Determination of Cohesive Energy Density of Polyacrylamide by Swelling Measurements

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SYNOPSIS

Polyacrylamide was prepared by a suitable redox system in oxygen atmosphere and its cohesive energy density (ced) was determined from swelling measurements. The molecular weight of polymer was also determined by viscosity measurements.

INTRODUCTION

The cohesive energy density (ced) of a polymer is the closest approximation of its solubility prediction provided that some specific interactions between the polymer and solvent are not present. The value of cohesive energy density also depends on the chemical structure and different constituent groups present in the polymer. Experimental determination of ced value for a number of polymers have been done by measuring the swelling coefficients in series of solvents.[1] Some other methods of ced determination involves the use of viscosity measurements.[2] The present paper deals with the determination of ced for polyacrylamide, which provides useful information about its solubility in the system, where it is to be used as a flocculating agent.

EXPERIMENTAL

Acrylamide (BDH) was recrystallized twice in methanol and dried under vacuum for a week. Polymerization was carried out in aqueous medium using a redox couple persulphate/ascorbic acid, catalyzed by Ag^+ ions at $35 \pm 0.2°C$ in oxygen atmosphere.[3] After a definite time interval, when the conversion was below 10%, the polymer was precipitated in methanol and dried after careful separation.

The polyacrylamide so obtained was supposed to be slightly crosslinked due to inter- and intramolecular immidization taking place during the polymerization.

For swelling measurements, polymers were cut into rectangular size having a weight of 0.1–0.2 g. They were then immersed in 25 mL of various organic solvents taken in well-stoppered boiling test tubes. The polymers were then taken out at regular interval of time, surface-dried by putting the piece between filter papers and pressing it, and weighed. The method was repeated till an equilibrium swelling was obtained which was indicated by constant weights observed. All the measurements were done at $20 \pm 0.2°C$. The swelling coefficient was calculated using the following relationship:

$$Q = \frac{m - m_0}{m_0} \times \frac{1}{d}$$

where m = weight of swollen polymer, m_0 = weight of polymer taken initially, and d = density of the solvent taken. The values of swelling coefficients Q for polymer in different solvents are given in Table I. Solubility parameters of different solvents were noted from the literature.[4] For molecular weight determination the samples of polyacrylamide were prepared and purified by two reprecipitations from methanol. The samples were then dried at 40°C. The viscosity of very dilute aqueous solution of the polymer (<0.4%) was determined at 25°C temperature. Finally, the molecular weight was determined

Table I   Results of Swelling Measurements of Polyacrylamide[a]

Solvent	δ_s	Q
Methanol	14.5	0.0025
Acetone	9.71	0.0506
Benzene	9.15	0.3290
1-Butanol	10.5	0.4500
Chloroform	9.24	0.0222
n-Hexane	7.24	0.3450
DMF	12.1	0.0170
CCl$_4$	8.58	0.0690

[a] δ = solubility parameter $(cal/mL)^{1/2}$. Q = swelling coefficient (mL/g).

by using the following relationship given by Swen et al.[5]:

$$[\eta] = 6.8 \times 10^{-4} M^{0.66}$$

where $[\eta]$ is the intrinsic viscosity of the polymer solution and M denotes the molecular weight of the sample.

RESULTS AND DISCUSSION

According to the treatment of Hilderbrand and Scott[6] and Scatchard[7] the heat of mixing per unit volume, when only dispersion forces are involved is

$$\Delta H = \phi_s \phi_p (\delta_s - \delta_p)^2 \qquad (1)$$

where ϕ_s and ϕ_p are the volume fractions of solvent and polymer, and δ_s and δ_p are solubility parameters given by

$$\delta = (\Delta E / V)^{1/2}$$

$\Delta E / V$, the energy of vaporization per unit volume, is also termed the cohesive energy density. From eq. (1), Gee[1] concluded that the maximum swelling of polymer will occur when $\delta_p \simeq \delta_s$. Hence a plot between the swelling coefficient Q and δ_s values of the solvent gives a Gaussian curve whose maxima will correspond to δ_p as shown in Figure 1. It was also shown that

