

Description of a High-Performance Density Cell. Application to New Investigations in the Field of Polymers Studies

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Synopsis

A new density cell based on the vibrating tube principle is described. This cell provides an accuracy of density measurements of 2×10^{-6} g/cm³ and presents a great stability with respect to temperature and time variations. In two experiments—measurement of self-diffusion coefficient of heavy water through membrane and determination of partial specific volume of polymers in very dilute solutions—it is shown that such a precision leads to new types of investigations.

INTRODUCTION

Until these last years, density measurements of liquids and gases were slow and difficult whatever the method used (picnometry as well as all other techniques based on the Archimedian principle). Recently, Kratky et al.¹ have conceived an automatic densimeter which makes such measurements easier and faster. The density is deduced from the natural vibration period of an oscillating glass tube filled with the liquid to be investigated. The theoretical accuracy of this apparatus should be 1×10^{-6} g/ml, but recent investigations² of its real performances have shown that this precision, often needed for physicochemical studies, cannot always be reached. For this reason, a high-precision flow densimeter, based on the same principle, has been built by Picker et al.,³ who have conceived a new cell and electrical drive circuit. They have been able to obtain the prescribed accuracy with this type of apparatus, but its use is restricted to solutions compatible with the stainless steel oscillator and needs 7 ml solution instead of 2 ml for the Kratky apparatus.

Our own purpose was to build a cell which retains the advantages of the Kratky cell and provides the expected accuracy. First, the concept of the cell and testing of its performance are discussed. Some experiments which become possible owing to its qualities are then described.

DESCRIPTION AND PERFORMANCES OF THE CELL

Principle

The electronic system provides a self-sustained and undamped oscillation of the tube. The period of vibration, T , can be written as

$$T = 2\pi(I/C)^{0.5} \quad (1)$$

where $I = I_0 + I_1$; I is the moment of inertia of the filled tube; I_0 is the moment

of inertia of the empty tube; I_1 is that of the liquid investigated, which is proportional to vd , v and d being the inner volume of the tube and the density of the liquid, respectively; and C is the elasticity constant of the tube.

There is a linear relationship between the density and the square of the period of vibration,

$$d = A + KT^2 \quad (2)$$

The constants A and K can be evaluated from the periods T_1 and T_2 corresponding to well-known densities d_1 and d_2 of two references. We shall discuss the choice of these references later. The vibrating period is determined with a precision of 1×10^{-5} sec.

Performance Testing

Temperature Dependence. Since the expansion coefficient of liquids is of the order of $10^{-3} \text{ ml g}^{-1} \text{ d}^\circ^{-1}$, the temperature of the cell must be maintained constant within a precision of $1 \times 10^{-3} \text{ d}^\circ$.

Atmospheric Pressure Dependence. In a previous work,² we have shown a dependence between the atmospheric pressure and the period of vibration of the tube filled with a liquid. This nonnegligible effect may introduce an error of $1 \times 10^{-4} \text{ g/ml}$ on the density measurement for a pressure variation of 10 mm of mercury. Figure 1 illustrates the effect of atmospheric pressure on the vibration period T . In order to confirm this phenomenon and to find its origin, we have applied various pressures of different gases (He, H₂, N₂, Ar) on the oscillator tube filled with pure water. Table I and Figure 2 show that the period of vibration is a linear function of the density of the gases in which the tube os-

