versus T, determine $d\gamma / dT$, and calculate E^S, the excess surface energy. Plot γ versus ln C, determine $d\gamma / d \ln C$ and calculate Γ_2, the excess surface concentration. From Γ_2, calculate the cross-sectional area of the surfactant molecule.

Calculate the error in measurements with the capillary rise and bubble pressure methods. Compare those results with literature values.

REFERENCES

1. Adamson, A. W., *Physical Chemistry of Surfaces*, 2nd ed., Wiley-Interscience, New York, 1967.
2. Adamson, A. W., *A Textbook of Physical Chemistry*, Academic Press, New York, 1973.
3. Alberty, R. A., *Physical Chemistry*, 7th ed., Wiley, New York, 1987.
4. Alexander, A. E., and J. B. Hayter, "Determination of Surface and Interfacial Tension," in A. Weissberger and B. W. Rossiter, eds., *Techniques of Chemistry*, vol. I, *Physical Methods of Chemistry*, pt. V, Wiley-Interscience, New York, 1971.
5. Butler, J. A. V., and A. Wighman, "Adsorption at the Surface of Solutions," *J. Chem. Soc.* 1932:2089.
6. Försterling, H.-D., and H. Kuhn, *Praxis der Physikalischen Chemie*, VCH, Deerfield Beach, Florida, 1985.
7. Harkins, W. D., and R. W. Wampler, "Activity Coefficients and the Adsorption of Organic Solvents," *J. Am. Chem. Soc.* 53:850, 1931.

Experiment 14

Viscosity of Solutions of Macromolecules

When a liquid flows, whether through a tube or as the result of pourin from a vessel, layers of liquid slide over each other. The force f require is directly proportional to the area A and velocity v of the layers, an inversely proportional to the distance d between them, as shown in Figur 14–1. The proportionality constant η is the coefficient of viscosity, o more commonly, the viscosity:

$$f = \eta \frac{Av}{d} \qquad \text{(14–}$$

Units of Viscosity

The traditional unit of viscosity is the **poise,** originally a cgs unit that ha the symbol P. The dimensions based on Equation 14–1 are the g cm sec^{-1}:

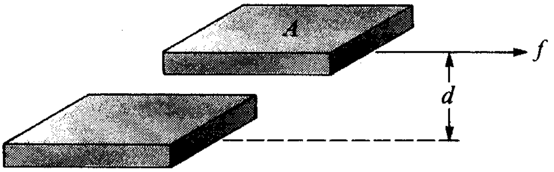

Figure 14–1 Origin of viscosity.

$$\frac{fd}{Av} = \frac{\text{g cm sec}^{-2}\text{ cm}}{\text{cm}^2\text{ cm sec}^{-1}} = \text{g cm}^{-1}\text{ sec}^{-1} = 1\text{ poise} = 1\text{ P} \qquad \textbf{(14–2)}$$

In SI units the poise has no special symbol and has units of kg m^{-1} s^{-1}. Thus, 1 P = 0.1 kg m^{-1} s^{-1}. Viscosities of gases and liquids are often reported in μP and cP, respectively. For example, at 25°C the viscosity of N_2 is 178 μP and the viscosity of water is 0.8937 cP.

Measurement

The rate of flow R (cm^3/sec) of a liquid through a cylindrical tube of radius r and length ℓ under a pressure head P is given by the Pousille equation:

$$R = \frac{V}{t} = \frac{\pi P r^4}{8\eta\ell} \qquad \textbf{(14–3)}$$

Measurement of P, r, t, V, and ℓ permits the calculation of the viscosity:

$$\eta = \frac{\pi P r^4 t}{8V\ell} \qquad \textbf{(14–4)}$$

It is easier to measure the viscosity of a liquid by comparing it with another liquid of known viscosity (presumably already measured with Eq. 14–4). Since $P = \rho g h$,

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \qquad \textbf{(14–5)}$$

The Ostwald viscometer (Fig. 14–2) is a simple device for comparing the flow times of two liquids of known density. If the viscosity of one liquid is known, the other can be calculated. After the reservoir is filled with a liquid, it is pulled by suction above the upper mark. The time required for the liquid to fall from mark 1 to mark 2 is recorded. Then the time required for the same volume of a liquid of unknown viscosity to flow under identical conditions is recorded, and the viscosity is calculated with Equation 14–5.

