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Interaction of Some Biomolecules with π- and σ-Acceptors

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Electrical conductance, refractometric and differential refractometric techniques have been used to study the charge-transfer interaction of some biomolecules with chloranil and iodine, and their ion-pair separation. A mechanism of transformation of outer complex to inner complex has been suggested. The coexistence of intimate and solvent-separated ion-pairs in equilibrium in binary mixtures of dioxan—*THF* is indicated for these complexes. The equilibrium constant (*K*) and solvation number (*n*) for the equilibria; $AAI^+, I_3^- + n\,THF \overset{K}{\rightleftharpoons} AAI^+//I_3^-$; $GBI^+, I_3^- + n\,THF \overset{K}{\rightleftharpoons} GBI^+//I_3^-$, have been calculated and it was found that a single *THF* molecule has managed to intercalate between cation and anion.

(Keywords: Charge-transfer complexes; Ion-pair separation; Aminoacids; Genetic bases)

Wechselwirkung einiger biologisch relevanter Moleküle mit π- und σ-Acceptoren

Unter Benutzung konduktometrischer, refraktometrischer und differenzrefraktometrischer Methoden wurde die Charge-Transfer-Wechselwirkung einiger biologisch relevanter Moleküle mit Chloranil und Jod und auch ihre Separation in Ionenpaare untersucht. Es wird ein Mechanismus zur Umwandlung des äußeren Komplexes in den inneren vorgeschlagen. Die Koexistenz von zusammenhaftenden und vom Lösungsmittel getrennten Ionenpaaren wird in binären Mischungen von Dioxan—*THF* nahegelegt. Die Gleichgewichtskonstante *K* und die Solvatationsnummer *n* wurde für folgende Gleichgewichte errechnet: $AAI^+, I_3^- + n\,THF \overset{K}{\rightleftharpoons} AAI^+//I_3^-$; $GBI^+, I_3^+ + n\,THF \overset{K}{\rightleftharpoons} GBI^+//I_3^-$. Dabei wurde herausgefunden, daß ein einzelnes *THF*-Molekül zwischen Kation und Anion eingeschoben ist.

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Introduction

Although spectrophotometric[1] and NMR[2] methods are used extensively to study molecular interactions, spectrophotometric techniques are difficult when there is overlapping of charge-transfer bands with the donor or acceptor bands[3]. In this report, we have studied the charge-transfer interaction of aminoacids (phenylalanine, tyrosine, alanine, tryptophan, valine, glycine) with iodine and genetic bases with iodine and chloranil using conductometric, refractometric and differential refractometric techniques.

Experimental and Data Analysis

All the materials were of AR grade and were used after further purification. The method of experimentation was essentially the same as described earlier[4–8].

Results and Discussion

Interaction of Aminoacids with Iodine

When excess of aminoacids are added to an aqueous solution of iodine, bleaching occurs, taking several minutes for tryptophan, and several hours for other aminoacids[9]. For the tryptophan—iodine system the process accompanied an increase in refractive index initially, followed by a decrease afterwards. From this observation it is clear that in case of tryptophan—iodine the outer complex (Stage I) is more dominating than in other aminoacids—iodine complexes. The refraction per cm^3 is directly related to the concentration of the complex which itself depends upon the concentration of donor and acceptor. If in solution the transformation of outer complex to inner complex takes place, the concentration of ionic species in solution increases. The dissociation ($DA \rightleftharpoons D^+ + A^-$) leads to a decrease in refraction per cm^3 of the system. Thus, after bleaching the tryptophan—iodine outer complex is transformed into the inner complex (Stage III). In other cases, where a direct decrease in refraction per cm^3 was observed, the life time of Stage I is very short. As soon as the outer complex is formed the system becomes tight showing an increase in refractive index. Other aminoacid—iodine complexes do not show an increase in refractive index values even during the bleaching process. This indicates an immediate transformation of outer to inner complex during the bleaching process (Stage III). On the basis of these observations, a mechanism of interaction between aminoacid and iodine may be proposed as shown in Scheme 1.

During the bleaching process the tryptophan—iodine complex shows an increase in conductance and for the same system after bleaching a decrease in conductance was noticed. We could not explain this drop in

Scheme 1

$$AA + I_2 \rightleftharpoons AA.I-I \quad \text{(Outer complex)} \qquad \text{Stage I}$$

$$AA.I-I + I_2 \rightleftharpoons (A.A.I^{+\delta} \ldots\ldots I^{-\delta}.I-I) \quad \text{(Transition stage)} \qquad \text{Stage II}$$

$$(AA.I^{+} \ldots\ldots I^{-} \ldots I-I) \rightleftharpoons (A.A.I^{+})\ (I_3^{-}) \quad \text{(Inner complex)} \qquad \text{Stage III}$$

AA = Aminoacid

conductance. But other aminoacids—iodine complexes show an appreciable increase in conductance value. From this observation it is clear that in case of the tryptophan—iodine complex the outer complex (Stage I) is more dominating than in other aminoacid—iodine complexes. The direct increase in the conductance value of other aminoacid—iodine complexes may be interpreted due to the short life time of Stage I.