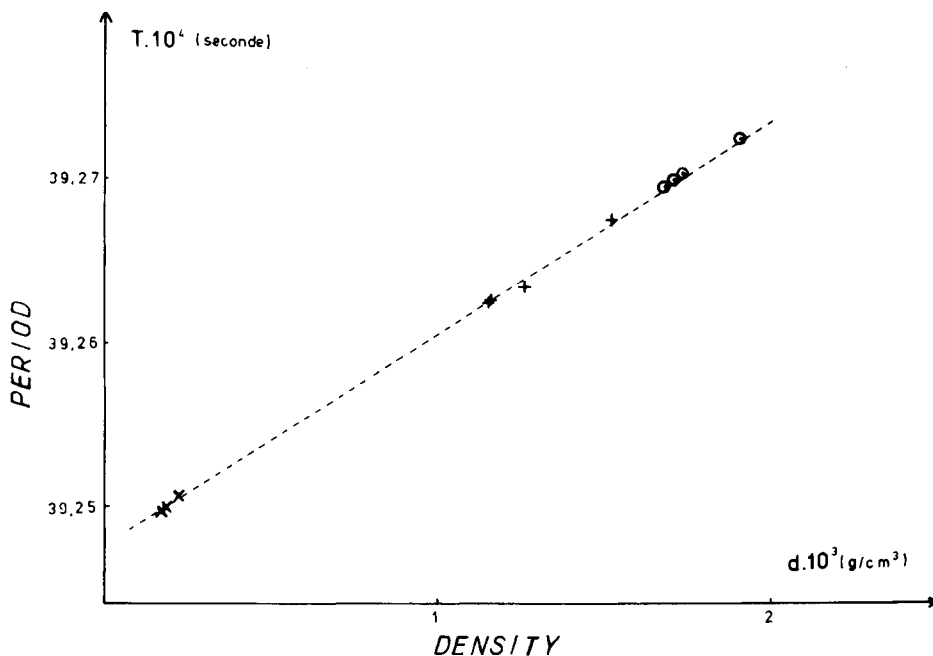


Fig. 1. Variation of period T vs atmospheric pressure p (tube filled with water).

TABLE I
Vibration Period of the Tube Filled with Water as a Function of Pressure and Density of the Gas in Which it Oscillates

Gas	Applied pressure, mm Hg	density $d \times 10^3$ of gas, g/ml	Vibration period $T \times 10^4$ of tube, sec
Argon	758.9	1.692	39.269463
	770.9	1.718	39.269813
	782.9	1.747	39.270160
	860.9	1.920	39.272320
Nitrogen	757.9	1.162	39.262413
	760.9	1.166	39.262483
	827.9	1.270	39.263315
Helium	1.006.9	1.532	39.267355
	757.9	0.169	39.249700
	767.4	0.171	39.249705
	784.9	0.175	39.249828
	802.9	0.179	39.249883
	837.9	0.187	39.249920
	1.00.9	0.223	39.250660

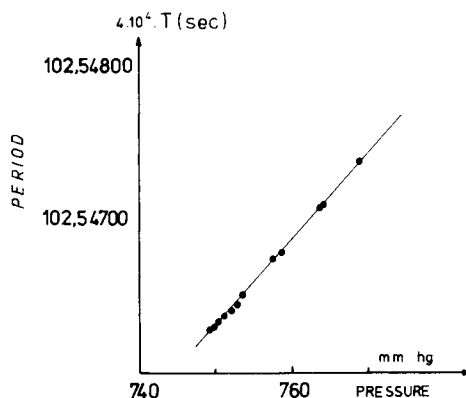


Fig. 2. Variation of period T vs pressure of different gas applied on the vibrating tube (H_2 , He, N_2 , Ar).

illates. This phenomenon can be qualitatively explained if we consider the damping of the tube which increases with the density of the applied gas.

These results demonstrate the necessity for the oscillator tube to be isolated from the variation of atmospheric pressure.

The Crystal-Controlled Timer. The measurement of the period of vibration is obtained using a vibrating quartz as reference. The variation of the frequency of this reference is about 10^{-7} Hz d°^{-1} and for the precision needed, we thought it advisable to thermostat the quartz as we did the cell.

Description of the Cell. The density cell requires the following characteristics: (a) a great weight to impart considerable inertia with respect to the vibrating tube and to reduce the influence of external vibrations; (b) good rigidity and tightness in order to isolate perfectly the oscillator from pressure variations; and (c) the possibility to regulate the cell with 10^{-3} d° .

