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INFERRING A MOLECULAR WEIGHT DISTRIBUTION, AN ILL-POSED PROBLEM; AND ESTABLISHING THE MOLECULAR WEIGHT SCALE USING MAGNETIC FLOAT TECHNIQUES

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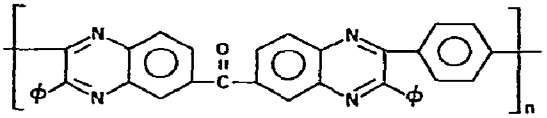
The ill-posed problem of inferring a molecular weight distribution from ultracentrifuge equilibrium sedimentation data at a single rotor velocity has been circumvented by application of a regularization and quadratic programming technique. This has been applied to polyphenyl-quinoxaline (PPQ)



dissolved in chloroform. Because the solvent is highly volatile, it was necessary to apply a newly designed magnetic float pycnometer in determining the partial specific volume which is necessary for establishing the molecular weight scale.

1. Introduction

Molecular weight averages and molecular weight distributions of synthetic polymers have profound affects on their physical and mechanical properties in the bulk state [1–3]. For example, if the weight average molecular weight is sufficiently high, a very small percentage of a high molecular weight fraction can greatly affect the mechanical properties [4]. The synthetic polymers of main interest to the authors about five years ago are soluble only in strong acids such as (97%) sulfuric acid or methanesulfonic acid. As a result standard gel permeation chromatography fractionation techniques used on most synthetic polymers was not applicable. Therefore, the need for developing a technique to infer a molecular weight distribution having more than just a gaussian or near gaussian distribution presented itself. The experimental technique chosen was sedimentation equilibrium using an analytical ultracentrifuge. The Fredholm integral of the first kind which was applied in determining the molecular weight distribution $f(M)$ from either concentration or concentration gradient data followed the Fujita formalism [5].

$$c(\xi) = C_0 \int_0^\infty \frac{\lambda M e^{-\lambda M \xi}}{1-e^{-\lambda M}} f(M)\,dM\,, \tag{1}$$

or

$$\frac{dc(\xi)}{d\xi} = -C_0 \int_0^\infty \frac{\lambda^2 M^2 e^{-\lambda M \xi}}{1-e^{-\lambda M}} f(M)\,dM\,, \tag{2}$$

where c is the concentration and $dc(\xi)/d\xi$ the concentration gradient at r, a radial distance; C_0, the concentration of the original solution; M, the molecular weight, ξ, the reduced coordinate, $(r_2^2-r^2)/(r_2^2-r_1^2)$ with r_1 and r_2 being the radial distances to the meniscus and bottom of the cell, respectively;

$$\lambda = (1-\bar{V}\rho)\,\omega^2 (r_2^2-r_1^2)/2RT\,, \tag{3}$$

with $\bar{V}$ the partial specific volume of the dissolved polymer; ρ the density of the solution, ω the rotor angular velocity, R the universal gas constant; and T the absolute temperature. Here it is assumed that the solution is pseudo-ideal and that the partial specific volumes and refractive index increments of all sample components are the same. In addition it is assumed that the buoyancy factor and refractive index increment are independent of pressure and concentration.

Many of the existing techniques for inferring $f(M)$ [6–8] did not provide sufficient distribution structure in order to reliably correlate $f(M)$ of homopolymers to their bulk state mechanical properties. Independently the application of continuous fractions and Frechet derivatives approaches both failed to yield the desired distribution structure. In the former the sought after distribution $f(M)$ is approximated by a quotient of two polynomials. In the latter the experimental data is approximated by a summation of exponentials such that the inverse transformation is easily performed. The linear programming approach taken by Scholte [9, 10] seemed for the first time to provide the required structure. However, the experimental requirement of achieving equilibrium at many rotor speeds was too demanding for the highly aggregating systems being studied.

Through efforts initiated by the authors, Lee [12] came to the conclusion that eqs. (1) and (2) are mathematically ill-posed problems. Subsequent research performed by the authors [13–15] dealt with application of Tikhonov's [16, 17] regularization technique to aid in inferring a reliable $f(M)$ by use of eqs. (1) or (2) with ultracentrifuge equilibrium sedimentation data obtained at a single rotor speed.