Viscosity of Solutions of High Polymers

While the viscosity of water and molasses arises from hydrogen bonding between flowing liquid layers, the viscosity of solutions of macromolecules

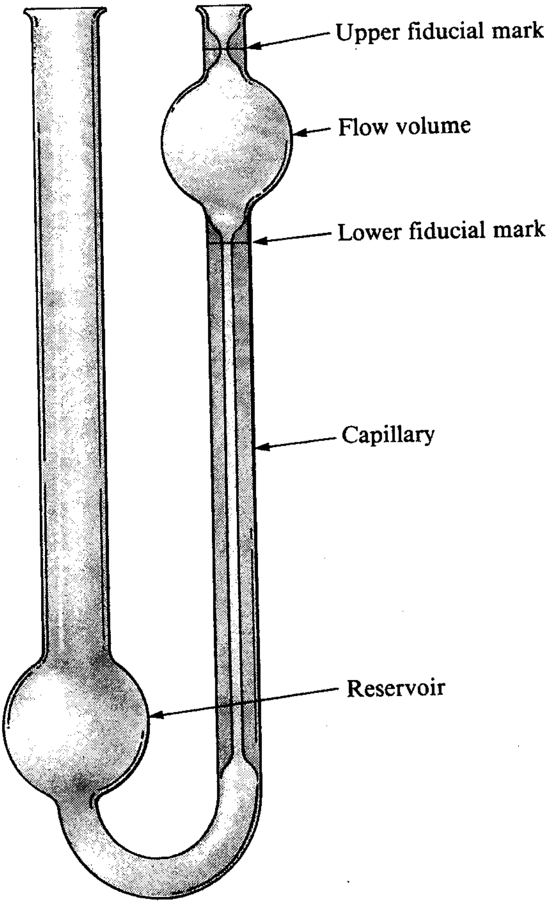

Figure 14–2 Ostwald viscometer.

arises from the entanglement of large molecules flowing along with the solvent. One would expect this effect to depend on the size, shape, and molecular weight of the macromolecules.

Indeed, the problem attracted the attention of Einstein, who showed that for large spherical molecules,

$$\eta_{\text{sp}} = 2.5(V/V_0) = 2.5\phi \tag{14-6}$$

where ϕ is the fractional volume occupied by the macromolecule and η_{sp}, the specific viscosity, is defined as

$$\eta_{\text{sp}} = \frac{\eta - \eta_0}{\eta_0} \tag{14-7}$$

where η and η_0 are the viscosities of the solution and solvent, respectively. Note that the specific viscosity is dimensionless.

Intrinsic Viscosity. The properties of individual macromolecules separated from their interaction with each other are found by extrapolating to infinite dilution:

$$[\eta] = \lim_{c\to 0} \frac{\eta_{\mathrm{sp}}}{c} = \lim_{c\to 0} \frac{1}{c} \ln \frac{\eta}{\eta_0} \tag{14-8}$$

The quantity $[\eta]$, the intrinsic viscosity, is important because it is most directly related to properties such as molecular weight and shape. Its dimensions are that of reciprocal concentration, usually expressed as 1/(g/100 ml). In dilute solution, both η_{sp}/c and $(1/c)\ln(\eta/\eta_0)$ are linearly dependent upon concentration c and can be extrapolated to infinite dilution to determine $[\eta]$.

Molecular Weight. It is found empirically that the intrinsic viscosity of a solution depends on the molecular weight of the solute:

$$[\eta] = KM^a \tag{14-9}$$

where a falls between 1/2 and 2 and is a parameter that is related to the shape of the molecule. When the solute molecule is nearly spherical, a is about 0.5, but when the solute molecule is long, extended, or rod shaped, its value may reach 1.7 to 1.8.

Both K and a must be determined from viscosity measurements with solutions of macromolecules of known molecular weight, determined by other methods, such as osmotic pressure measurements. Some typical values of K and a are listed in Table 14–1.

Because chain termination in polymerization reactions occurs randomly, polymers have a distribution of molecular masses about an average value. Experimental measurement of viscosity or colligative properties like osmotic pressure leads to M_{n}, the **number average molecular weight.** If the polymer sample is considered to be made up of a large number of fractions consisting of n_1 moles of mass M_1, n_2 moles of mass M_2, and so on, the number average molecular weight is defined as

$$M_{\mathrm{n}} = \frac{n_1M_1 + n_2M_2 + \cdots}{n_1 + n_2 + \cdots} = \frac{\sum_i n_iM_i}{\sum_i n_i}$$

Colligative properties such as osmotic pressure depend on the number of particles in solution but not on the individual mass. Light scattering of polymer solutions, however, depends on the mass and number of particles and leads to the **mass average molecular weight** M_{w} (Matthews, 1984) where

TABLE 14–1

Parameters for Molecular Weight Determination (units of $[\eta]$ and K are 1/(gm/100 ml)) $[\eta] = KM^a$

Macromolecule	Solvent	$K \times 10^4$	a
Cellulose acetate	Acetone	1.49	0.82
Methyl methacrylate	Benzene	0.94	0.76
Polystyrene	Toluene	3.7	0.62
Polyvinyl alcohol	Water	2.0	0.76

$$M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

If all the molecules have the same molecular mass, the polymer is said to be monodisperse and $M_w/M_n = 1.0$. Synthetic polymers with M_w/M_n as low as 1.04 have been prepared. Vinyl polymers have M_w/M_n ratios from 2 to about 10 and low-density polyethylene has M_w/M_n as high as 20 (Rudin, 1969).

