Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Viscodensitometer Studies on Gelatine and the Sorption of Gelatine on Glass

G. R. Dobson[a b]; M. Gordon[a c]
[a] CHEMISTRY DEPARTMENT, IMPERIAL COLLEGE, LONDON, ENGLAND [b] B. P. Research Centre, Sunbury-on-Thames, England [c] Department of Pure and Applied Chemistry, University of Strathclyde, Glascow, Scotland

To cite this Article Dobson, G. R. and Gordon, M.(1967) 'Viscodensitometer Studies on Gelatine and the Sorption of Gelatine on Glass', Journal of Macromolecular Science, Part A, 1: 3, 517 — 538

To link to this Article: DOI: 10.1080/10601326708053987

URL: http://dx.doi.org/10.1080/10601326708053987

J. MACROMOL. SCI. (CHEM.), A1(3), 517–538 (1967)

Viscodensitometer Studies on Gelatine and the Sorption of Gelatine on Glass

---

G. R. DOBSON* and M. GORDON†
CHEMISTRY DEPARTMENT,
IMPERIAL COLLEGE,
LONDON, ENGLAND

Summary

The sorption of polymers on glass surfaces, and the effects produced thereby on measurements of intrinsic viscosity, hitherto studied in capillary viscometers, is here analyzed by the sensitive viscodensitometric technique, based on the principle of the moving-sphere viscometer. By working with several spheres of *equal* size, the errors in viscometry due to sorption can be practically eliminated. The use of two spheres differing in radius by a factor of 10 allows the direct weighing of the polymer sorbed per unit geometric surface. In this way the sorption isotherm of an alkali-bone gelatin on Pyrex glass from 0.17 M KCl solution was found to rise to a plateau of 3 mg/m^2 at a gelatin concentration of 0.1 g/dl. The plateau extends from this lower limit to 0.5 g/dl. The partial specific volume of gelatin, directly obtained in the viscodensitometer along with the viscosity, was found to be 0.702 cc/g in water and 0.725 cc/g in 0.95 M KCl.

In 1960 Gordon et al. (9) introduced a new type of viscometer, based on the moving-sphere principle, which is capable of measuring viscosities with an accuracy of 0.2%, densities with an absolute accuracy of 10^{-4} g/ml, and density differences with an accuracy of 10^{-6} g/ml, using 4-cc samples of liquid. The instrument essentially consists of small hollow Pyrex glass floats moving under gravity in a precision-bore Pyrex tube. To evaluate both viscosity and density, at least two floats are necessary. The instrument of Gordon et al. suffered from some difficulty in so manipulating the

---

[*] Present address: B. P. Research Centre, Sunbury-on-Thames, England.

[†] Present address; Department of Pure and Applied Chemistry, University of Strathclyde, Glascow, Scotland.

floats that the desired one could be timed moving along the axis of the tube while the others were stationary. In fact, because of this difficulty only two floats could reasonably be included in the instrument.

These difficulties have now been overcome by the development of a technique for making floats with magnetizable cores. With magnetic control the sorting, positioning, and centering of floats in the tube is simple. The tube may be kept sealed during measurements, thus minimizing the risk of dirt entering the solution. Furthermore, any number of floats can be included in one instrument, thus making measurements possible over a wider range of densities (about 0.0035 gm/cc for the seven floats used in one instrument described below).

Use of capillary viscometers and very dilute solutions led many workers (*1,20–22,29,32–34,* and others) to conclude that there are anomalies in the measured dilute-solution viscosities of polymers. In all cases an upswing of the $\eta_{sp/c}$ vs. c curve was observed in very dilute solutions (ca. < 0.001 g/cc). The origin of the anomalies has been a subject of considerable discussion; for example, Kawai and Saito (*12*) proposed that the anomalies are due to a "critical" solution effect in dilute solution on the basis that polymer coils will expand with dilution when they lose contact with each other.

In his paper of 1955 and subsequently in other papers, Öhrn (*20–22*) proposed a convincing explanation for the observed anomalies based on purely experimental consideration, viz., that the diameter of the capillary of the viscometer diminishes in the presence of an adsorbed layer of polymer. If the apparent relative viscosity is η_{rel}^*, the capillary radius a and the thickness of the layer δa, then the true relative viscosity is

$$\eta_{rel} = \eta_{rel}^* \left(\frac{a - \delta a}{a}\right)^4 \simeq \eta_{rel}^* \left(1 - 4\,\frac{\delta a}{a}\right) \qquad (1)$$

which leads to

$$\eta_{sp}/c \simeq \eta_{sp}^*/c - 4\delta a/ca \qquad (2)$$

In a high-precision study of viscosity in capillary viscometers with different diameters, Öhrn (*20*) was able to explain all the observed anomalies in terms of his adsorption hypothesis and produced adsorption isotherms which have the same general shape as those measured by more direct methods. His results indicated a film thickness of 1500 A for polystyrene ($M = 800{,}000$) in toluene. The anomalous upsweeps occur at concentrations less than 0.001 g/cc, which is less than concentrations normally used in the determination of intrinsic viscosity. Nevertheless, a conventional linear plot of η_{sp}/c vs. c is no criterion for the absence of an adsorption effect, because if Öhrn's analysis is correct, such plots would be displaced by several per cent toward higher values of η_{sp}/c. In these circumstances quite serious errors will be present in the determination of intrinsic viscosity by capillary viscometers.

The object of the present work is to measure the amount of a polymer adsorbed on a glass surface and to study its effect in viscometry. The work also serves to illustrate the use of the viscodensitometer in the study of dilute polymer solutions.

THEORY OF MEASUREMENT WITH FLOATS

The limiting speed of a sphere of radius a, and apparent (over-all) density σ, moving through a viscous fluid of viscosity η and density ρ along the axis of a tube of radius R is given by the Stokes-Faxen equation,

$$v = 2a^2g(\sigma - \rho)F/9\eta \tag{3}$$

where F (Faxen's constant) is

$$F = 1 - 2.104a/R + 2.09(a/R)^3 \tag{4}$$

Equations (3) and (4) are approximations applying only to the motion of a perfect sphere moving with a low Reynolds number ($\mathrm{Re} = va\rho/\eta$). However, if we write Eq. (3) as

$$v = K(\sigma - \rho)/\eta \tag{5}$$

where K is a constant, we may describe the motion of a "float," which is only approximately spherical, at appreciable Reynolds numbers. We have tested the validity of Eq. (5) up to a Reynolds number of ±0.3, a good linear fit being obtained; the standard deviation in ρ was 0.0000013 g/cc over a total range of 0.0003. (By convention, a negative Reynolds number here signifies a rising sphere.) The equivalent radius of a float may be obtained by comparing Eqs. (3), (4), and (5). In this work we have used a tube of 6 mm diameter and floats of mean diameter 1.2 mm, the largest being 1.5 mm and the smallest 0.9 mm.