The cell, represented in Figure 3, is obtained from a cylinder of brass selected for its high density and its good thermic conductivity. In its center and its upper part, there is a compartment in which are set the vibrating tube A, the reference quartz B, and the two exciting coils C. The tube is attached in front of this part, and a tight pin for electrical connections is held behind. We have selected a glue resistant to shear vibrations and thermal effects. The compartment is isolated from external pressure by a Plexiglas cap screwed on a toric joint. The coils are rigidly held with two staples. The circulating, thermostated water passes through the Plexiglas cap and the jacket surrounding the oscillator compartment. The size of this jacket is great enough to ensure good circulation. A quartz thermometer probe is introduced at the outlet of the cell.

The natural oscillating period of the tube is about 4 msec. For our experiments, we have generally used a 1-MHz reference quartz well thermostated inside the cell.

The frequency meter included in the original Anton Paar densimeter has a resolution of 10 μ sec, and to get a precision of 10^{-6} g/ml on the density, it is necessary to measure about 4×10^4 periods, which corresponds to a time of 135 to 200 sec. We have also used as detector a Metrix frequency meter DX 446 A with a 100-nsec resolution and equipped with a reference quartz of 10-MHz frequency. We thus are able to obtain the same accuracy averaging only 4×10^3 periods (3 sec) if the room temperature is maintained constant with a precision of 1° .

Performance of the Cell. The reproducibility of the measurements is about 20 μ sec for a counting time of 150 sec. In a space of time of about four months, we have observed a discrepancy of 130 μ sec on the mean value of the period, which does not correspond to systematic errors or to a possible drift of the apparatus. This incertitude may be simply due to impurities in the water used for calibration from time to time.

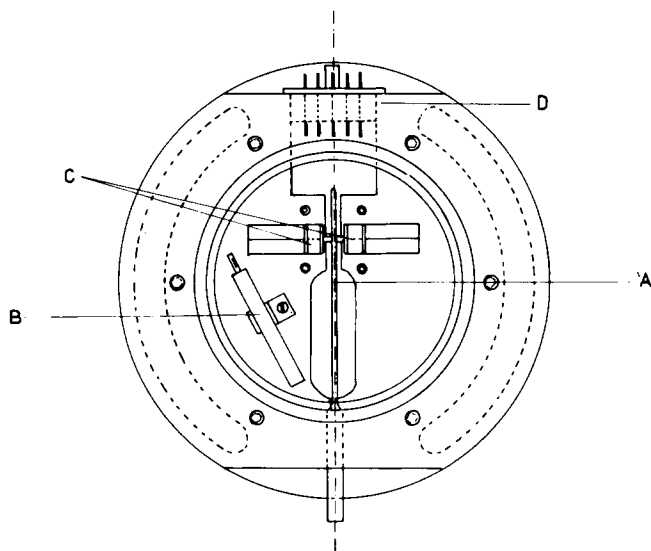


Fig. 3. Design of the cell.

Calibration

Test of the Calibration Law $T^2 = A + kd = f(d)$. We have checked the validity of this law in a density range from 10^{-3} to 2 g/ml. In Table II are reported the different values obtained with two oscillator tubes; we used for this purpose liquids of well-known densities and spectroscopic-grade purity. The curve $T^2 = f(d)$ can be considered linear. The differences between experimental values and the straight line drawn, determined by the least-squares method, are lower than 10^{-4} g/ml and seem to be statistical. Moreover, the curve fitted with a higher polynomial degree does not provide better results. Let us note here that this discrepancy is of the same order of magnitude as found for the differences in the density value of a pure liquid reported in the literature.

Kratky et al. calibrate the densimeter with water and atmospheric air, and Picker et al. with aqueous sodium chloride solutions at 25°C in a concentration of 0.2M. We have used the Kratky method, justified by the preceding results. The density of water is well known within an accuracy of 1×10^{-6} g/ml, and that of moist air can be calculated from the atmospheric pressure and relative humidity with a precision of 1×10^{-7} g/ml. The constant's value is equal to 6306.3 ± 0.2 at 25°C.

