The Energetics of Ion Transport in the Presence of Polymeric Compounds which Alter the Rheological Properties of Water

Certain polymeric compounds such as poly(vinyl methyl ether) (Gantrez) increase the viscosity of water and aqueous solutions and have commercial use as thickening agents. On the other hand, other polymers, such as polyethylene oxide (Polyox), appear to reduce the turbulent friction in water even when added in small concentrations;[1] this phenomenon is sometimes called the Toms phenomenon.[2] Two mechanistic explanations of the Toms phenomenon suggest themselves: (*a*) the long polymeric chains simply alter the small-scale hydrodynamics of the fluid by virtue of their shapes, tending to straighten out the flow lines, and (*b*) the polymers induce profound changes in the structure of liquid water.

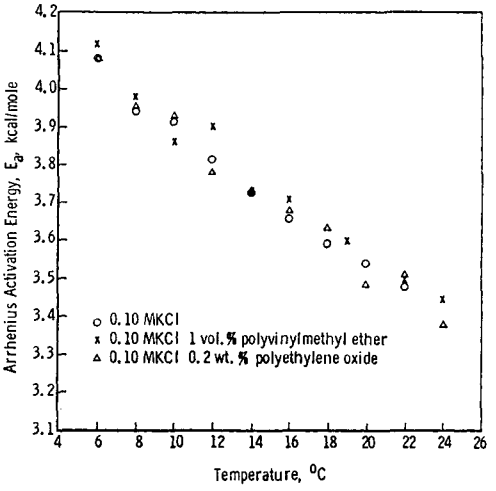

Fig. 1. Temperature dependence of Arrhenius activation energy of electrical conductivity of aqueous 0.10*M* KCl solutions with and without addition of rheological active additives.

We have found that the Arrhenius energy of activation of such transport processes as electrical conductivity and viscous flow is particularly sensitive to structural changes in the solvent,[3] and we have accordingly examined the electrical conductivity of aqueous 0.10*M* KCl solution to which the above polymeric substances had been added. The results (Fig. 1) indicate that, well within the limits set by experimental uncertainties, the temperature dependence of the Arrhenius activation energy of electric conduction is not affected by the addition of rheologically active polymers; from this it follows that either these polymers at the concentrations studied do *not* appreciably alter the structure of water or, if the structure is perturbed, the perturbation is patchy and the ion transport process avoids the patchy areas in much the same way as protonic conduction avoids the structured regions (Frank-Wen cluster) in liquid water.[4]

The addition of 1 vol.-% poly(vinyl methyl ether) lowered the conductance of the aqueous 0.10*M* KCl solution by about 2% at all temperatures studied, and the addition of 0.2 wt.-% polyethylene oxide lowered it by about 0.2%.

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References

1. G. E. Gadd, *Nature*, **212**, 874 (1966).
2. B. A. Toms, *Proc. 1st Intern. Congr. Rheol*, **2**, 130 (1948).
3. R. A. Horne, R. A. Courant, and D. S. Johnson, *Electrochim. Acta*, **11**, 987 (1966).
4. R. A. Horne and R. A. Courant, *J. Phys. Chem.*, **69**, 2221 (1965).

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