For two floats, use of Eq. (5) leads to

$$\eta = K_1 t_1 \beta \tag{6}$$

and

$$\rho = \sigma_1 - \beta \tag{7}$$

where

$$\beta = (\sigma_1 - \sigma_2)/[1 - (K_1 t_1)/(K_2 t_2)] \tag{8}$$

t_1 and t_2 being reciprocal velocities, i.e., the times taken by floats 1 and 2 respectively, to traverse 1 cm.

The shear rate caused by a sphere of radius a falling through a liquid at a speed v [Lamb (*18*)] has a maximum value of $1.5v/a$ on the surface of the sphere. The radius of a typical float is 0.06 cm, and the maximum speed used is about 0.05 cm/sec, and so the maximum shear rate is less than 1.5 sec^{-1}. Fox et al. (*7*) studied in capillary viscometers the viscosities of polymer solutions at shear rates ranging between 150 and 5000 sec^{-1}. As a result of this investigation they introduced the procedure of extrapolating measured intrinsic viscosities to zero shear rate, to allow for the change of molecular configuration of the polymer in a shear gradient. Such extrapolation clearly is unnecessary in the viscodensitometer.

An adsorbed film will affect the behavior of a float in two ways; its bouyancy will effect the density and its thickness will change the K value. The new density of a float of original density σ and radius a, in the presence of a mass m, per unit geometric surface area, of a polymer film of density ψ is

$$\sigma^* = \frac{(4/3)\pi a^3 \sigma + 4\pi a^2 m}{(4/3)\pi a^3 + 4\pi a^2 m/\psi} \tag{9}$$

$$\sigma^* \simeq \sigma + \frac{3m}{a}\left(1 - \frac{\sigma}{\psi}\right) \tag{10}$$

Since ψ is a measure of the bouyancy of the film, it is best represented by the reciprocal of the partial specific volume ($\tilde{v}$) of the polymer in solution, which is a measure of the contribution of the polymer to the density. Thus Eq. (10) becomes

$$\sigma^* = \sigma + (3m/a)(1 - \tilde{v}\sigma) \tag{11}$$

For two floats, we have

$$(\sigma_1^* - \sigma_2^*) = (\sigma_1 - \sigma_2)(1 + \phi') \tag{12}$$

where

$$\phi' = 3m(1 - \bar{\sigma}\bar{v})(1/a_1 - 1/a_2)/(\sigma_1 - \sigma_2) \tag{13}$$

If two floats have the same radius, the effect of the adsorbed film on the density difference is zero, whereas with floats of widely differing radii there is a marked effect, which will be used later to determine *m*.

The effect of the film on the *K* value of the float is given by

$$K^* = K\left(\frac{a + \delta a}{a}\right)^2 \simeq K(1 + 2\delta a/a) \equiv K(1 + \phi'')$$

where $\bar{a}$ is the mean radius of the float and δa is the effective hydrodynamic thickness of the adsorbed layer. Hence

$$\eta_{sp}/c = \eta_{sp}^*/c + (\phi' + \phi'')/c \tag{15}$$

The term in ϕ'' is, of course, subject to the same uncertainty as Öhrn's correction for capillary viscometers. However, in capillary instruments the corresponding term takes the form $4\delta a'/a'$, and the capillary diameter a' is usually 0.4 mm or less, compared to $a = 1.2$ mm for the floats. Accordingly, the effect of the thickness of the adsorbed layer on the floats is only one-sixth or less of that for a capillary viscometer. Indeed, the effect in the viscodensitometer is smaller than the experimental error, but is systematic and therefore worth correcting.

MANUFACTURE OF THE FLOATS

The floats used in the viscodensitometer are made by the self-inflation in a flame of a length of sealed Pyrex capillary. The method used is based on that of Gordon and McNab (8) and of Gordon et al. (9) but with modifications to allow for the inclusion of nickel in the float. Also, more refined etching procedures are used. Plates 1 and 2, p. 538, show individual steps in the process, a small gas-air flame being used for all heating operations. First a length of fine Pyrex capillary (diameter ca. 1 mm) is sealed in the middle (A). A piece of nickel, from Henry Wiggins Ni tape, "bright, soft, annealed" (about 0.02 × 0.02 × 0.002) is inserted in the capillary and pulled down magnetically to the seal (B). The capillary is then sealed off above the nickel, and a bulb produced by partial self-inflation in a flame (C). At this stage the nickel is still free to move inside the bulb and may be seen (unavoidably out of focus) in C. The thickened base of the bulb is necessary, since it later gives the finished float a preferred vertical orientation in the solution, provides a platform on which to seal the nickel by careful heating, and allows considerable etching to adjust the density (see below). D shows the nickel (dark line) sealed to the base of the bulb, which is then *lightly* attached to a Pyrex "matchstick" and the capillary stem drawn off (E). The finished float is then broken away easily from the end of the matchstick.

The density of the finished float is determined by the ratio of air to glass, and it is largely a matter of experience to judge the "sealing

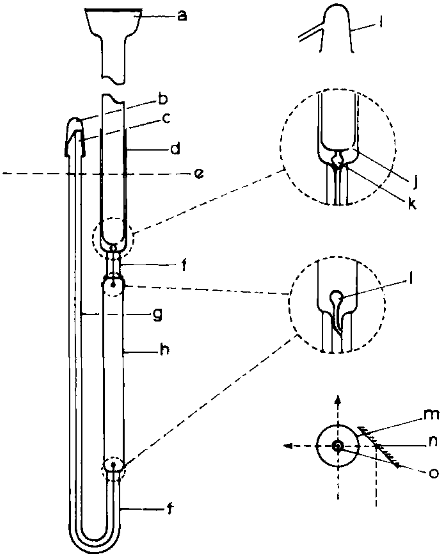

FIG. 1. Schematic drawing of Pyrex glass viscodensitometer. a, glass frit (No. 3); b, B10 cap; c, B10 capillary cone, partly ground away; d, inner tube sliding fit to outer tube; e, thermostat water level; f, positions of clamps; g, 1-mm capillary; h, precision-bore fall tube, 6 mm diameter, containing the floats; i, modified B10 socket for emptying; j, hole; k, ground-in glass stopper; l, Pyrex "matchsticks," sealed to capillary; m, section of 6-mm tube; n, mirror; o, float. Floats are sorted and centered using small magnets. Accurate centering is checked using the mirror n. The viscodensitometer is filled and emptied through the cone b. By opening the ground-glass stopper, solutions flow in under gravity. To empty the instrument the specially modified socket is placed over the cone, the stopper is opened, and suction is applied by a filter pump. During measurements the cone is sealed by a cap and the stopper closed. The apparatus was placed in a thermostat, the temperature of which was controlled to ±0.001°C.

