpies and entropies of formation of the complexes of Vitamin **1** with [60]- and [70]fullerenes

Acceptor	Temperature (K)	Formation constant (K) (mol^{-1} dm^3)	ε'(dm^3 mol^{-1} cm^{-1})	ΔH_f^0 (kJ mol^{-1})	ΔS_f^0 (kJ mol^{-1})
[60]Fullerene	293	80 ± 1.0	700 ± 8.0	−13.80 ± 0.79	−10.74 ± 2.55
	298	70 ± 2.0			
	303	65 ± 1.0			
	308	60 ± 2.0			
	313	55 ± 2.0			
[70]Fullerene	293	1050 ± 7.0	2000 ± 21	−32.47 ± 0.78	−52.88 ± 2.58
	298	850 ± 6.0			
	303	700 ± 14			
	308	550 ± 12			
	313	450 ± 20			

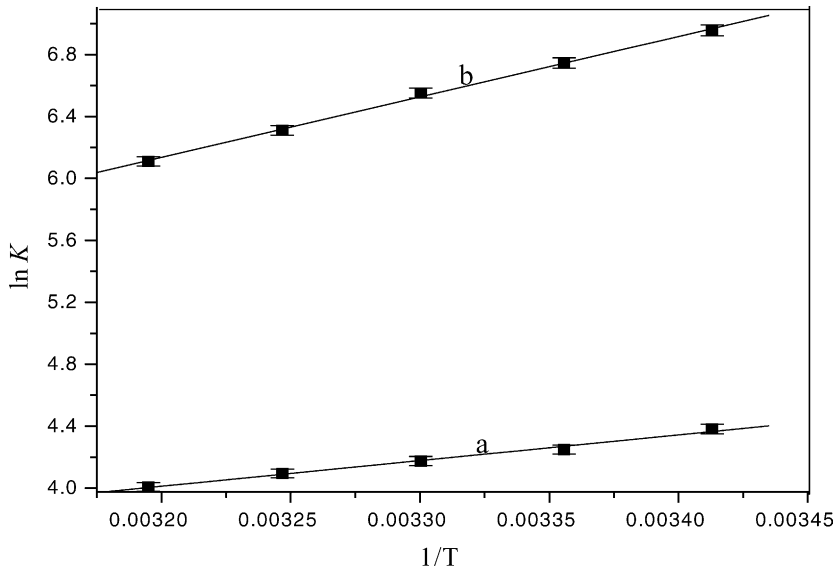

Fig. 8. van't Hoff plots for complexes of Vitamin **1** with (a) [60] fullerene and (b) [70]fullerene.

to 10^6). The values of ln K for both the complexes exhibit excellent linear correlation with $1/T$ in accordance with van't Hoff equation as shown in Fig. 8. The regression equations are:For [60]fullerene **1** complex

$$\ln K = \frac{1660 \pm 95}{T} + (-1.30 \pm 0.31); \quad r^2 = 0.99 \qquad (12)$$

For [70]fullerene. **1** complex

$$\ln K = \frac{3905 \pm 94}{T} + (-6.36 \pm 0.31); \quad r^2 = 0.99 \qquad (13)$$

The enthalpies (ΔH_f^0) and entropies (ΔS_f^0) of formation of the complexes determined from Eqs. (12) and (13) are shown in Table 4.

4. Conclusion

The present study yields the vertical ionisation potential of retinol palmitate and this result may be of some value in pharmacodynamical interpretation of biochemical processes

involving this vitamin. Moreover, the CT complex formation of [60]- and [70]fullerenes with the vitamin may be used to solubilise the fullerenes in Vitamin A oil as solvent and this solution may be of pharmaceutical utility in testing the biological activity of the fullerenes in vivo.

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