It is the purpose of this investigation to discuss briefly the procedure of incorporating Tikhonov's regularization into quadratic programming. Then apply this to infer a molecular weight distribution of polyphenyl-quinoxaline (PPQ) polymer [18]. In addition a unique feature of this investigation was the application of a magnetic float pycnometer to establish the molecular weight scale. This special instrument was required because the solvent (chloroform), being very volatile, yielded erratic data by conventional pycnometry approaches.

2. Regularization

Since in practice the upper limit of integration in eqs. (1) and (2) can usually be some finite number, consider them as represented by a Fredholm integral of the first kind

$$u(\xi) = Q[\xi, f(M)] = \int_{M_0}^{M_1} K(\xi, M) f(M)\, \mathrm{d}M \,, \tag{4}$$

where $\xi_0 \leqslant \xi \leqslant \xi_1$. This can further be written as

$$Q[\xi, f(M)] = u = Af \,, \qquad u \in U \text{ and } f \in F \,, \tag{5}$$

where F and U are some complete metric spaces and Af is a function having domain F and range U. The problem of solving eq. (5) for a set $\{f\}$, given a set $\{u\}$ and knowing the functional form of A is a properly posed problem if the following conditions are satisfied:

(a) The solution of eq. (5) exists for any $u \in U$.

(b) The solution of eq. (5) is unique in F.

(c) The solution of eq. (5) depends continuously on u in the metrics of F and U. In such a case there exists a function Tu defined and continuous over all U and T is an inverse operator of A, where

$$Tu = A^{-1}u = f = R[M, u(\xi)] \,. \tag{6}$$

If even one of the conditions (a), (b) or (c) is not satisfied [$u = Af$] is an ill-posed problem (IPP) or mathematically incorrectly formulated problem. That is, when $u(\xi)$ functions exist which do not have corresponding $f(M)$ solutions then eq (4) or eqs. (1) and (2) are IPPs. However, even in such a case upon application of Tikhonov's ideas of regularization a special function $\bar{u}(\xi)$ may exist which has a corresponding solution:

$$\bar{f}(M) = R[M, \bar{u}(\xi)] \,. \tag{7}$$

In order to describe the application of this regularization technique, consider an approximating function $\tilde{u}(\xi)$ be given for $\bar{u}(\xi)$, such that $\|\tilde{u} - \bar{u}\| < \delta$ where δ is known. It is then required to find $\tilde{f}(M)$ an approximation, to $\bar{f}(M)$ with help of parametrical functionals $R[\tilde{u}, \alpha]$ in which the parameter α is connected with the δ-precision of the input data; $\alpha = \alpha(\delta)$ [19]. Let us assume that $M_0 = 0, M_1 = M_{\max}, \xi_0 = 0, \xi_1 = 1$ and that $K(\xi, M)$ is integrable. Also for $\bar{u}(\xi) = 0$ there must exist just one solution, namely, $\bar{f}(M) = 0$. Then instead of using the conventional functional of calculus of variations

$$N[f(M);\bar{u}(\xi)] = \int_0^1 \{Q[\xi, f(M)] - \bar{u}(\xi)\}^2 \, d\xi \tag{8}$$

Tikhonov suggests application of the functional

$$M_n^\alpha[f(M);\bar{u}(\xi)] = N[f(M);\bar{u}(\xi)] + \alpha\Omega^{(n)}[f(M)] \,, \tag{9}$$

where $\Omega^{(n)}$ is the regularizing functional

$$\Omega^{(n)}[f(M)] = \int_0^{M_{\max}} \left\{\sum_{i=0}^{n+1} P_i(M)[f^{(i)}(M)]^2\right\} dM \,. \tag{10}$$

Here the $P_i(M)$ are positive continuous functions, $f^{(i)}(M)$ is the ith derivative with respect to M, and α is an arbitrary parameter which for various values the corresponding sets $\{\widetilde{f^\alpha}\}$ are determined. For any specific α, a set $\{\widetilde{f^\alpha}\}$ minimizes M_n^α.