off" process from D to E in order to obtain approximately the required density. Finished floats are collected in a density gradient tube which allows preliminary sorting.

The further adjustment in density, to about 10^{-5} g/cc, is by controlled etching of the thick base of the float successively in 40%, 8%, and 2% HF, with intermittent testing in a calibrated density gradient tube. As shown in F, only the base of the float contacts the "mountain" of HF raised with the aid of surface tension. Using 80% HF, the mean rate of change of density was typically 0.0006 ± 0.0002 g/cc/min. The final etching is in 2% HF, monitoring the density by the measurement of the float's balance temperature in a solution of known density. The finished set of floats is sealed into the fall tube of a viscodensitometer, which is illustrated in Fig. 1.

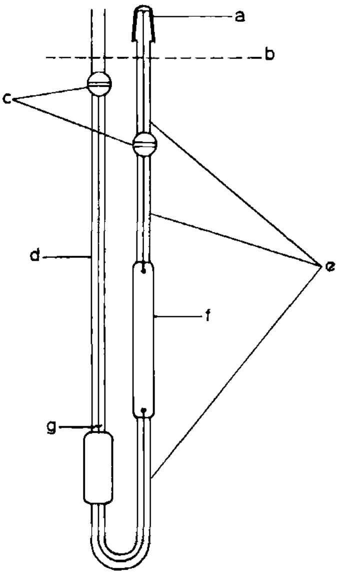

FIG. 2. Apparatus for the calibration of the second float set: cf. Fig. 1. a, cap; b, thermostat water level; c, taps; d, 0.38-mm precision-bore capillary; e, 1-mm capillary; f, precision-bore fall tube (6 mm) with floats; g, etch mark.

CALIBRATION

The first viscodensitometer for use at densities of about 1 g/ml was calibrated with degassed, triply distilled water. Water being the primary standard, viscosities were calculated from temperature by interpretation of smoothed literature data (*Handbook of Chemistry and Physics*). A dilatometer of capacity 28 cc, and with capillary diameter 1 mm, was constructed to check the thermal expansion of the water sample against densities tabulated in the *Handbook*. Coefficients of expansion found agreed with literature data to better than 0.2%, and so henceforward temperature was taken as a measure of density. At higher temperatures (above 30°C) the literature data are insufficiently accurate. Therefore, the table was extended by use of dilatometer measurements.

Floats were timed over measured distances at various temperatures. At several temperatures two floats were timed to check the calibration (see below). The temperatures at which the floats had zero bouyancy (balance point) were found by interpolation. Float constants (K and σ) were obtained by least-squares fitting of the equation

$$K(\sigma - \rho) - 0.00001017K(t - b) = \eta v \qquad (16)$$

where in addition to symbols already defined, b is the balance point, t the temperature, v the velocity at t (upward velocities taken negative), and 0.00001017 the coefficient $d\rho/dt$ of thermal expansion of Pyrex glass. A typical fitting is shown in Table 1. Finally,

TABLE 1

A Typical Float Calibration[a] [Float 5, $b = 28.72$, $\phi = 0.00001017\ (t - b)$]

t, °C	ϕ, g/cc	ρ_{lit}, g/cc	η_{lit}, cp	v, cm/sec	ρ_{calc}[b]
26.716	−0.0000204	0.996589	0.8573	−0.026981	0.9965873
28.050	−0.0000068	0.996218	0.8327	−0.009440	0.9962168
28.464	−0.0000025	0.996099	0.8250	−0.003674	0.9960995
28.593	−0.0000013	0.996063	0.8228	−0.001874	0.9960635
28.747	0.0000003	0.996016	0.8200	0.000408	0.9960181
28.878	0.0000016	0.995979	0.8175	0.002333	0.9959800
29.041	0.0000033	0.995932	0.8147	0.004742	0.9959326
31.127	0.0000244	0.995301	0.7799	0.038535	0.9952993

[a] Least-squares fit of Eq. (16) gives $K = 42.78$, $\sigma = 0.9960262$.

[b] Density calculated from Eq. (16) to show the goodness of fit.

the calibration was checked for self-consistency by recalculation [using Eqs. (6), (7), (8)] of ρ and η wherever two floats had been measured at one temperature. The result of this is shown in Table 2.

TABLE 2

Self-Consistency of Calibration[a]

a	b	v_a, cm/sec	v_b, cm/sec	ρ_{lit}, g/cc	ρ_{calc}, g/cc	η_{lit}, cp	η_{calc}, cp
1	2	0.002531	−0.02523	0.997938	0.9979374	0.9724	0.9766
1	2	0.004850	−0.02307	0.997892	0.9978919	0.9677	0.9641
1	2	0.02538	−0.001703	0.997499	0.9974992	0.9294	0.9319
2	3	0.003257	−0.04638	0.997413	0.9974124	0.9217	0.9210
2	3	0.005913	−0.04365	0.997367	0.9973664	0.9177	0.9180
3	5	0.005356	−0.02698	0.996589	0.9965902	0.8573	0.8615
3	4	0.02242	−0.004344	0.996345	0.9963451	0.8410	0.8371
4	5	0.002343	−0.009440	0.996218	0.9962177	0.8326	0.8360
4	5	0.008671	−0.003674	0.996099	0.9960996	0.8251	0.8235
5	6	0.004742	−0.02933	0.995932	0.9959328	0.8147	0.8145
5	6	0.03853	−0.005383	0.995301	0.9953004	0.7799	0.7790
6	7	0.002913	−0.02562	0.995095	0.9950940	0.7690	0.7690
6	7	0.01399	−0.003979	0.994826	0.9948265	0.7562	0.7565
6	7	0.01972	−0.007220	0.994691	0.9946909	0.7498	0.7512