$$Q = Q_{max} e - (\delta_s - \delta_p)^2 \phi_s$$

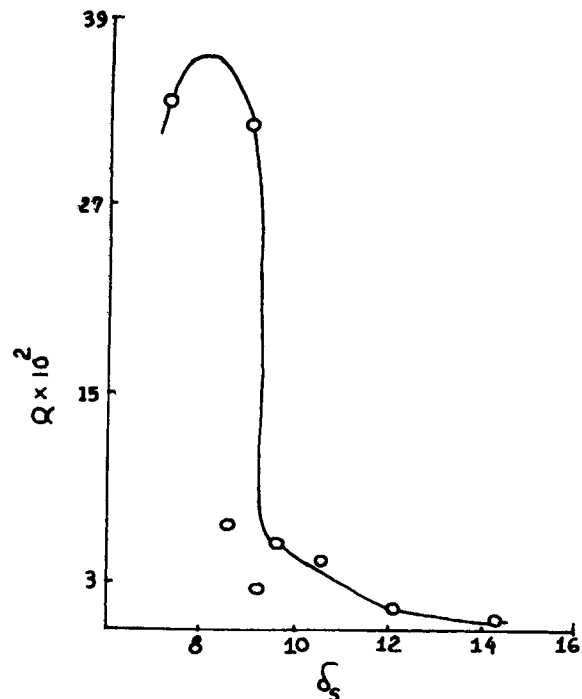Thus, by plotting $[(1/\phi_s) \ln(Q_{max}/Q)]^{1/2}$ versus δ_s,

Figure 1   A plot between swelling coefficient Q and δ_s.

a straight line is obtained whose intersection point with the abscissa will give δ_p. The values for Q versus δ_s have been plotted and shown in Figure 1. From the plot Q_{max} was obtained and $[(1/\phi_s) \times \ln Q_{max}/Q]^{1/2}$ was calculated and plotted against δ_s as shown in Figure 2. It is clear that the value of
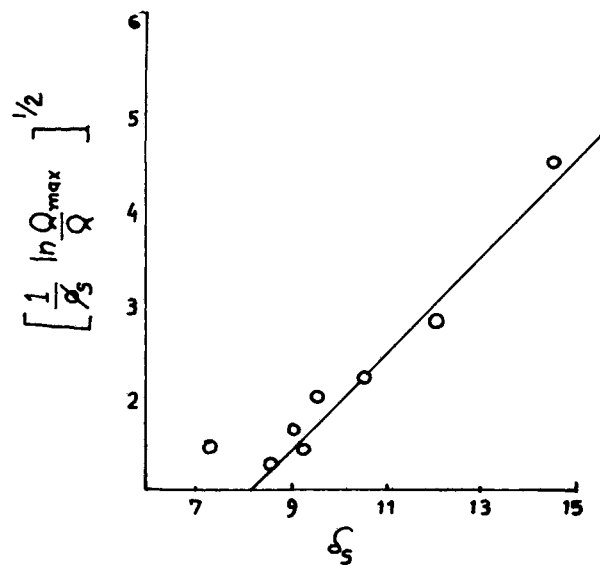

Figure 2   A plot between $[(1/\phi_s)\ln(Q_{Max}/Q)]^{1/2}$ and δ_s.

δ_p obtained from Figures 1 and 2 are quite the same (8.0).

The molecular weight of resulting polyacrylamide was found to be nearly 30,000 from viscosity measurements.

REFERENCES

1. G. Gee, G. Allen, and G. Wilson, *Polymer*, **1**, 456 (1960).
2. G. C. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1931, 1742 (1958).
3. U. D. N. Bajpai, Alka Jain, and A. K. Bajpai, *Revue Roumaine de Chimie*, **33**(6), 629 (1988).
4. D. J. Brandrup and E. H. Immergutgut, *Polym. Handbook*, Wiley, New York, 1975.
5. T. J. Suen, Y. Jen, and J. Lockwood, *J. Polym. Sci.*, **31**, 481 (1958).
6. J. Hilderbrand and R. Scott, *The Solubility of Non-Electrolytes*, 3rd ed. Van Nostrand Reinhold, New York, 1949.
7. G. Scatchard, *Chem. Rev.*, **8**, 321 (1931).