Apparatus

This experiment requires an Ostwald viscometer with a water flow time of about 100 sec; a 25°C thermostat; 10- and 25-ml pipets; a rubber bulb and tube; two or more 50-ml volumetric flasks; cleaning solution; polystyrene (the peanut-sized pieces used as protective packing material are satisfactory); and 300 ml toluene.

SAFETY CONSIDERATIONS

None.

EXPERIMENTAL PROCEDURE

Dissolve about 1 g polystyrene in toluene in a 50-ml volumetric flask. While the polymer is dissolving, clean the viscometer with cleaning solution. If it is not available, prepare the cleaning solution by dissolving 12 g sodium dichromate ($Na_2Cr_2O_7$) in 12–15 ml hot water. Cool. Cautiously, slowly, and with stirring, add 225 ml concentrated sulfuric acid. Store in a 250-ml glass-stoppered bottle. Use carefully on glassware that has previously been cleaned with detergent and rinsed with water.

Calibration. After cleaning the viscometer with cleaning solution, rinse it with distilled water; then add a 10-ml aliquot of water and let it come to thermal equilibrium with the thermostat. Both fiducial marks should be below the water level of the thermostat. With a rubber bulb, pull the water in the viscometer above the upper fiducial mark and measure the time it requires to flow from the upper to the lower mark. Repeat to determine the uncertainty in measuring time. The flow time with water, along with its density at 25°C (0.99777 g/cm^3) and viscosity (0.8937 cP) are used with Equation 14–5 to determine the viscosities of toluene η_0 and the polystyrene solutions η.

Drain the water from the viscometer; rinse it first with a few milliliters of acetone, then with toluene. Add a 10-ml aliquot of toluene, and after the viscometer and toluene are at thermal equilibrium, measure the flow time as before.

Measurements. Take a 25-ml aliquot of the polystyrene solution and dilute to 50 ml with toluene in a volumetric flask. Again measure the flow time. Dilute repeatedly until the final solution is 1/8 the original solution concentration; measure the flow time of each solution.

Results and Calculations

The density of toluene at 25°C is 0.866 g/cm^3. The density of the solutions may be assumed to be that of toluene. Tabulate c, η_0, η_{sp}, η_{sp}/c, and $(1/c) \ln (\eta/\eta_0)$. On a single sheet of graph paper, plot both η_{sp}/c and $(1/c) \ln (\eta/\eta_0)$ versus c. Extrapolate to $c = 0$ to obtain $[\eta]$. If your extrapolation is linear, you may run a least-squares analysis of the data. Calculate the molecular weight of your polystyrene sample with Equation 14–9 and the parameters listed in Table 14–1. The parameter K in Table 14–1 requires the concentration c to be expressed in g/100 ml.

REFERENCES

1. Allcock, H. R., and F. W. Lampe, *Contemporary Polymer Chemistry,* Prentice-Hall, Englewood Cliffs, New Jersey, 1981.
2. Bradbury, J. H., "Polymerization Kinetics and Viscometric Characterization of Polystyrene," *J. Chem. Educ.* 40:465–468, 1963.
3. Carraher, Jr., C. E., "Generation of Poly(vinyl alcohol) and Arrangement of Structural Units," *J. Chem. Educ.* 55:473–475, 1978.
4. Flory, P. J., *Principles of Polymer Chemistry,* Cornell University Press, Ithaca, New York, 1953.
5. Flory, P. J., and F. S. Leutner, "Occurrence of Head-to-Head Arrangements of Structural Units in Polyvinyl Alcohol," *J. Poly. Sci.* 3:880, 1948.
6. Goldberg, A. I., W. P. Hohenstein, and H. Mark, "Intrinsic Viscosity–Molecular Weight Relationships for Polystyrene," *J. Poly. Sci.* 2:502, 1947.
7. Johnson, J. F., J. R. Martin, and R. S. Porter, in A. Weissberger and B. W. Rossiter, eds., *Techniques of Chemistry,* vol. I, *Physical Methods of Chemistry,* pt. VI, chap. 2, Wiley-Interscience, New York, 1977.
8. Mathias, L. J., "Evaluation of Viscosity–Molecular Weight Relationship," *J. Chem. Educ.* 60:422, 1983.
9. Matthews, G. P., "Light Scattering by Polymers," *J. Chem. Educ.* 61:552–554, 1984.
10. Rabek, J. F., *Experimental Methods in Polymer Chemistry,* Wiley-Interscience, Chichester, England, 1980.
11. Rudin, A., "Molecular Weight Distributions of Polymers," *J. Chem. Educ.* 46:595, 1969.
12. Swindells, J. F., R. Ullman, and H. Mark, in A. Weissberger, ed., *Technique of Organic Chemistry,* vol. 1, pt. 1, chap. XII, Interscience, New York, 1959.
13. Tanford, C., *Physical Chemistry of Macromolecules,* Wiley, New York, 1961.