[a] Viscosities and densities calculated using pairs of floats, compared with literature values calculated at the same temperature (a and b signify float numbers)

After some use it was found that the calibration had changed considerably, leading to anomalous results. It was found that K values had not changed appreciably, but it was necessary to recalibrate the floats for density by measurement of balance points. The results of these repeated calibrations are shown in Tables 3 to 5. It may be seen that subsequent to the first large change, the floats

TABLE 3

Density Calibrations of Floats in First Viscodensitometer

Float pair	11/8/62	6/20/63	7/25/63	8/29/63	10/10/63	11/15/63	2/3/64	2/12/64
1, 2	4.961[a]	5.147	5.180	5.194	5.142	5.182	5.156	5.178
2, 3	7.674	7.699	7.695	7.692	7.720	7.708	7.687	7.660
3, 4	3.929	3.829	3.870	3.875	3.885	3.905	3.845	3.899
4, 5	2.275	2.520	2.510		2.535	2.525	2.515	2.517
5, 6	8.318	8.266	8.243		8.232	8.190	9.230	8.204
6, 7	3.574	3.537	3.539		3.595	3.590	3.587	3.581
1, 7	30.731	30.998	31.037		31.109	31.110	31.020	31.039

[a] The figures are the density differences between pairs of floats, multiplied by 10^4.

TABLE 4

K Values and Radii of Floats

Float	*K*, cm^3/sec^2 × 10^2	*a*, mm	1/*a*, cm^{-1}
1	50.60	0.636	15.72
2	55.07	0.678	14.75
3	59.94	0.727	13.75
4	45.55	0.589	16.98
5	42.78	0.563	17.76
6	32.22	0.466	21.45
7	64.20	0.762	13.12

did not change their densities substantially relative to each other. Moreover, no systematic decrease in float density with time was found, indicating that no significant etching of the floats by the cleaning mixture occurs. In no other case but with this set of floats was a large initial change in float densities found to occur. Results indicate that removal of gelatin films by a nitric acid cleaning mixture is complete and reproducible. It may be seen that variations in the density differences between floats may be as much as 1% in successive calibrations, and so to obtain the full precision of the instrument it seems necessary to calibrate for density before any set of measurements. The cause of these fluctuations is not clear.

The second set of three floats calibrated in the apparatus shown in Fig. 2 using a 0.86-*M* solution of potassium chloride in the temperature range 20 to 30°C. Viscosities of the same potassium chloride were measured over a range of temperature in a suspended level viscometer; density changes (uncorrected for the expansion of Pyrex) were obtained from dilatometer readings.

TABLE 5

Calibration of Floats in Second Viscodensitometer

Float	*K*, cm^3/sec^2 × 10^2	*a*, mm	1/*a*, cm^{-1}	$\Delta\rho$, g/cc
9[a]	50.60	0.636	15.72	0.0005434
10	39.55	0.533	18.76	0.0005729
11	41.88	0.555	18.02	

[a] The absolute density of float 9 is 1.0365 g/cc.

DISCUSSION OF PRECISION

Because of the thermal expansion of the solution, temperature control is one factor limiting precision. Consideration of density changes produced by the temperature fluctuations of ±0.001°C in comparison with the density differences between floats leads to an expected precision in viscosity measurements of ±0.1% and in density measurements of ±0.0000003 g/cc. Measured times are never less than 100 sec with an expected accuracy of 0.05 sec while floats of average speed (0.02 cm/sec) are timed over a distance of 2 cm, which may be measured with an expected precision of ±0.1%. A sequence of float timings to test repeatability gave a standard deviation of 0.09% for five out of seven readings (actual time in seconds, 92.59, 95.11, 94.59, 95.11, 95.37, 95.23, 95.14). Table 2 shows that in a series of viscosity and density measurements the standard deviations were approximately 0.2% for viscosity and 10^{-6} g/cc for density.

MATERIALS USED

A sample of deionized first-extract alkali-bone gelatin ($\bar{M}_w = 120{,}000$), supplied by Kodak Ltd., was the polymer studied. Solvents were distilled water and a solution of potassium chloride in distilled water, all degassed at 50°C before use. The pH of all solutions was 5.1 ± 0.1. Solutions were made up by weight of gelatin in a given weight of solvent, weighings being performed on an analytical balance with an accuracy of ±0.1%. After weighing out, the solutions were maintained at 50°C for approximately 12 to 20 hr, with occasional shaking, before use. The water content of the gelatin, determined by drying to constant weight in vacuo over silica gel, was found to be 13.5%. All concentrations given refer to weight of dry gelatin.

MEASUREMENT OF THE AMOUNT OF ADSORPTION

Using techniques described above, two floats were made to have the same density (1.0012) to within 0.000016 g/cc, but with widely differing radii (0.49 mm and 5.4 mm). The equivalent radius of the small float was determined from its K value and that of the big float from its volume, assuming it, too, to be a sphere.

These floats, in the dilatometer apparatus illustrated in Fig. 3, were used to measure the weight of gelatin adsorbed on unit geometric surface of glass from a solution of 0.168 M potassium chloride at 40°C. From the difference in dilatometer readings (ΔL)

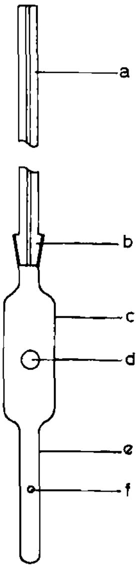

FIG. 3. Dilatometer/float apparatus for the measurement of the adsorption isotherm. a, 1-mm precision-bore capillary; b, B10 capillary cone; c, tube, inner diameter 2 cm; d, big float; e, precision-bore fall tube (6 mm) with: f, small float.

between the balance points of the floats, we find the apparent density difference between them ($\Delta\sigma$) to be

$$\Delta\sigma = \bar{\sigma} A \, \Delta L / V \qquad (17)$$

where A is the cross-sectional area of the capillary and V is the volume of the dilatometer. V was found by volumetric methods to be 32.43 cc, while A was calculated as the cross section of the 1-mm precision-bore capillary to be 0.00785 cm^2. Also $\bar{\sigma} = 1.0012$, and so

$$\Delta\sigma = 0.000242 \, \Delta L \qquad (18)$$

and

$$m = |0.0000149(\Delta L^* - \Delta L)| \qquad (19)$$

ΔL may be measured with an accuracy of ±0.002 cm, which corresponds to an accuracy of ±0.0000005 g/cc in $\Delta\sigma$. Density changes ($\Delta\sigma - \Delta\sigma^*$) found were approximately 0.000005 g/cc, and so the

