A styrylpyridinium salt in aqueous solution: unusual solution behaviour

N. J. Crowther and D. Eagland*

School of Pharmacy–Pharmaceutical Chemistry, University of Bradford, Bradford, UK BD7 1DP

The results of a series of physico-chemical experiments are presented which show that 4-(4-formylphenylethenyl)-1-methylpyridinium methanesulfonate, one example of a styrylpyridinium salt, undergoes a micellar type aggregation as a function of concentration in aqueous solution.

The photosensitivity of the styrylpyridinium group was first reported by Williams and coworkers,[1,2] subsequently photoreactive styrylpyridinium salts have achieved widespread use in the production of photoresists for screen printing, since their use in this role was first patented by Ichimura and coworkers in 1988.[3,4] The reported mode of action of such salts is by an acid-catalysed aldol condensation reaction with the polymer poly-(vinyl alcohol), and subsequently a photoinduced dimerisation, using UV light, of the attached pendant styrylpyridinium groups on adjacent polymer molecules.

Several papers have since been published[5–7] on various aspects of the fundamental photodimerisation reaction of styrylpyridinium, and related compounds, in solution and in the crystal form,[8,9] and of photodimerisation following the solubilisation of these compounds into micellar materials such as aerosol OT[10] but, as far as we are aware, nothing has been reported on the physico-chemical behaviour of such compounds in aqueous solution.

The structure of a molecule of the styrylpyridinium type is such that we considered that unusual aqueous solution behaviour might be expected, thus we report here a series of physico-chemical studies of one such compound, 4-(4-formyl-phenylethenyl)-1-methylpyridinium methylsulfonate, SbQ, in aqueous solution.

The sample of SbQ was kindly supplied by Sericol plc, purified by a recrystallisation procedure, with a quoted purity of better than 99.5% m/m, which was confirmed by the lack of a minimum in the observed surface tension data. Density measurements were made using previously reported techniques[11] and had a precision of 1×10^{-4} kg m^{-3}; the microcalorimetric measurements, also using previously reported procedures,[12] had a precision of 1×10^{-7} J. Surface tension measurements were undertaken using a drop profile measurement procedure, developed in this laboratory, with a precision of ±0.05 mN m^{-1}. Light-scattering measurements were made using a Sofica photogoniometer, model 42 000, modified to use a Uniphase 1 mW He–Ne laser, operating at 543 nm. Vapour-pressure measurements were made with a Knauer vapour-pressure osmometer, standardised against Analar NaCl solutions. Heats of dilution measurements were carried out using an LKB flow microcalorimeter, model 2107-121/127.

The vapour-pressure measurements, obtained at 37 °C, are presented in Fig. 1, where the ratio $\Delta t/c$ represents the difference in temperature between the solvent reference probe and the solution probe at a concentration c in g kg^{-1}. The plot shows two linear regions, both with good correlation coefficients of 0.996 and 0.998, intersecting at a concentration value of 1.25% m/m. The intercept of the low range of solution concentrations was utilised in the usual manner to determine a value for the number average molar mass for SbQ of 341, close to the expected value of 335. The difference of slope at the higher concentrations suggests that, above the concentration of 1.25% m/m, some form of aggregation has occurred.

An analysis of the energy of the structure of the SbQ molecule, minimised in water, was performed, using a Hyperchem molecular modelling package, based on MM+ force-field calculations,[13] which produced a very planar structure. Such a structure for the molecule easily allows for the possibility of stacking of the molecules with the hydrophobic regions one above the other, with the aldehyde and NMe groups alternating, to produce an aggregate, shown energy minimised in water for four space-filled SbQ molecules in Fig. 2.

Taking the difference between the intercepts in Fig. 1 for the two concentration regions as being due to the aggregate, this yields a molar mass for the SbQ aggregate of about 2800, suggesting that the aggregate stack consists of about eight monomer units, with a critical concentration for the change of 1.25% m/m, close to 0.04 **m**

Surface tension measurements, as a function of concentration, for a series of solutions of SbQ, at 25 °C, are shown in Fig. 3; the pattern seen is the classic one for micellisation of a surfactant with the break occurring at about 0.06 **m**. This evidence therefore suggests that the SbQ aggregate is in fact a stacked rod-like micelle, with a c.m.c. value of 0.04 to 0.06 **m**, depending on the experimental measurement. The somewhat
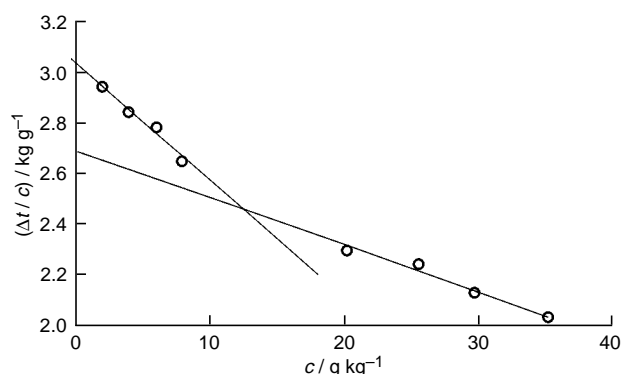

Fig. 1 Vapour-pressure measurements on solutions of SbQ, at 37 °C, as a function of concentration
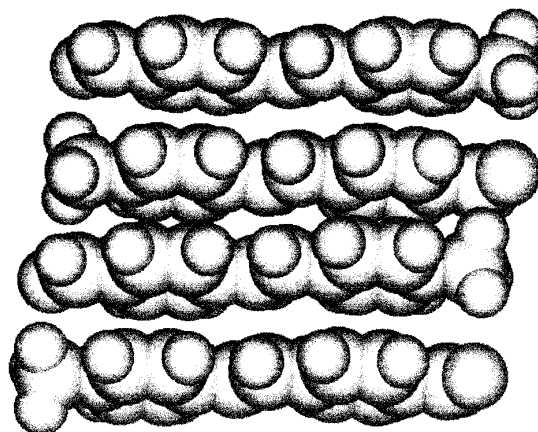