In all applications of Tikhonov's reguliarization technique to solve problems in our laboratory the $P_i(M)$'s in eq. (10) were equated to constants. Therefore, the functional in eq. (9) to be minimized is

$$M_n^\alpha[f(M);\bar{u}(\xi)] = N[f(M);\bar{u}(\xi)] + \sum_{i=0}^{n} \alpha_i \Omega^{(i)}[f] \,, \tag{11}$$

where now

$$\Omega^{(i)}[f] = \int_0^{M_{\max}} [f^{(i)}(M)]^2 dM \,, \tag{12}$$

$f^{(i)}(M)$ being the ith derivative of $f(M)$ with respect to M.

3. Regularization and quadratic programming

If one assumes a constant increment, h, associated with the mesh for M, then a $f_j^{(i)}$; i.e., $f^{(i)}(M)$ at a particular point M_j, can be approximated by

$$f_j^{(i)} = \frac{1}{h^i}\sum_{k=0}^{i}\binom{i}{k}\left(-1\right)^k f_{j-p+k} \,, \tag{13}$$

where $\binom{i}{k}$ are the binominal coefficients and $p = i$ for i odd and $p = i-1$ for i even. Then eq. (12) becomes

$$\Omega^{(i)}[f] = \frac{1}{h^{i-1}} \sum_{g=1}^{J}\sum_{r=1}^{J}\sum_{k=0}^{n}\sum_{l=0}^{n}\binom{n}{k}\binom{n}{l} \times (-1)^{l+k} f_{g-p+k} f_{r-p+l} \,, \tag{14}$$

which in matrix notation will be

$$\Omega^{(i)}[f] = f^1 \Lambda^{(i)} f \,, \tag{15}$$

where $\mathbf{\Lambda}$ is a matrix whose elements are zero except for diagonal and near off diagonal elements for which if $t = q-p+k$ and $s = r-p+l$, then

$$\lambda_{t,s}^{(n)} = \sum_{k=0}^{n}\sum_{l=0}^{n}\binom{n}{k}\binom{n}{l}(-1)^{l+k} \,, \tag{16}$$

with the boundary conditions $1 \leqslant t \leqslant J$ and for $s < 1$, then $s = |s| + 1$ or if $s > J$ then $s = 2J - s + 1$.

Next consider eq. (8). Express this in matrix notation, where as in eq. (5), the operator (kernel multiplied by appropriate integration constants for numerical evaluation) will be designated by $\mathbf{A} = \{a_{ij}\}$; $u = \{u_i\}, i = 1, 2, ..., I$; and $f = \{f_j\}, j = 1, 2, ..., J$. Thus eq. (8) can be expressed as

$$\sum_{i=1}^{I}\left(\sum_{j=1}^{J} a_{ij} f_j - u_i\right)^2 = f'\mathbf{A}'\mathbf{A}f - 2u'\mathbf{A}f + u'u \,. \tag{17}$$

Neglecting the last term in eq. (17) which is a constant and using the result of eq. (15), the functional M_n^α of eq. (11) expressed in matrix notation is

$$M_n^\alpha = f'\mathbf{A}'\mathbf{A}f - 2u'\mathbf{A}f + \sum_i \alpha_i f'\Lambda^{(i)} f \,. \tag{18}$$

This can be written so as to be in a more obvious form for application of quadratic programming algorithms [20], i.e., minimize

$$M_n^\alpha = f'\left[\mathbf{A}'\mathbf{A} + \sum_i \alpha_i \Lambda^{(i)}\right] f - 2u'\mathbf{A}f \,. \tag{19}$$

4. Application of the theory

Using the kernel as expressed by eq. (1), computer experiments were performed to verify the theory. Numbers analogous to the experimental data $C(\xi)/C_0$, i.e., $\{\bar{u}: \bar{u} = A\bar{f}\}$ were generated from an assumed molecular weight distribution $\{\bar{f}\}$. The back