Variations with Temperature of Constants A and K. Repeated temperature variations between 4° and 60°C have shown that value of K , determined for 25°C, remains constant with an accuracy of 2×10^{-5} . Successive measurements then have allowed us to confirm the stability and the reproductibility of K at every temperature. Figure 4 shows the variation of K with temperature. We have established an equation of K versus temperature with a third-degree polynomial regression which accounts for all the experimental values with a precision of 0.02%. In the same way, we have determined an algebraic expression for the A term of the calibration eq. (1) and obtained the following equation relating T^2 to D :

$$T^2 = (18416.36 - 1.0106t - 0.032t^2 + 0.0006t^3) + (6317.69 - 0.4429t - 0.0035t^2 + 0.0001t^3)d \quad (3)$$

This result demonstrates the great stability of our cell with respect to temperature and time variation. We have tested the validity of this relationship over several months, and it should be emphasized that it provides the density value directly, without fastidious and numerous calibration experiments.

TABLE II
Experimental and Calculated Values of the Vibration Period Determined by the Least-Squares Method versus Densities of Various Liquids

Compounds	Experimental period T , sec	Calculated period T , sec	Density d at 25°C, g/ml
Water	157.09014	157.08415	0.997075 ⁴
Heavy water	159.22938	159.22665	1.10445 ⁵
Hexane	150.06654	150.05054	0.6548 ^{7,8}
Carbon tetrachloride	168.46742	168.46943	1.58434 ⁵
Air	135.60448	135.60890	0.0011687 ⁶
Benzene	154.56191	154.57859	0.8733 ⁹
Cyclohexane	152.54118	152.54284	0.7748 ⁹

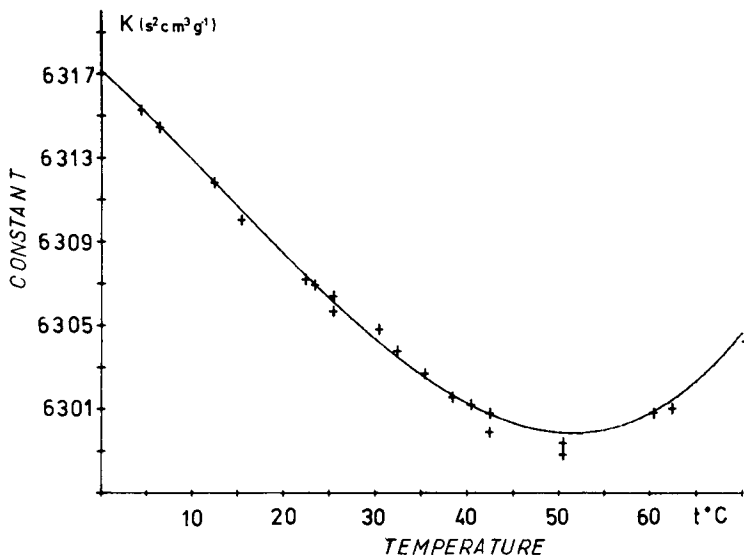


Fig. 4. Variation of constant K vs temperature t : (x) experimental points; (—) calculated curve.

APPLICATIONS OF THE APPARATUS TO THE STUDIES OF POLYMERS

The accuracy of the measurements obtained with the densimeter let us to detect low variations in concentration of a solute and small volume changes. We will give here two examples in which we have used its great performance in the field on macromolecular studies.

The first example is relative to the measurement of the self-diffusion coefficient of heavy water through membranes. The second concerns the measurement of apparent specific volume of polymers in very dilute solutions. In addition, this density cell has been adapted as detector at the outlet of a gel chromatography apparatus. This will be reported in the next communication.

