Comparison of Results obtained in Kinetic Studies of the Interaction between Cationic Dyes and Sodium Carboxymethylcellulose using the Joule-heating Temperature-jump and Laser Temperature-jump Methods

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Summary It has been shown that the large electric field change generated in the Joule-heating temperature-jump apparatus produces effects which can be erroneously attributed to the temperature jump.

IN recent years, a number of kinetic studies have been made of the interaction between metachromatic dyes and polyelectrolytes in solution.[1] Much of this work has been done using commercially available Joule-heating temperature-jump (T-jump) apparatus employing spectrophotometric detection. Interest in these studies has been motivated by a desire to understand the mechanism by which ligands bind to charged polymers.

We report herein some results of a study of the interaction between the cationic dyes Acridine Orange-(AO) and Toluidine Blue (TB) (obtained from BDH Chemicals Ltd.; purified by recrystallisation from ethanol), and the polyanion, sodium carboxymethylcellulose (NaCMC) (obtained from Hercules Powder Co.; dried; mean number of anionic sites per cellulose unit 0·7, concentration given as molarity of anionic sites), using conventional Joule-heating T-jump (commercially available, Hartley Instruments Ltd., England) and laser T-jump (described previously[2]) apparatuses. Both types of equipment employed spectrophotometric detection in which the change in absorbance of the solution being studied was monitored following the temperature jump. In both cases the detection system operated with light sources which produced unpolarized light, and the measurements were made on solutions thermostated at 25 °C.

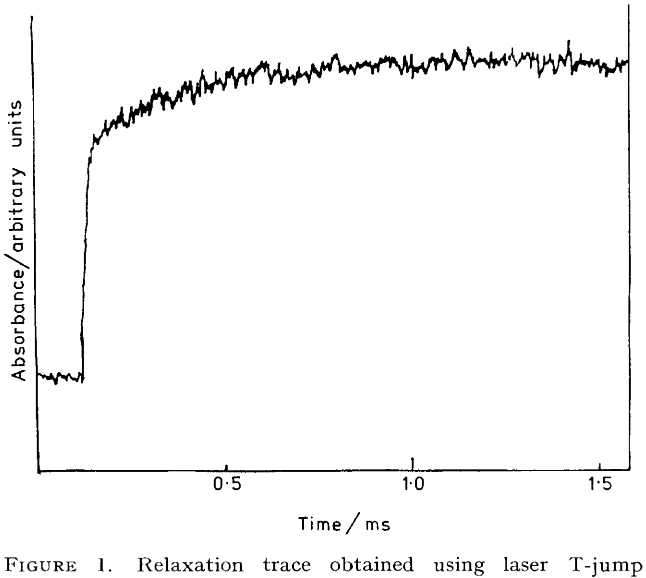

FIGURE 1. Relaxation trace obtained using laser T-jump apparatus; [AO] 10^{-4} M, [NaCMC] 4×10^{-3} M, [NaCl] 10^{-3} M. Light absorption was monitored at λ 492 nm. The relaxation time for the faster of the two processes was found from a separate trace which was obtained on an expanded time scale. Relaxation times are 8·8 μs and 310 μs.

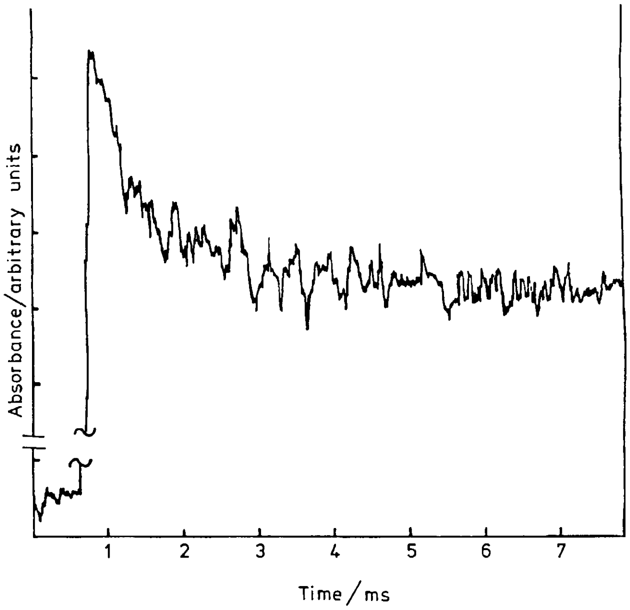

FIGURE 2. Trace obtained using Joule-heating T-jump apparatus. The solution and conditions were as described for Figure 1; relaxation time 1·06 ms.

