ASSOCIATION OF POLOXAMER BLOCK COPOLYMERS IN AQUEOUS SOLUTION

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Polyoxyethylene-polyoxypropylene ABA block copolymers (poloxamers or Pluronics) are surface-active emulsifying agents of low toxicity whose solution behaviour appears complex and unresolved (Prasad & others, 1979). It has been suggested that at low concentration conformational changes in the polymer result in monomolecular 'micelles' and that at higher concentrations more conventional multimolecular micelles are formed. Light scattering evidence (McDonald & Wong, 1977) for these events is equivocal. We have now measured the diffusion coefficients of poloxamers in solution using photon correlation spectroscopy (PCS, at 441.6 nm) and from this data have obtained equivalent spherical hydrodynamic radii, r. Some results are presented in Table 1 for poloxamer L64 (molecular weight of hydrophobe 1750; 40% hydrophile; cloud point 60°) along with values of intrinsic viscosity, $[\eta]$ (ml g^{-1}).

Table 1. Equivalent spherical hydrodynamic radii (r) of poloxamer L64 (8% solution)

Temp (°C)	r(nm)	$[\eta]$	Temp (°C)	r(nm)	$[\eta]$	NaCl(M)	r	$[\eta]$
25	9.7	10.3	45	6.4	7.6	0.25	8.8	-
35	6.6	9.1	50	9.5	-	0.5	8.6	-
40	5.9	-	55	15.4	16.0	1.0	6.5	9.1
						1.5	6.2	-

McDonald & Wong (1977) found that L64 formed multimolecular micelles and it is likely that the 9.7 nm observed for the 8% solution of this polymer represents the radius of aggregates. The decrease in size due to increase in temperature up to 40° and addition of salt may be ascribed to desolvation. Solvent exclusion leading to compact micelles has been observed by Tuzar & Kratochvil (1976) in non-aqueous systems of block copolymers. Uptake of hexane in L64 solutions at 35° increased r to 8nm, adding weight to the concept of aggregation in this system. Poloxamer F68 (cloud point > 100°C) behaves differently: r increases with increasing temperature and increasing NaCl concentration. Measurements on other poloxamers leads us to explain the discrepancies in the literature as due to the temperature dependence of the solution properties especially as the temperature approaches the cloud point. With L64 an initial decrease in r is followed by an increase as temperature is elevated; with L42 (cloud point 39°) only the increase in size is seen from measurements in the accessible temperature range. On the other hand, Pluronic F87 (cloud point > 100°) exhibits only the decrease as the region of the cloud point is not accessible. F68 (80% hydrophile) probably does not form multimolecular aggregates.

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