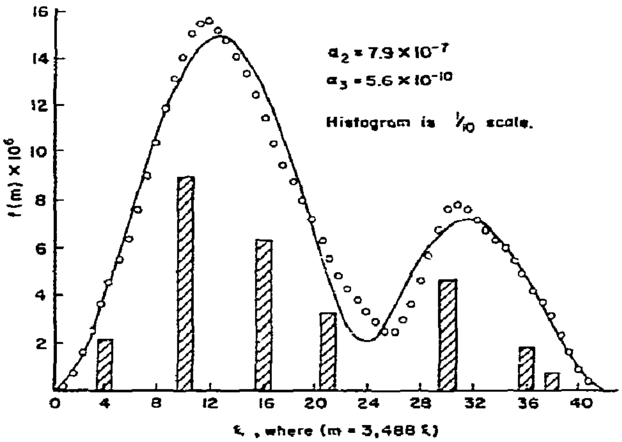


Fig. 1. Asymmetrical bimodal distribution, solid line represents the original distribution, circles the distribution using a 41 point mask and regularization with quadratic programming. The histogram to 1/10 scale represents results using quadratic programming without regularization.

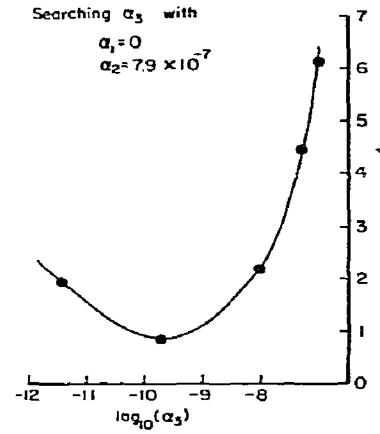


Fig. 2. A typical plot of the error criterion $\|\bar{u}-\widetilde{u}^\alpha\|$ versus the logarithm to the base ten of α. Such a plot could be obtained for each α_i while holding previous α_i's constant.

solution, i.e., determining a set $\{\widetilde{f}^\alpha\}$ from $\{\bar{u}\}$ was peformed. Pictorially viewed, the plots of $\{\bar{f}\}$ and $\{\widetilde{f}^\alpha\}$ could be compared, e.g., see fig. 1. However, with real equilibrium sedimentation data $\{\bar{f}\}$ would not be available for comparison with $\{\widetilde{f}^\alpha\}$. Therefore, the set of α_n's which minimized $\|\bar{u}-\widetilde{u}^\alpha\|$ determined the $\widetilde{f}^\alpha(M)$ which best represented the experimental data. That is, the chosen $\widetilde{f}^\alpha(M)$ was in correspondence with inf $\{\|\bar{\mu}-\widetilde{\mu}^\alpha\|\}$ where

$$\|\bar{u}-\widetilde{u}^\alpha\| = \left\{\int_0^1 [\bar{u}(\xi)-\widetilde{u}^\alpha(\xi)]^2 \, d\xi\right\}^{1/2} . \qquad (20)$$

Such a determination is shown graphically in fig. 2.

To perform this with real data, an ultracentrifuge equilibrium sedimentation experiment was performed. A 0.3% by weight solution of PPQ in chloroform was prepared. It was inserted into a 12 mm, 2° single sector Kel-F centerpiece, which was appropriately assembled in a cell and inserted into a AN-J rotor. A similar cell was assembled but contained only solvent. The two menisci were adjusted to the same height by careful weighing of the two cells. This meant that when using a Beckman Model E Analytical ultracentrifuge schlieren optical system, the solvent and solution gradient curves appeared simultaneously on the same photograph. After spinning at 10000 RPM for two weeks and at 25°C, equilibrium was reached. Photographs were taken at the same schlieren angle and compared with those taken two days prior. When the two curves coalesced, we agreed that equilibrium was achieved. The molecular weight distribution inferred from the obtained experimental data is shown in fig. 3.