Interaction of Genetic Bases with Chloranil and Iodine

The charge-transfer interaction between genetic bases (donor) with chloranil (acceptor) in *DMSO* has been studied using equations (1–7) of Ref.[4]. But no appreciable change, neither in conductance nor in refractive index, was noted by applying these equations. This may be due to the low solubility of the solutes in *DMSO* and also to the weak interaction. By applying *Gutmann*'s technique [equation (8) of Ref.[4]] for these systems, a measurable change was noted. Therefore σ_P, σ_O and σ_M values were

Table 1. *Conductance data for charge-transfer complexes of genetic bases with chloranil in DMSO at 30 °C*

Complex	Conductance (μ mho)*			σM
	σ_P	σ_O	$(\sigma_P - \sigma_O)$	
Adenine	220	40	180	900.00
Guanine	480	70	410	1 464.28
Cytosine	440	85	355	835.29
Thymine	415	80	335	1 046.87
Uracil	330	60	270	760.00

* A standard deviation of $\pm$ 0.1% was calculated.

calculated and recorded in Table 1. From this table it is evident that the σ_P value for the guanine—chloranil complex is greater than for other complexes. This indicates a better donor capability of guanine than for other genetic bases. Theoretical calculations[10] are also in agreement with this observation.

On mixing an aqueous solution of genetic bases with iodine in aqueous solution of iodine, a decrease in refractive index was observed while in other systems [e.g. aminoacid—iodine, chloranil, Ph_3M—I_2[12,13], $M(acac)_n$—I_2[14]] an increase in refractive index was noted. This abnormal behaviour of genetic bases—iodine complexes may be interpreted due to the immediate formation of ion-pairs. This immediate transformation of outer complex to inner complex may be due to the high dielectric constant of the medium. Thus, a mechanism for the transformation may be proposed (Scheme 2).

Scheme 2

$$GB + I_2 \rightleftharpoons GBI{-}I$$
(Outer complex)

$$GBI{-}I + I_2 \rightleftharpoons GBI^+, I_3^-$$
(Inner complex)

GB = Genetic bases

In the above mechanism the outer complex was not detected because of the direct decrease of the refractive index. This mechanism finds further support from the spectrophotometric data of *Slifkin*[15].

Intimate and Solvent-Separated Ion-Pairs

A binary mixture of dioxan and tetrahydrofuran (*THF*) has been used to monitor the solvent-separated and intimate ion-pairs. A plot of n^2 or $\Delta\Omega C_{SS}$ or Λ *versus* mole fraction of *THF* shows a sigmoid curve with two plateaus. This may be due to the co-existence of two distinct species in the equilibrium (Scheme 3).

Scheme 3

$$AAI^+, I_3^- + n\,THF \overset{K}{\rightleftharpoons} AAI^+ // I_3^-$$

$$GBI^+, I_3^- + n\,THF \overset{K}{\rightleftharpoons} GBI^+ // I_3^-$$

Intimate ion-pair — Solvent-separated ion-pair

Table 2. *Solvation number (n) and equilibrium constant (K) data for the intimate and solvent-separated ion-pairs in the systems according to Scheme 3*

System		Solvation number (n)*			Equilibrium constant (K)* $dm^3\ mol^{-1}$		
		A	B	C	A	B	C
AA							
	Phenylalanine	1.10	1.10	1.05	1.12	1.09	1.10
	Tyrosine	1.20	1.15	1.05	1.20	1.09	1.16
	Tryptophan	0.85	0.85	1.00	1.24	1.20	1.22
	Valine	0.80	0.82	0.96	1.60	1.25	1.51
	Leucine	0.92	1.10	0.98	1.30	1.10	1.25
	Glycine	1.15	1.15	1.05	1.22	1.17	1.20
	Alanine	1.15	1.05	1.05	1.20	1.16	1.14
GB							
	Adenine	1.01	0.90	1.10	1.24	1.60	1.65
	Guanine	1.12	0.95	0.90	1.28	1.30	1.30
	Cytosine	1.08	1.10	1.08	1.08	1.20	1.34
	Thymine	0.85	1.15	1.12	1.12	1.25	1.20
	Uracil	0.90	1.20	1.14	1.24	1.40	1.30

A = calculated from conductometric data; B = calculated from refractometric data; C = calculated from differential refractometric data.

* A standard deviation of $\pm$ 0.1% was calculated.

The equilibrium constant (K) and solvation number (n) for these equilibria have been calculated by using equations (2–4) of Ref.[4]; the values are recorded in Table 2. From this table it is evident that a single *THF* molecule has managed to intercalate itself between anion and cation. These results are similar to those reported by *Chan* and *Smid*[16] for the intimate and solvent-separated ion-pairs of carbanions using a spectrophotometric method, and are in good agreement with those obtained by NMR[17], refractometric and conductometric techniques[18] of different systems.

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