Fig. 2 Energy-minimised structure of an SbQ aggregate in water

high equilibrium value of the surface tension, at 51 mN m^{-1}, is possibly due to the strongly hydrophilic groups present at each end of the molecule.[14]

Values of the apparent molar volume of the SbQ molecule, obtained from the density measurements at 25 °C, are also shown in Fig. 3; the sharp change of slope seen at 0.04 **m** means that the SbQ molecule adopts a more compact form above this concentration, exactly what might be expected to happen when aggregating to form a micelle. Such a change of slope at the c.m.c. of a surfactant has been reported by Perron *et al.*[15]

Values for the Rayleigh scattering at an angle of 90°, measured at a temperature of 25 °C, as function of concentration, are shown in Fig. 3; the sharp increase in scattering which occurs at concentrations approaching 0.04 **m** indicates the appearance of larger particles, the micelles in fact.

Heats of dilution measurements, at 25 °C, as a function of the initial concentration of the solution, Fig. 3, also show a sharp change of slope, in this case at 0.035 **m**, yet again indicating a major change in the solution state of the solute, from monomer to micelle[15] has occurred.

In conclusion, the close correlation between the concentration dependence behaviour of all the experimental measure-ments is good confirmation of the existence of a monomer–micelle equilibrium in the aqueous solutions of SbQ.

The SbQ molecule is one example of quite a large group of styrylpyridinium and styrylquinolinium compounds, all of similar structure; it is therefore very likely that, in general, compounds of this type will exhibit similar micellar behaviour. With regard to the broader implications of this behaviour, we are grateful to one of the referees for drawing our attention to the work of Tiddy *et al.*[16,17] who have reported what may be similar stacked aggregates in dilute aqueous solutions of azo and cyan dyes.

References

1 D. G. Borden and J. L. R. Williams, *Makromol. Chem.*, 1964, **73**, 203.
2 J. L. R. Williams and D. G. Borden, *Makromol. Chem.*, 1977, **178**, 3053.
3 K. Ichimura, *UK Pat.* GB 2 030 575 B, 1978.
4 K. Ichimura, M.Ito, M. Yamana and H. Ito, *US Pat.* 4 777 114, 1988.
5 K. Ichimura, *Makromol. Chem.*, 1987, **188**, 2973.
6 K. Ichimura and N. Oohara, *J. Polym. Sci.: Part A, Polym. Chem.*, 1987, **25**, 3064.
7 M. Y. Li, E. M. Pearce, A. Reiser and S. Narang, *J. Polym. Sci.: Part A, Polym. Chem.*, 1988, **26**, 2517.
8 M. Hasegawa, K. Saigo, T. Mori, H. Uno, M. Nohara and H. Nakanishi, *J. Am. Chem. Soc.*, 1985, **107**, 2788.
9 M. Hasegawa, H. Arioka, H. Harashina, M. Nohara, M. Kubo and T. Nishikubo, *Isr. J. Chem.*, 1985, **25**, 302.
10 K. Takagi, B. R. Suddaby, S. L. Vadas, C. A. Backer and D. G. Whitten, *J. Am. Chem. Soc.*, 1986, **108**, 7865.
11 F. F. Vercauteren, W. A. B. Donners, N. J. Crowther and D. Eagland, *Eur. Polym. J.*, 1987, **23**, 711.
12 D. Eagland, N. J. Crowther and C. J. Butler, *Polymer*, 1993, **34**, 2804.
13 U. Burkert and N. L. Allinger, *Mol. Mech., ACS Monogr.*, 1982, **177**.
14 A. R. Pitt, S. D. Morley, N. J. Burbridge and E. L. Quickenden, *Colloids Surf. A: Physicochem. Eng. Aspects*, 1996, **114**, 321.
15 G. Perron, F. Yamashita, P. Martin and J. E. Desnoyers, *J. Colloid Interface Sci.*, 1991, **144**, 222.
16 G. J. T. Tiddy, D. L. Mateer, A. P. Ormerod, W. J. Harrison and D. J. Edwards, *Langmuir*, 1995, **11**, 390.
17 W. J. Harrison, D. L. Mateer and G. J. T. Tiddy, *J. Phys. Chem.*, 1996, **100**, 2310.
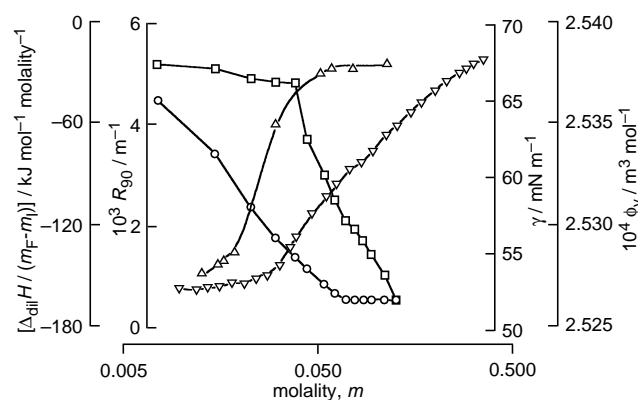
Fig. 3 Surface tension measurements (○), apparent molar volume values (□), Raleigh scattering values at 90° (△) and heats of dilution (▽) of SbQ solutions at 25 °C, as a function of concentration