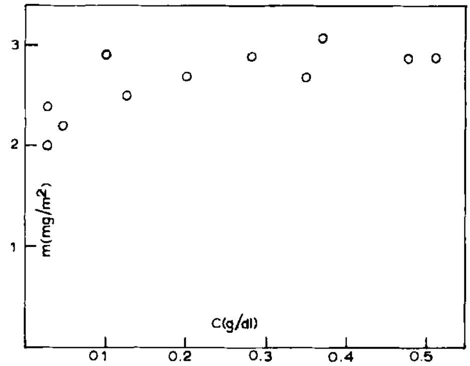

FIG. 4. Adsorption isotherm of gelatin on Pyrex glass from 0.17 *M* KCl.

estimated accuracy of individual measurement of *m* is ±10%. The results of these measurements are shown in the adsorption isotherm of Fig. 4. The adsorption is seen to rise very quickly with increasing solution concentration, and then levels off to a plateau at gelatin concentrations greater than 0.1%.

Janus and Darlow (*10*) and Langston (*19*) pointed out that after a solution of gelatin has been passed through a capillary viscometer, an increase in the characteristic constant of the viscometer is observed. The viscometer may be restored to its original condition by treatment with nitric acid. This "conditioning" effect was attributed to the presence of an adsorbed layer of gelatin on the wall of the capillary and may be used to estimate the effective hydrodynamic thickness of the gelatin film. A suspended level viscometer with a capillary of 0.38 mm precision bore was soaked in chromic-nitric acid cleaning mixture, and then the time of flow of 0.093 *M* potassium chloride solvent at 40°C was measured. The viscometer was filled with a $\frac{1}{10}$% solution of gelatin in the potassium chloride solvent at 40°C, the solution being passed through the capillary. It was then emptied, rinsed with saline solvent, and the time of flow of the solvent redetermined. The effective hydrodynamic thickness of the film was calculated, using Eq. (1), from the increase of flow time (Table 6). It may be seen that the effect of the "conditioning" is marked and reproducible, leading to a film thickness of 1820 A ± 10%. This result agrees qualitatively with that of Langston (2000 A) and is consistent with the results of Janus and Darlow, which indicate a film thickness of approximately 3000 A.

TABLE 6

Conditioning Effect of Film on Suspended Level Viscometer with 0.038-cm Precision-bore Capillary

	Acid cleaned, sec	Conditioned, sec
	548.6[a]	550.8
	548.8	550.9
	548.8	550.5
	548.6	550.9
Mean	548.7	550.8

[a] Figures are flow time of 0.093 potassium chloride solution at 40°C. These results, with Eq. (4), lead to a film thickness of 1820 A.

MEASUREMENT OF SOLUTION VISCOSITIES

Viscosities were measured with the viscodensitometer of gelatin solutions in water at 34.32°C using floats 5, 6, 7; in 0.093 *M* potassium chloride/water at 40.00°C using floats 1, 2, 3, 4; and in 0.947 *M* potassium chloride/water at 40°C using floats 9, 10, 11. Plots of specific viscosity are shown in Fig. 5 [values plotted are those found with Eq. (15)].

The corrected specific viscosity curves (Fig. 5) are as expected for a polyampholite. At the isoelectric point, no changes in configuration with dilution arising from electrical effects are expected, and the viscosity plot should have its normal linear form. Measurements in water were made at the isoelectric point and show a linear

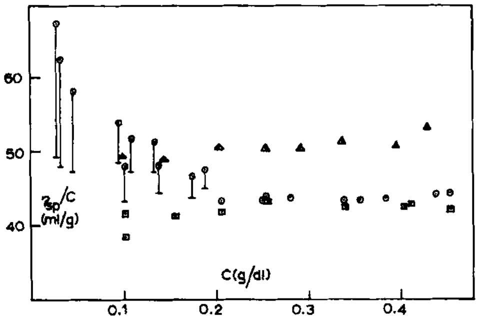

FIG. 5. Specific viscosity plots for gelatin solutions in various solvents. □, Water; ○, 0.093 *M* KCl; △, 0.95 *M* KCl. The vertical lines show the effect of a ½% error in the measured viscosities.

plot, while measurements in molar potassium chloride show a linear plot displaced toward higher values of η_{sp}/c. This displacement is attributed to the screening effect of the salt on attractive forces between oppositely charged groups on the gelatin chain [Pouradier and Venet (*24*)]. Results for solutions in 0.093 *M* potassium chloride show an anomalous upsweep at low concentrations, whereas no such anomalies are apparent in water or in 0.95 *M* KCl. It is possible that the apparent anomalies are due to systematic errors, and the effect of a $\frac{1}{2}$% error in viscosity is shown. The magnitude of the effect is large, however, and it is probably real, even though the capillary viscometer measurements (Fig. 6) do not show any such effect at concentrations down to 0.1 g/dl. The viscosities of the very dilute gelatin solutions were measured with the same float pair that was used to measure the viscosity of the potassium chloride solvent. Therefore, any systematic errors would also be present in the viscosity of the solvent and would cancel in the specific viscosity. Furthermore, the viscosity of the solvent measured by the viscodensitometer was not significantly different from that measured with a capillary viscometer.

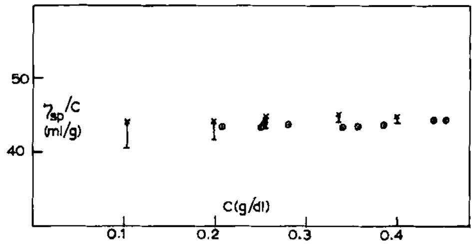

FIG. 6. Comparison of viscodensitometer results (⊙) with those (×) of a capillary viscometer. The points for low concentrations are omitted. The vertical lines show the effect of Öhrn's correction for capillary viscometer results. Solvent 0.093 KCl.

One possible cause is that the isoelectric point of the gelatin moves toward lower pH as electrolyte concentration is increased [Stainsby (*28*)]. The solutions of gelatin in decimolar potassium chloride are therefore not at their isoelectric point, but at the same time there is insufficient added electrolyte to prevent coil-expansion effects with dilution by the screening effect mentioned.

