Spectroscopic and Viscosimetric Studies of Aqueous Polyethylene Oxide Solutions

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As part of a general investigation into the properties of aqueous solutions containing polyethylene oxide (PEO, Polyox Resin, *ex* Union Carbide, $\overline{M}\text{v} = 2{\cdot}98 \times 10^5$), we have examined the viscosities of the three-component system, water + alcohol + PEO. Our results may be compared with those for other polymer + water + alcohol mixtures[1,2] and linked to a model for the aqueous PEO solution.

The properties of the systems PEO + water, and water + t-butyl alcohol show the following trends:—

(*a*) Addition of PEO to water at 25° results in a very marked increase in viscosity, *e.g.* 0·133% by weight PEO increases viscosity by 47·6%. Indeed, a solution containing >3% by weight PEO is difficult to pour. A similar, though much less marked increase in viscosity occurs when t-butyl alcohol is added to water over the range $0 < x_2 \leqslant 0{\cdot}1$, where x_2 is the mole fraction of alcohol; *e.g.* 7·76% by weight ($x_2 = 0{\cdot}02$) of t-butyl alcohol increases the viscosity by 48·2%.

(*b*) Addition of 0—1% by weight of PEO to water containing potassium iodide (2×10^{-4} M) results in a slight shift of < 30 cm.$^{-1}$ to higher energies of the charge-transfer-to-solvent (c.t.t.s.) absorption band of iodide ion. When compared with concentrations of t-butyl alcohol required to give a similar increase in viscosity in water, this is a much smaller shift in the c.t.t.s. band.[3-5]

(*c*) The relative intensities of the absorption bands at 1·556 and 1·416 μ (assigned respectively to "bonded" and "free" O–H)[6] in the spectra of HOD (6 M) in D_2O were not comparably affected by added PEO. Also D_2O was much less sensitive to addition of PEO than to t-butyl alcohol ($0 < x_2 < 0{\cdot}03$ or $0 <$ wt % $< 11{\cdot}3$) when compared to changes in viscosity.[3,7]

(*d*) Addition of PEO has little effect on the ^1H n.m.r. spectra of water, and the spectra due to the protons of the polymer were unaffected by increase in PEO concentration. This confirms observations reported by Kang-Jen Liu.[8] In contrast, addition of t-butyl alcohol shifts the water proton resonance initially to lower fields.[9]

Recent summaries of the thermodynamic, spectroscopic and ultrasonic absorption properties of monohydric alcohol–water mixtures[10,11] have shown that in dilute alcohol solution, the structure resembles a liquid clathrate hydrate. However, the results for the PEO system indicate neither a comparable structure enhancement nor the general breakdown of water structure found when methyl cyanide is added.[12]

The effect of added alcohol and PEO was further probed by measuring the intrinsic viscosity, $[\eta]$, and Huggins constant, k', for the three-component system PEO–water–alcohol (Figure). When t-butyl alcohol or n-propyl alcohol was added, $[\eta]$ first increased and then decreased to a minimum at $x_2 = 0{\cdot}0375$ and 0·09 respectively. The Huggins constant shows a reversed trend in both systems. A similar trend in $[\eta]$ and k' occurs for aqueous solutions of polyvinyl alcohol containing n-propyl alcohol, with a fall in $[\eta]$ where k' shows an increase at $x_2 = 0{\cdot}09$.[1] Methyl alcohol added to aqueous solutions (at pH 3·0) of polymethacrylic acid produces a minimum in $[\eta]$ near $x_2 = 0{\cdot}15$.[2]

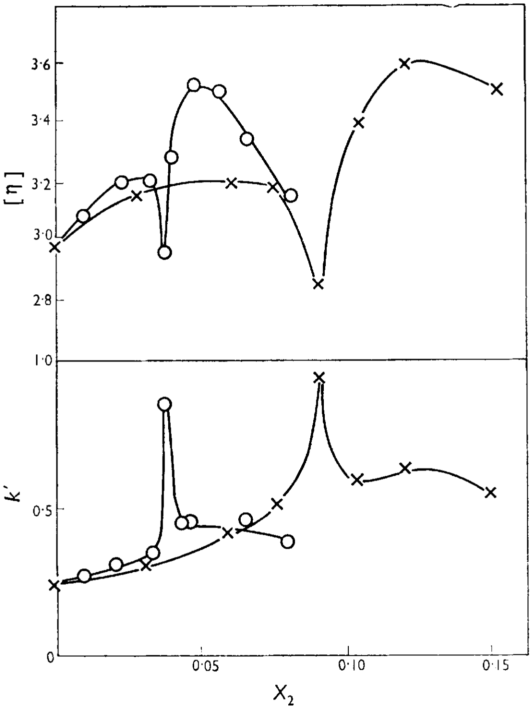

FIGURE. *Variation of intrinsic viscosity and Huggins constant with mole fraction of alcohol.* × ; *water–n-propyl alcohol.* ○; *water–t-butyl alcohol*

