Formation of Silver–Adenine Long-chain Aggregates in Neutral Aqueous Solution: Study of Flow Linear Dichroism

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The existence of long, linear adenine–silver clusters in neutral, very dilute solutions has been demonstrated by flow linear dichroism.

We are engaged in a study of the interaction of some metal ions with nucleic acids, the component bases, and their derivatives. Recently we have found that in aqueous solution the interaction of silver ions with some guanine derivatives[1] leads to the formation of dimeric species of the heterocyclic bases where the complexed silver ions provide the crosslinks between them. An extension of this work to adenine and its derivatives has now been carried out and we have found that, as was the case with guanine derivatives, silver ions produce association between the bases in aqueous solution. Here we report that in neutral dilute solutions we detected the existence of long, linear adenine–silver clusters.

Absorption of light by electric transition dipoles of chromophores corresponds to interactions between vectorial quantities and is, accordingly, anisotropic on the molecular level; however, in isotropic solution the random orientation of the molecules masks this inherent anisotropy. Conversely, anisotropic absorption implies a non-random distribution of the chromophoric transition moments. When solutes are of macromolecular dimensions a partial orientation of such molecules can be achieved by flow and with suitable instrumentation the consequent optical anisotropy may be determined.[2] We have measured the linear dichroism (*LD*) defined at any wavelength by equation (1), where $A_{\parallel}$ and $A_{\perp}$ represent the absorbances of the solutions measured with light polarised, parallel with and perpendicular to the direction of the flow, respectively. A convenient, closely related quantity is the reduced linear dichroism defined by $LD_r = LD/A$, where A is the isotropic absorption of the solution.[3]

$$LD = A_{\parallel} - A_{\perp} \qquad (1)$$

No flow dichroism is detectable with a pure adenine solution. When silver ions are added gradually, up to a molar ratio of silver to adenine of approximately 1.4:1, flow dichroism is observed as shown in Figure 1. As more silver is added the *LD* persists up to a silver to adenine molar ratio of about 2.2:1 above which it rapidly diminishes and it completely disappears at a ratio greater than 2.5:1.

A general requirement for flow orientation under the conditions employed here is the presence of aggregates of at least 50 nm in one dimension; thus the above observation can only be interpreted in terms of a flow-orientable, presumably

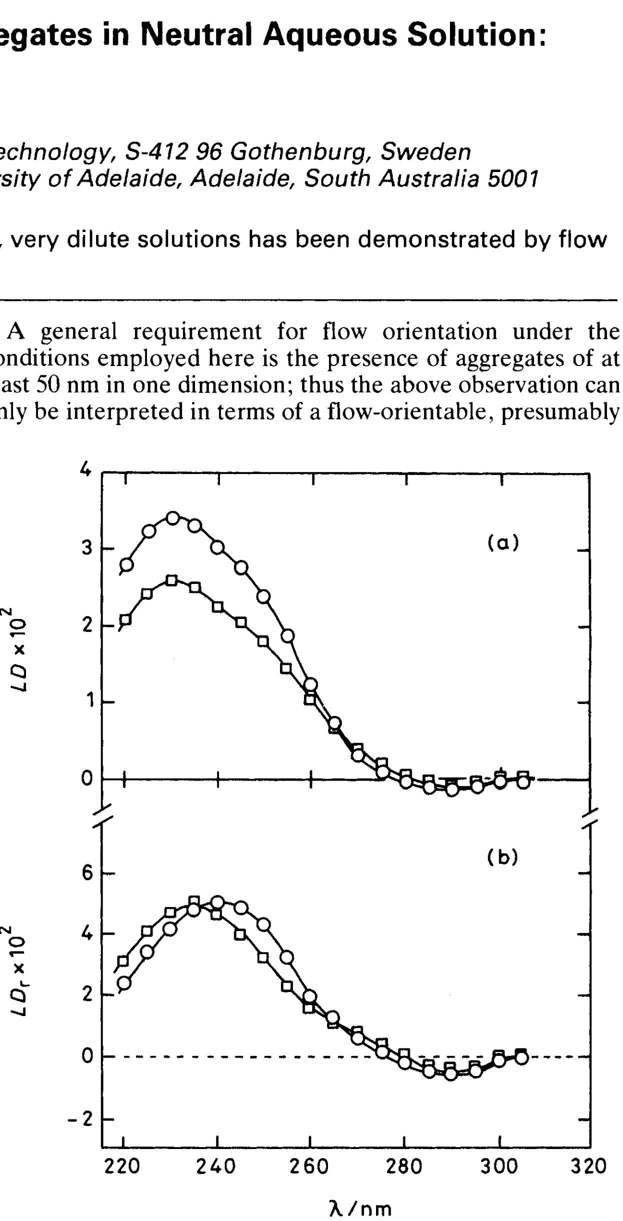

Figure 1. (a) Linear dichroism (b) reduced linear dichroism of adenine-silver complex in 1 mM cacodylate buffer solution. Adenine concentration: 7.9×10^{-5} mol dm^{-3}; molar ratio of silver to adenine = 1.5:1 (□) and 2.0:1 (○); rate of shear = 600 s^{-1}, optical path length = 1 cm.

long-chain, polymeric adenine–silver species. The disappearance of the polymer in the presence of a large excess of silver ions, as implied by the disappearance of *LD* under these conditions, would be compatible with a structure for the polymeric species where 'monomeric' adenine moieties were crosslinked by complexed silver ions. We have found from the shape of the *LD* curves, that the ratio between the positive and negative peaks near 230 and 290 nm, respectively, is independent of the flow gradient in the range of 200—1200 s^{-1}. This lends support to the conjecture that the polymeric structure is maintained by relatively strong silver to base complexing rather than by weaker van der Waals interactions which may become disrupted by the application of hydrodynamic fields of increasing intensity.

Further discussion concerning these results and the likely structure of the polymeric complexes is reserved for a subsequent paper. Here we stress two points. First, the results demonstrate the important role that flow dichroism plays in the detection and characterisation of long aggregates in solution. Secondly, the discovery of the formation of a 'polypurine' in the presence of a metal ion may have relevance to the problem of prebiotic chemical evolution of biological macromolecules.

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