Viscosities of gelatin solution in 0.093 *M* potassium chloride also were measured in a suspended-level viscometer. Figure 6 show the comparison between capillary viscometer and viscodensitometer results. The plot for the capillary viscometer is displaced toward higher values of η_{sp}/c from the curve for the viscodensitometer (but shows no upsweep). Assuming the adsorption hypothesis [Öhrn (20)] and applying the necessary corrections, the uncorrected curve for the viscodensitometer is not very different from the corrected one if the floats are of similar size in the concentration range of interest ($c > 0.2$ g/dl), whereas applying relevant corrections to the capillary results brings them into agreement with viscodensitometer results. This provides evidence in favor of Öhrn's adsorption hypothesis and indicates that whereas adsorption in capillary viscometers may lead to serious errors in measured intrinsic viscosity, the errors are less serious in moving-sphere viscodensitometers.

Solution densities also may be calculated from viscodensitometer results. These densities will be depressed slightly (ca.-0.000005 g/cc) by the effect of the film. Such an error is not significant in the determination of partial specific volume ($\bar{v}$). A typical density vs. concentration plot is shown in Fig. 7 which leads to $\bar{v}$ 0.699. For

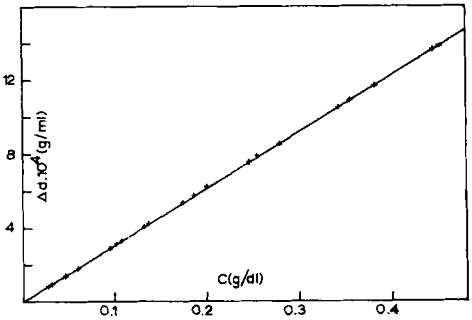

FIG. 7. Density plot for gelatin solutions in 0.093 *M* KCl, at 40°C.

gelatin in water at 34°C we find $\bar{v} = 0.702$, and at 40°C in 0.95 *M* KCl, $\bar{v} = 0.725$. Charlwood (2) found that for gelatin in water at 30°C, $\bar{v} = 0.695$, and this agrees well with our results. Incidentally, once the partial specific volume of the polymer has been determined, accurate knowledge of solution concentration prior to viscosity measurements is unnecessary, because the density as measured simultaneously with viscosity in the viscodensitometer is an adequate measure of solution concentration.

DISCUSSION

The adsorption theory of Öhrn (*20*) provides a very simple explanation for anomalies in measured dilute solution viscosities of polymers and was successfully used to explain his results [Öhrn (*22*)]. The evidence for the adsorption hypothesis is, however, conflicting, and indeed it is not certain that this is the only affect contributing to anomalies. Streeter and Boyer (*29*) attributed observed effects to disentanglement of polymer chains at low concentrations. Kooy and Hermans (*14*) found no anomalies down to concentrations of 0.003 g/dl, whereas Tuijnman and Hermans (*33*), using the same apparatus, found anomalies which they attributed to non-Newtonian effects. On the adsorption hypothesis, their results indicate a layer 5000 A thick, and in adsorption experiments they found very high adsorbance of 100 mg/m^2. Öhrn (*22*) attempted to repeat this work with a lower-molecular-weight sample of the same polymer and found no shear-gradient dependence of viscosity and an adsorption layer of 500 A.

The amount of adsorption found in the present work (Fig. 4) agrees well with that found by Pouradier and Roman (*25*), who found between 3 and 6 mg/m^2 for fractionated gelatin in the molecular-weight range 30,000 to 190,000 adsorbed on silver halides, the surface area being determined by particle-size counting. Kragh and Langston (*17*), for gelatin adsorbed on quartz, found less molecular-weight dependence and adsorption of 2.1 mg/m^2, the surface area being determined by nitrogen adsorption.

It is difficult to correlate the amount of adsorption measured by various workers, owing to the difficulty of assessing the surface area available to the polymer. With a porous substrate, areas determined by nitrogen adsorption obviously are unrealistic, since nitrogen will adsorb on internal surface not available to polymer segments. Perkel and Ullman (*23*) use areas determined by palmitic acid adsorption but point out that even these may be too high. For smooth surfaces, such as those of our Pyrex floats, the geometric surface area is as good as any estimate of surface and is by far the easiest to measure. What emerges from most studies is that there is much more polymer adsorbed than may be accommodated in a monomolecular layer [e.g., Pouradier and Roman (*25*), Koral et al. (*15*), Perkel and Ullman (*23*), Ellerstein and Ullman (*3*), and Kragh (*16*)] without any corresponding evidence in the isotherm shape for multilayer formation. Jenckel and Rumbach (*11*) proposed that this behavior is due to the tendency of the polymer to be adsorbed at a few segments only, the rest of the molecule looping into the solution. The apparent irreversibility of polymer adsorption is attributed to the statistical improbability of all segments simultaneously becoming desorbed even though individual segments are adsorbing quite reversibly.

Simha et al. (*27*) proposed a model for polymer adsorption which fits the observed data well. Their model predicts only a few segments adsorbed and hence thick layers with dimensions of the same order as those of the free molecule in solution [but probably greater, owing to lateral compression of molecules on the surface; see, e.g., Koral et al. (*15*)]. This treatment has been criticized by Silberberg (*26*), whose theory predicts that, even in the presence of quite weak adsorption energies, a significant proportion of polymer segments will be adsorbed with loops of only a hundred or so segments, leading to layers only 30 A thick. Experimental evidence supporting Silberberg's theory is provided by Fontana and Thomas (*6*), who, from infrared measurements, concluded that as many as 36% of chain segments is close to the surface. A tentative explanation for these results was proposed by Perkel and Ullman (*23*). The polymer may be adsorbed in two stages with the first molecules adsorbed lying flat on the surface, but, with greater adsorption, molecules are adsorbed with only a few segments. This mechanism, proposed earlier by Pouradier and Roman (*25*) for gelatin adsorption, would account for many-segment adsorption combined with thick layers but is difficult to reconcile with mobility of the adsorbed molecules [Kragh (*16*)]. Silberberg points out that attainment of the equilibrium predicted by his treatment may be slow, and in the early stages long loops would be present.