The greatest difficulty in determining this distribution was in establishing the molecular weight scale. This enters the calculation through the experimental constant given by eq. (3). First attempts at determining the buoyancy factor $(1-V\rho)$ involved the banana shaped pycnometer described in ref. [21] and

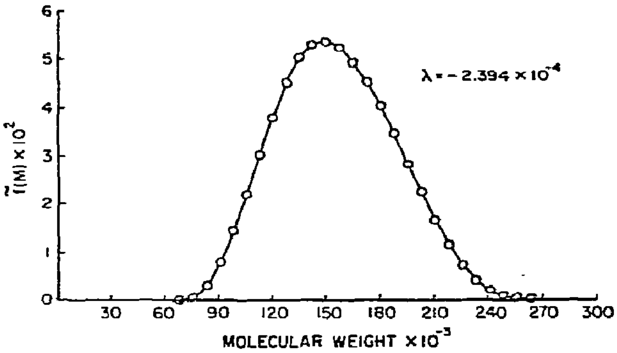


Fig. 3. The molecular weight distribution of polyphenylquinoxaline polymer in chloroform at 0.3% by weight concentration and 25°C. This was inferred using the regularization incorporated into quadratic programming technique.

application of the theory of Lewis and Randall [22]. Because the solvent (chloroform) is so volatile the required accuracy in weighing the pycnometer was beyond our experimental technique. It was for this reason that the following magnetic float pycnometer was applied.

5. Magnetic float pycnometer

A magnetic float can be defined as a buoyant float, containing a permanent magnet, submerged in a liquid under consideration. The system is surrounded by a solenoid with well controlled current (see fig. 4). Therefore, a magnetic field can be created which combines with gravity and buoyancy of the float to control the float's movements up or down. To measure the density one must stabilize the float at a certain constant height and measure either the magnetic field necessary for such a stabilization, or obtain a reading R which is proportional to this magnetic force.

The equilibrium of the float at constant height can be characterized by the following equation:

$$M_F(1-V_F\rho)+f_FR+K_F=0\,. \tag{21}$$

where M_F is the weight of the float, V_F the reciprocal

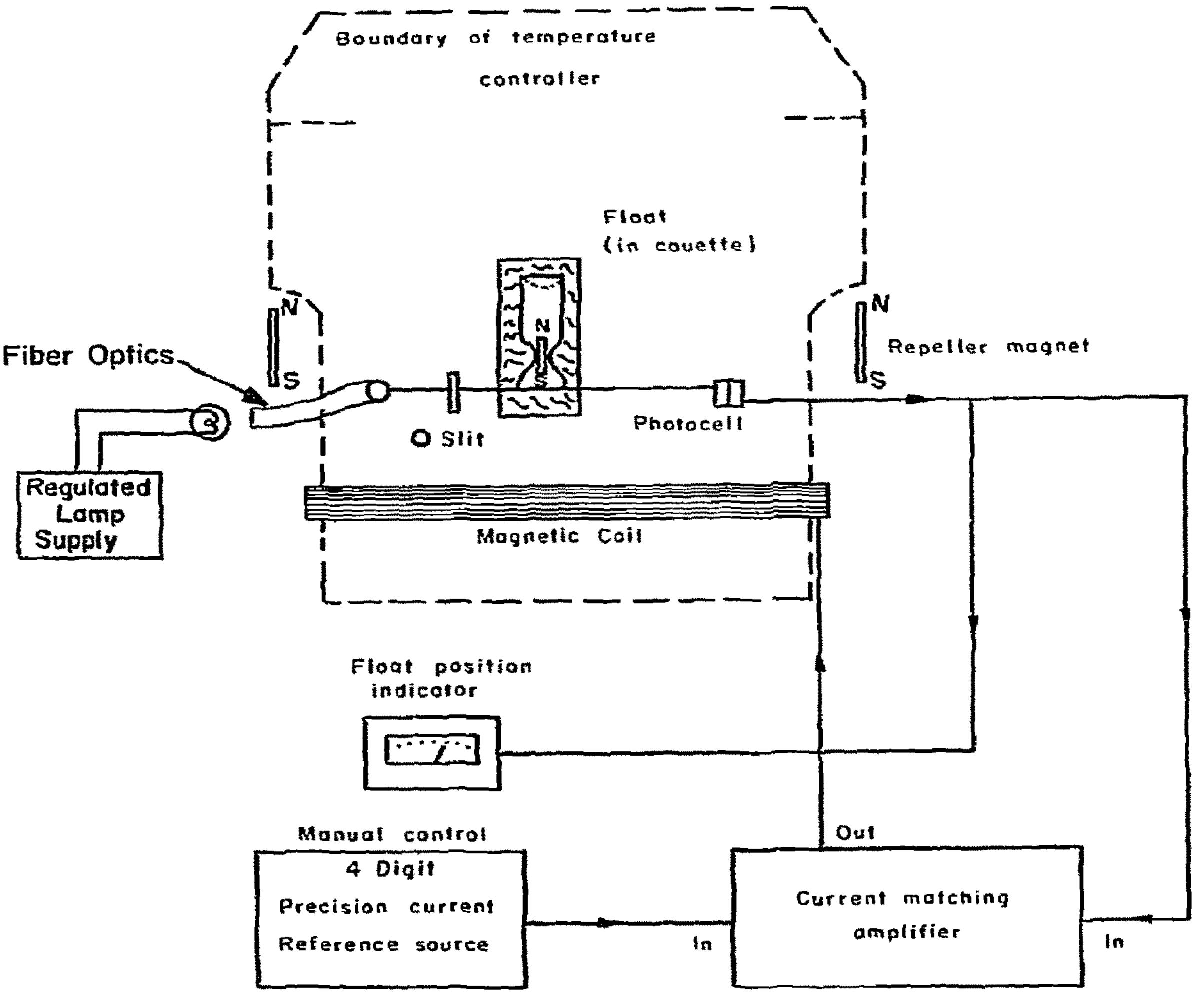


Fig. 4. Schematic of magnetic float system with emphasis on the vertical stabilization control.

of its density, ρ the density of the liquid, f_F a constant for a given float which transforms the reading R into a weight equivalent to the magnetic force, and K_F a constant characteristic of the float.

The advantages of this method are: (1) Since the float is entirely submerged in the liquid, the humidity cannot influence the measurement; (2) there is no need to weigh or adjust the volume of the liquid; (3) the theory as expressed by eq. (21) is very simple. The quantity M_F can be measured by weighing the float, and quantities, V_F and f_F and K_F have to be calibrated.

Another advantage of this method is its ability to measure directly differential values. Assuming that one deals with a slightly higher density than previously ($\rho + \Delta\rho$), eq. (21) becomes

$$M_F(1-V_F\rho)-M_F V_F \Delta\rho + f_F R + f_F \Delta R + K_F = 0\,. \tag{22}$$

By subtracting eq. (21) from eq. (22) one will obtain:

$$\Delta\rho = (f_F/M_F V_F)\,\Delta R\,. \tag{23}$$

Therefore, if the quantity $(f_F/M_F V_F)$ is known, one can immediately and easily determine the density increase $\Delta\rho$ (and therefore a new density) from the increase of instrument reading ΔR.

The absolute value of ρ can be found from eq. (21):

$$\rho = (M_F + f_F R + K_F)/M_F V_F\,. \tag{24}$$

A successful application of magnetic float depends on the prevention of several of the following technical difficulties appearing in previous designs.

(1) Proper centering of the float. The float tends to drift from its center. In such a case the geometry of the magnetic field is perturbed and the readings are not reliable.

(2) The float tends to touch the walls of the container, causing friction and adhesive effects which make measurements unreliable.

(3) While rising and descending, the float drifts by its inertia and it is difficult to stabilize at a desired height. If not stabilized, the geometry of the magnetic field is perturbed and the readings are not reliable.

(4) The solenoid dissipates heat which may critically influence the thermal equilibrium of the liquid.

(5) Precise thermal equilibrium requires equipment, such as a stirrer, electric motor, heater, relay, etc. Some of these are fabricated from magnetic materials and disturb the delicate magnetic field balance, as well as the thermal equilibrium.

(6) Other appliances and instruments (especially movable instruments in the laboratory) may have a deleterious influence on the stability of the magnetic field within the pycnometer. Therefore, the main objective of the new attempt was to eliminate the above mentioned inadequacies.