Aqueous solutions of PEO exhibit a lower critical solution temperature,[13] and in this solvent the polymer has the ***gauche*** configuration.[14] In this form, molecular models show that alternate oxygen atoms are spaced approximately 4·8 Å apart. Warner has shown[15] that this repeating distance is extremely important in the structures of biochemically important macromolecules, since this is the next nearest neighbour distance between oxygen atoms in the ice ***Ih*** structure. Therefore, in aqueous solutions, PEO may be linked substitutionally into the water lattice. However, no such comparisons with the structure of water can be drawn in the cases of polymethylene, polytrimethylene, and polytetramethylene oxides of high molecular weight, all insoluble in water.

In the three-component systems PEO + alcohol + water, the alcohol initially enhances water–water interactions, but it is suggested that water–polymer interactions are diminished.[16] A competition between alcohol and polymer for accommodation within the clathrate structures is envisaged. In alcohol + water systems, clathrate sites are most fully occupied by alcohols when the partial molar volumes of alcohol in water are at a minimum ($x_2 = 0{\cdot}15$ for methyl alcohol, 0·09 for n-propyl alcohol, and 0·0375 for t-butyl alcohol). At these values of x_2, $[\eta]$ for polymer–alcohol–water systems is found to be a minimum.

At higher concentrations of alcohols, the simple hydrate clathrate structures break up and, following the development of an excess ultrasonic absorption, a number of equilibria between different hydrate clathrates have been envisaged.[11] In these systems, past the minimum in $[\eta]$, the polymer chain is more flexible, and the subsequent increase in $[\eta]$ following the addition of more alcohol is expected from the rheology of the system.[16]

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[1] D. W. Levi, P. C. Scherer, W. L. Hunter, and K. Washimi, *J. Appl. Polymer. Sci.*, 1959, **1**, 127.

[2] V. N. Tsvetkov, and E. N. Zakharova, *Vestnik. Leningrad Univ.*, 1967, **22** (10), 41.

[3] M. J. Blandamer, D. E. Clarke, T. A. Claxton, M. F. Fox, N. J. Hidden, J. Oakes, M. C. R. Symons, G. S. P. Verma, and M. J. Wootten, *Chem. Comm.*, 1967, 273.

[4] M. J. Blandamer, M. F. Fox, and M. C. R. Symons, *Nature*, 1967, **214**, 163.

[5] J. Kenttämaan, E. Tommila, and M. Martti, *Ann. Acad. Sci. Fennicae*, 1959, **4**, A2, 92.

[6] I. Klotz and J. D. Worley, *J. Chem. Phys.*, 1966, **45**, 2868.

[7] M. J. Blandamer, *Chem. Comm.*, in the press.

[8] Kang-Jen Liu, *J. Chem. Phys.*, in the press.

[9] D. N. Glew, H. D. Mak, and N. S. Raith, *Chem. Comm.*, 1968, 264.

[10] F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, **20**, 1.

[11] M. J. Blandamer and M. C. R. Symons, Symposium on Equilibria and Reaction Kinetics in Hydrogen-bonded Systems, Newcastle 1968, in the press.

[12] D. A. Armitage, M. J. Blandamer, M. J. Foster, N. J. Hidden, K. W. Morcom, M. C. R. Symons, and M. J. Wootten, *Trans. Faraday Soc.*, 1968, **64**, 1193.

[13] F. E. Bailey and R. W. Callard, *J. Appl. Polymer Sci.*, 1959, **1**, 56.

[14] T. M. Connor and K. A. McLaughlan, *J. Phys. Chem.*, 1966, **69**, 1888.

[15] D. J. Warner, *Ann. New York Acad. Sci.*, 1965, **125**, 605.

[16] M. J. Blandamer, M. F. Fox, E. Powell, and J. W. Stafford, to be published.