The molecular-weight dependence of the maximum adsorption (A_s) [e.g., Pouradier and Roman (*25*), Perkel and Ullman (*23*)] is consistent with a relation $A_s = KM^a$, where a lies between 0.20 and 0.45. Perkel and Ullman (*23*) showed that such behavior is consistent with many possible models for adsorption and, therefore, is not a very good guide.

Recently Stromberg et al. (*30,31*) have studied the thickness of adsorbed polymer films by ellipsometry, which provides a means of measuring directly the thickness of the film. It is not certain that the thickness obtained by this method will correspond to the hydrodynamic thickness, but it will be at least a guide.

They studied the adsorption of polystyrene from solutions at the theta temperature. Their results show that the film thickness is proportional to the square root of the molecular weight, indicating that the polymer is adsorbed as a random coil. For the molecular weight used by Öhrn (22) they find a root-mean-square film thickness of approximately 600 A. Bearing in mind the difference in the type of measurement, this agrees qualitatively with the effective hydrodynamic thickness of 1500 A found by Öhrn.

Previous methods for weighing adsorbed films have involved the use of very small particles of adsorbent in order to get measurable effects on the concentration of the mother liquor. The resulting uncertainties in surface area due to heterogeneities of particle size, flocculation, or methods of surface determination are avoided in our big-float/small-float experiment. Here the geometric surface area (which from consideration of the mechanism of polymer adsorption is the one of interest) may be determined with sufficient precision, and the film is weighed directly by measurement of its effect on apparent float densities.

The weight of gelatin adsorbed on unit surface area of glass (Fig. 4) is more than can be packed into a monolayer [see Keenan (*13*)] but there is no evidence for multilayer adsorption. It seems likely, therefore, that gelatin, like other polymers, is adsorbed in a looped structure. Results obtained from the "conditioning" effect of the film on a capillary viscometer indicate an effective hydrodynamic thickness for the gelatin film of 1800 A. Figure 6 shows that this result accounts for differences of viscosities measured in capillary viscometers compared with those obtained in the viscodensitometer. The value of 1800 A seem surprisingly high, however, since Öhrn found only 1500 A for a polymer of much higher molecular weight. There is some evidence [Kragh (*16*)] that polymers like gelatin, which contain many types of groups, some of which may adsorb preferentially, form thicker layers.

The effect of the adsorbed film on capillary viscometers results in systematic errors which may be serious and which are difficult to detect without elaborate experimentation. The apparently excellent accuracy which has been achieved with these instruments can, therefore, be misleading. Uncertainties due to the thickness of the adsorbed film are much smaller in viscodensitometry, and exact correction may be made for the effect of the film on the float densities. With floats of similar size, the error induced in measured viscosity by this effect is negligible.

The effect of solid particles in the test solution, which causes serious trouble in capillary viscometers, is not so serious in the viscodensitometer, and it is unnecessary to take elaborate precautions against dust. Other advantages in operation of the viscodensitometer are the very low shear rate and the ability to measure solution concentrations (from density) simultaneously with the viscosity.

Acknowledgments

We gratefully acknowledge a grant for equipment from the Royal Society, and a gift of the gelatin, together with the technical information quoted, from Dr. Janus of Kodak Ltd.

REFERENCES

1. H. Batzer, *Makromol. Chem.*, **12**, 145 (1954).
2. P. A. Charlwood, *J. Am. Chem. Soc.*, **79**, 776 (1956).
3. S. Ellerstein and R. Ullman, *J. Polymer Sci.*, **55**, 123 (1961).
4. P. J. Flory and T. G. Fox, *J. Polymer Sci.*, **5**, 745 (1950).
5. P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904, 1909 (1951).
6. B. J. Fontana and J. R. Thomas, *J. Phys. Chem.*, **65**, 480 (1961).
7. T. G. Fox, J. C. Fox, and P. J. Flory, *J. Am. Chem. Soc.*, **73**, 1901 (1951).
8. M. Gordon and I. A. McNab, *Trans. Faraday Soc.*, **49**, 31 (1953).
9. M. Gordon, C. S. Hope, L. D. Loan, and R. J. Roe, *Proc. Roy. Soc. (London)*, **A258**, 215 (1960).
10. J. W. Janus and R. L. Darlow, *Nature*, **194**, 1075 (1962).
11. E. Jenckel and B. Rumbach, *Z. Electrochem.*, **55**, 612 (1951).
12. T. Kawai and K. Saito, *J. Polymer Sci.*, **26**, 213 (1957).
13. A. L. Keenan, *J. Phys. Chem.*, **33**, 371 (1929).
14. J. Kooy and J. J. Hermans, *J. Polymer Sci.*, **16**, 417 (1955).
15. J. Koral, R. Ullman, and F. R. Eirich, *J. Phys. Chem.*, **62**, 451 (1958).
16. A. M. Kragh, *J. Phot. Sci.*, **12**, 191 (1964).
17. A. M. Kragh and W. B. Langston, *J. Colloid. Sci.*, **17**, 101 (1962).
18. H. Lamb, *Hydrodynamics*, Cambridge, New York, 1932.
19. W. B. Langston, *Supplement to Research Series* A2, British Gelatine and Glue Research Association, London, 1962.
20. O. E. Öhrn, *J. Polymer Sci.*, **17**, 137 (1955).
21. O. E. Öhrn, *J. Polymer Sci.*, **19**, 199 (1956).
22. O. E. Öhrn, *Arkiv Kemi*, **12**, 397 (1958).
23. R. Perckel and R. Ullman, *J. Polymer Sci.*, **54**, 127 (1961).
24. J. Pouradier and A. M. Venet, *J. Chim. Phys.*, **47**, 11 (1950).
25. J. Pouradier and J. Roman, *Sci. Ind. Phot.*, **23**, 4 (1951).
26. A. Silberberg, *J. Phys. Chem.*, **66**, 1872 (1962).
27. R. Simha, H. L. Frisch, and F. R. Eirich, *J. Phys. Chem.*, **57**, 584 (1953).
28. G. Stainsby, *Nature*, **169**, 662 (1952).

29. D. J. Streeter and R. F. Boyer, *J. Polymer Sci.*, **14,** 5 (1954).
30. R. R. Stromberg, E. Passaglia, and D. J. Tutas, *J. Res. Natl. Bur. Std.*, **A67,** 431 (1963).
31. R. R. Stromberg, D. J. Tutas, and E. Passaglia, *J. Phys. Chem.*, **69,** 3955 (1965).
32. M. Takeda and E. Turuta, *Bull. Chem. Soc. Japan*, **25,** 80 (1952).
33. C. A. F. Tuijnman and J. J. Hermans, *J. Polymer Sci.*, **25,** 385 (1957).
34. H. Umstätter, *Makromol. Chem.*, **12,** 94 (1954).