A new magnetic float pycnometer for precise density measurements and determination of partial specific volume of polymer in solution was thus fabricated [23,24]. A repeller system located outside the thermostat prevents the float from drifting and stabilizes it on the axis of a solenoid. The vertical stability is achieved by photoelectric feedback. As the float moves up or down within a light beam, the light passing to a photocell controls the stabilizing photoelectric current and brings the float to a chosen position. A dry thermostat comprised of sandwiched thermal insulators and conductors completely encloses the float and liquid. The temperature inside the thermostat is controlled to ± 2.0×10^{-4}°C with the actual temperature setting known to ± 0.01°C. The reproducibility in density measurements is about 1.0×10^{-6} g/cm^3.

The instrument has been calibrated and used to measure the partial specific volume of polystyrene in cyclohexane at 35°C [24]. The same solutions were also subjected to conventional pycnometric measurements. The results have been found to be in a very good agreement [24].

The application of the computational formula by Svedberg and Pedersen [25] for determining the partial specific volume of the polymer in solution ($\bar{V}$) and thus the ultracentrifugal bouyancy factor

$$(1-\bar{V}\rho) = (\mathrm{d}W_1/\mathrm{d}\rho)\,\rho/W_2 \tag{25}$$

to the present PPQ polymer in chloroform was achieved.

Here ρ denotes the density of the solvent, W_1, the experimental weight concentration of the solutions, and $W_2 = 1-W_1$. The results of this are shown in fig. 5. Since the cuvette containing the solution and magnetic float was sealed, no problem with evaporation of chloroform was encountered.

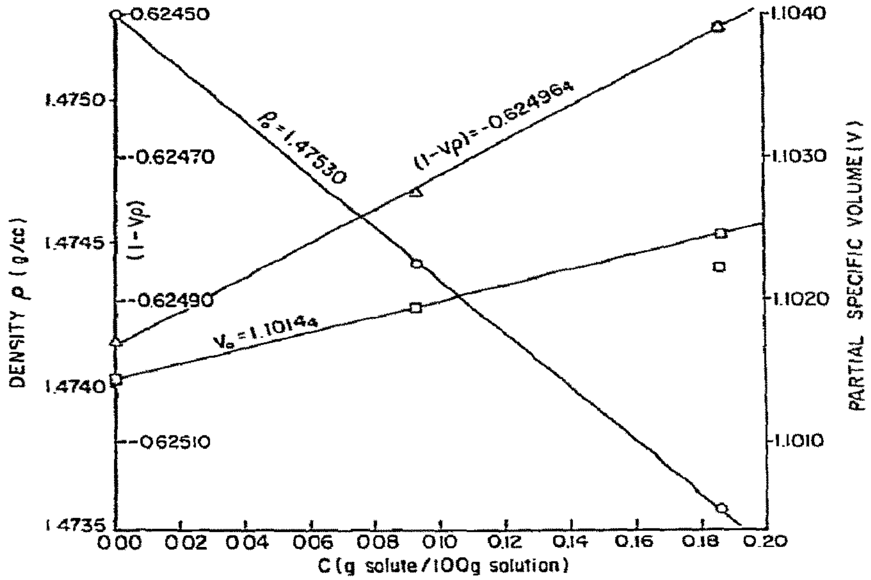


Fig. 5. Results from magnetic float pycnometry of polyphenyl-quinoxaline (MW = 150 000) in chloroform at 25°C.

6. Conclusion

The utility in using a magnetic float pycnometer in determining the partial specific volume of a synthetic polymer dissolved in a highly volatile solvent has been discussed. Without this instrument it would have been very difficult to determine the molecular weight scale of a molecular weight distribution determination. Inferring a molecular weight distribution from ultracentrifuge equilibrium-sedimentation data collected at a single rotor velocity has been accomplished by use of Tikhonov's regularization incorporated by the authors into quadratic programming. Since this class of polymers exhibits strong aggregating phenomena, it should not be surprising that the obtained molecular weight distribution was unimodal. In order to circumvent this high aggregation phenomena, the authors plan to perform a similar ultracentrifuge experiment with a solution concentration ten thousand times more dilute. This will naturally necessitate use of the absorption optical system rather than the schlieren optical system.

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