Figures 1 and 2 are examples of traces which have been obtained with the two types of T-jump apparatus for identical solutions. The absorption spectrum of AO–NaCMC solutions shows a peak at λ 492 nm, which is attributed to absorption by monomer dye, and a broad peak at *ca.* 450 nm which is attributed to absorption by dye aggregates on the polyanion.[3] The traces shown were obtained under conditions in which, initially, the greater proportion of the dye would be bound to the polyelectrolyte and these results indicate the change in absorbance due to dye in monomer form. The concentration of simple electrolyte in these solutions is lower than that usually employed with Joule-heating equipment. The laser T-jump traces always show a monotonic increase in absorbance characterized by two well separated relaxation times. The Joule-heating trace exhibits a high amplitude increase in absorbance, which occurs within the discharge time of the capacitor, followed by a slow decay towards the final equilibrium position. This slow decay is much slower than the decay of the electric field across the cell and is slower than either of the relaxation processes found with the laser T-jump. The conspicuous difference in shape between the traces is only found when measurements are made at low ionic strength. Similar traces were obtained when TB was substituted for AO. At higher ionic strength the traces obtained by the different techniques are qualitatively similar, both showing a monotonic increase in absorbance, but with different relaxation times. An example of such a trace is shown in Figure 3 for a TB–NaCMC solution. The laser T-jump trace is characterized by a single relaxation time of 11·2 μs. With the laser apparatus, there was found to be no evidence for any slower relaxation process when the observation time was extended to 10 ms. (These results are under investigation). The Joule-heating traces, however, always showed evidence of two relaxation processes for the TB–NaCMC solution referred to in Figure 3. The faster of these two processes was too fast to be analysed using this equipment.

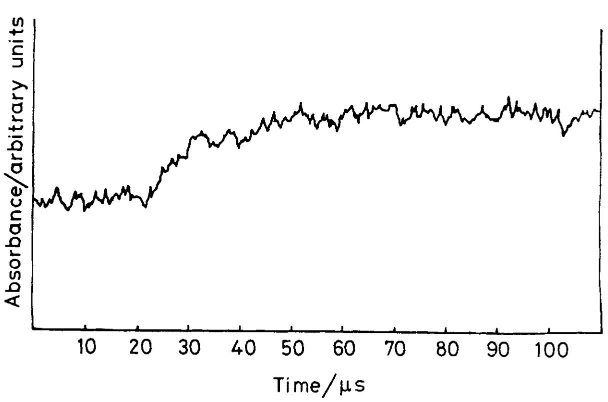

FIGURE 3. Laser T-jump trace obtained with a TB–NaCMC solution. Observation was made at λ 630 nm corresponding to the monomer absorption peak for TB; [TB] 6·4 × 10^{-5} M, [NaCMC] 6·4 × 10^{-4} M, [NaCl] 0·025 M; relaxation time 11·2 μs.

The slower process had a relaxation time of 15 ms. Results very similar to ours have been obtained by other workers using Joule-heating equipment to study dye–polyelectrolyte solutions at low ionic strength.[4,5] We have also obtained traces with the Joule-heating apparatus at the aggregate peak wavelength, 450 nm, for AO–NaCMC solutions. The traces obtained are identical to Figure 2, but are inverted showing a large amplitude drop in absorbance followed by a slow rise towards final equilibrium.

To explain these results we must note that, with the Joule-heating technique, the solution under study is subjected to a high electric field for a short period of time. In our experiments, the magnitude of the field was in the region of 40 kV cm^{-1} and its duration was *ca.* 100 μs when used with solutions in which the simple electrolyte concentration was 10^{-3} M. As the ionic strength of the solution is increased the duration of the field decreases. It is known that such fields can orientate polyelectrolyte molecules and render their solutions optically anisotropic. For this reason caution has been urged in the interpretation of Joule-heating T-jump traces obtained with dye–polyelectrolyte solutions. It has been suggested that a possible solution to this problem is to use plane polarised light in the detection system.[6] However, the dichroic effect in itself cannot explain our observations. In particular, it is difficult to see how induced optical anisotropy could give rise to an increase in absorbance at the monomer wavelength and a similar decrease in absorbance at the aggregate wavelength. We believe that a more plausible and simpler explanation is that the transient electric field perturbs the equilibria which prevail in the dye–polyelectrolyte system.[7] It may be that orientation of the polyelectrolyte molecules plays a part in this perturbation, but what is observed is a real increase in monomer dye at the monomer wavelength accompanied by a corresponding reduction in aggregate dye at the aggregate wavelength. Furthermore, we note that in a previous study[4] of dye–polyelectrolyte kinetics using Joule–heating apparatus, anomalous traces similar to ours were obtained, but there was no evidence of a dichroic effect. We do not know what the effect of a high electric field on a dye-polyelectrolyte complex is. However, it would be wrong to assume that it is small. For example, recent observations indicate that the second Wien effect is much greater for polyelectrolytes than for simple electrolytes.[8] We believe that the effect of the field is greater at low ionic strength, partly because the duration of the field is longer under these conditions, thus allowing any relatively slow field-induced changes to occur to a greater extent. Also, more dye is bound to the polyion under these conditions. It would seem that the observed relaxational behaviour is a mixture of field-induced relaxation and relaxation due to the temperature change. As the detailed shape of the field transient is not usually known any attempt to analyse such relaxation behaviour in terms of chemical processes is likely to be unreliable.

The Joule-heating T-jump technique is, therefore, likely to produce misleading results when applied to systems which are perturbed by high electric fields. We believe that this is the case in Joule-heating T-jump studies of dye–polyelectrolyte systems. To what extent it is true for other systems requires further study.

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