Zusammenfassung

Die Sorption von Polymeren an Glasoberflächen und die dadurch sich ergebenden Effekte auf die Messung der grundmolaren Viskosität (die bisher im Kapillarviskosimeter untersucht wurde) wird hier mit Hilfe der empfindlichen viskodensitometrischen Methode analysiert, wobei letztere auf dem Prinzip des Viskosimeters mit der sich bewegenden Kugel beruht. Durch Verwendung mehrerer Kugeln *gleicher* Grösse kann der auf Sorption beruhende Fehler bei der Viskosimetrie praktisch eliminiert werden. Die Verwendung von zwei Kugeln deren Radius sich um den Faktor 10 unterscheidet, erlaubt ein direktes Auswiegen des pro Flächeneinheit sorbierten Polymeren. Auf diese Weise wurde die Sorptionsisotherme eines Alkaliknochengelatins auf Pyrexglas in 0.17 *M* KCl Lösung bestimmt. Es ergab sich, dass dieselbe ein Plateau von 3 mg/m^2 bei einer Gelatinkonzentration von 0.1 g/dl erreicht. Dieses Plateau erstreckt sich von dieser unteren Grenze bis zu 0.5 g/dl. Das im Viskodensitometer direkt zusätzlich zu der Viskosität erhaltenen partielle spezifischen Volumen der Gelatine ergab sich zu 0.702 cc/g in Wasser und 0.725 cc/g in 0.95 *M* KCl.

Résumé

La sorption des polymères sur des surfaces de verre et l'effet produit sur les mesures de viscosité intrinsèque, etudiés jusqu'ici dans des viscosimètres capillaires, sont analysés par la méthode viscodensitométrique sensible, basée sur le principe d'un viscosimètre à sphères mobiles. En utilisant plusieures sphères de dimensions égales, on peut éliminer pratiquement les erreurs dues à la sorption. L'emploi de deux sphères, leur rayon étant différent par un facteur de dix, permet de peser directement le polymère sorbé par une unité géometrique de surface. De cette manière on a trouvé que la sorption isotherme d'une gelatine osseuse alcaline sur un verre de Pyrex d'une solution KCl de 0.17 *M* augmente jusqu'au palier de 3 mg/m^2 à une concentration de gelatine de 0.1 g/dl. Ce palier s'étend à partir de cette limite inférieure jusqu'à 0.5 g/dl. Le volume spécifique partiel de la gelatine, obtenu directement dans le viscosimètre avec la viscosité, était 0.702 cc/g dans l'eau et 0.725 cc/g dans 0.95 *M* KCl.

Received by editor July 15, 1966
Submitted for publication November 14, 1966

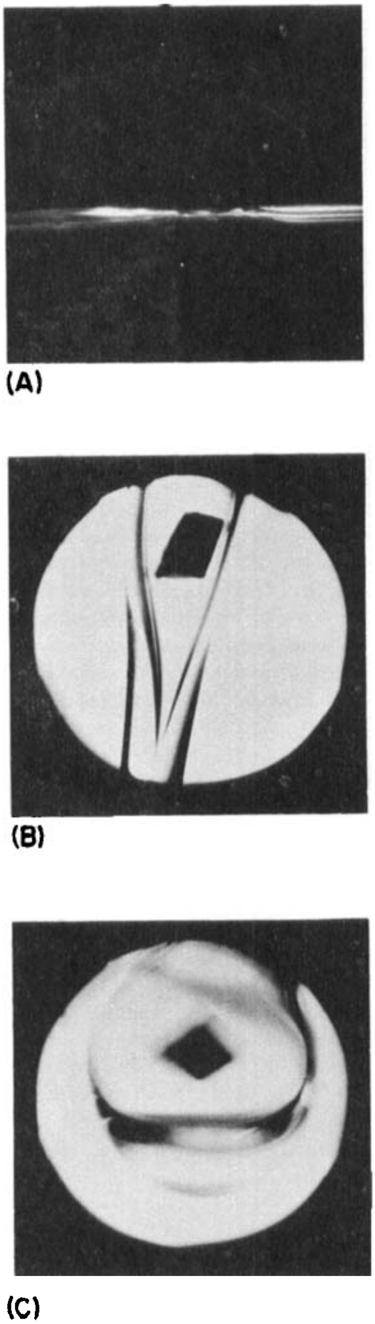

Plate 1

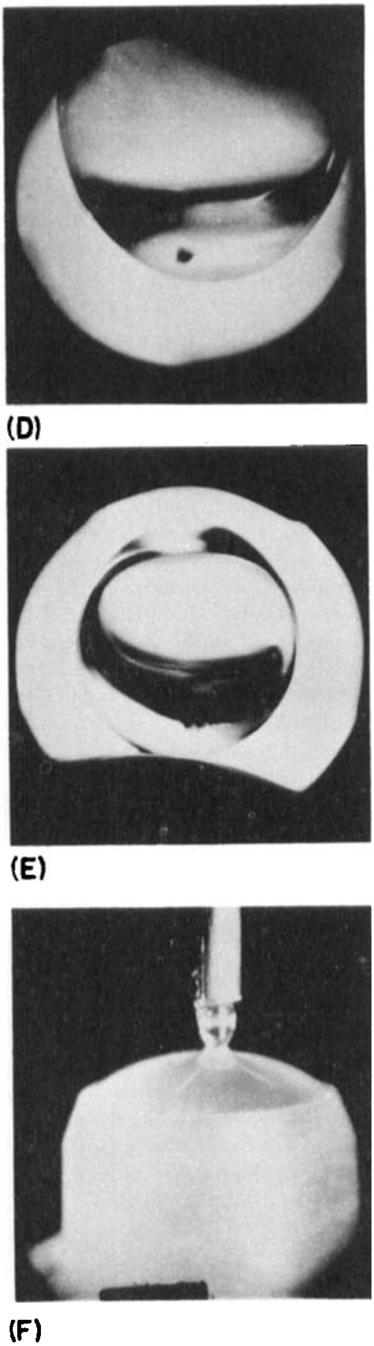

Plate 2