Measurements of Permeability of Self-Diffusion of Heavy Water Through Membranes

Radioactive tracers such THO are generally used for the study of the self-diffusion coefficient of water through membranes.¹⁰ In order to avoid the difficult manipulation of a volatile radioactive substance, the use of heavy water is sometimes preferred. Some authors,¹¹ for example, have used spectroscopic detection to measure the concentration of the diffusing species. In our case, we have determined this concentration with the densimeter, and we shall describe the experimental arrangement and give some preliminary results obtained with grafted poly(vinyl alcohol) membranes.

Experimental Arrangement

The experimental arrangement schematized in Figure 5 is similar to that described by Klein, Smith, and Wendt.¹¹ The membrane is placed in a Plexiglas

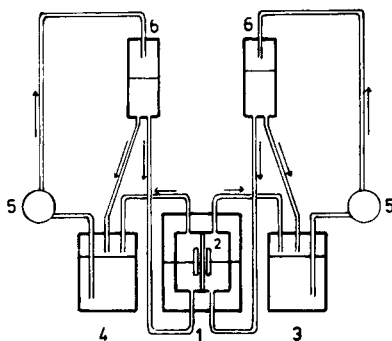


Fig. 5. Schematic representation of the dialysis device for measurement of D_2O self-diffusion permeability of membrane: (1) diffusion cell; (2) stirrers; (3) H_2O reservoir; (4) $D_2O + H_2O$ reservoir; (5) pumps; (6) reservoir.

cell of which each chamber has a volume of 25.5 cm^3 . A nylon screen is used as membrane support. Vigorous stirring assures the homogeneity of the solutions and reduces the thickness of the diffusing layers on the two faces of the membrane.

The total volume of liquid (250 cm^3) on each side circulates in the cell by gravitation from reservoirs 6. In order to equilibrate the hydrostatic pressure on the membrane, the levels of the two solutions were carefully adjusted according to their density difference. The circulation rate is great enough to consider the whole solution as homogeneous (4 l./min) and is obtained with the centrifuge pumps 5.

Procedure and Materials

The preparation and characterization of the grafted poly(vinyl alcohol) membranes are published elsewhere.¹² The purity of the heavy water is 99.4%. The weight concentrations of heavy water of the solutions are between 0.20 and 0.30 g/g, and the experiments were so designed that the total change in heavy water concentration was not more than 1% of the original concentration. Samples (2.0 cm^3) were taken at 30-sec intervals and their densities were measured at 25°C , with temperature fluctuations lower than 0.002°C . All the diffusion experiments were carried out at 25°C in a thermostated room.

The weight concentration W_H of heavy water of each sample is calculated, assuming the additivity of molar volumes of the two kinds of water, from the following relationship:

$$W_H = \frac{1/d_w - 1/d_s}{1/d_w - 1/d_H}$$

where d_s represents the density of the solution, and d_H and d_W are those of heavy water and pure water (H_2O), respectively. The d_H and d_W values are those given in Table II.

Since the conditions of steady state are realized in our experiments, we can use Fick's first law for diffusion across a membrane:

$$J = -P(C_2 - C_1) = -P \Delta C$$

where J is the solute flow, and C_2 and C_1 are the concentrations of the diffusing

species, on either side of the membrane (in our case $C_2 \approx 0$). The slopes of the plot of the total amount M of D_2O passing through the membrane versus time t let us calculate the permeability P .

Two examples of experiments carried out with the same sample membrane are represented in Figure 6 and correspond to two different values of ΔC . The plots of M versus t are linear according to Fick's law, in spite of the inaccuracy of the zero time. Since the mean dispersion of experimental points is lower than 0.01 g, we could obtain a precision of the permeability much better than 5%, if the measurements of thickness and surface of the membrane did not introduce other appreciable errors. In this case, the two experiments provide P values of 4.65 and 4.73 cm^2/sec .

Thus, this method is well adapted to the study of water transport through

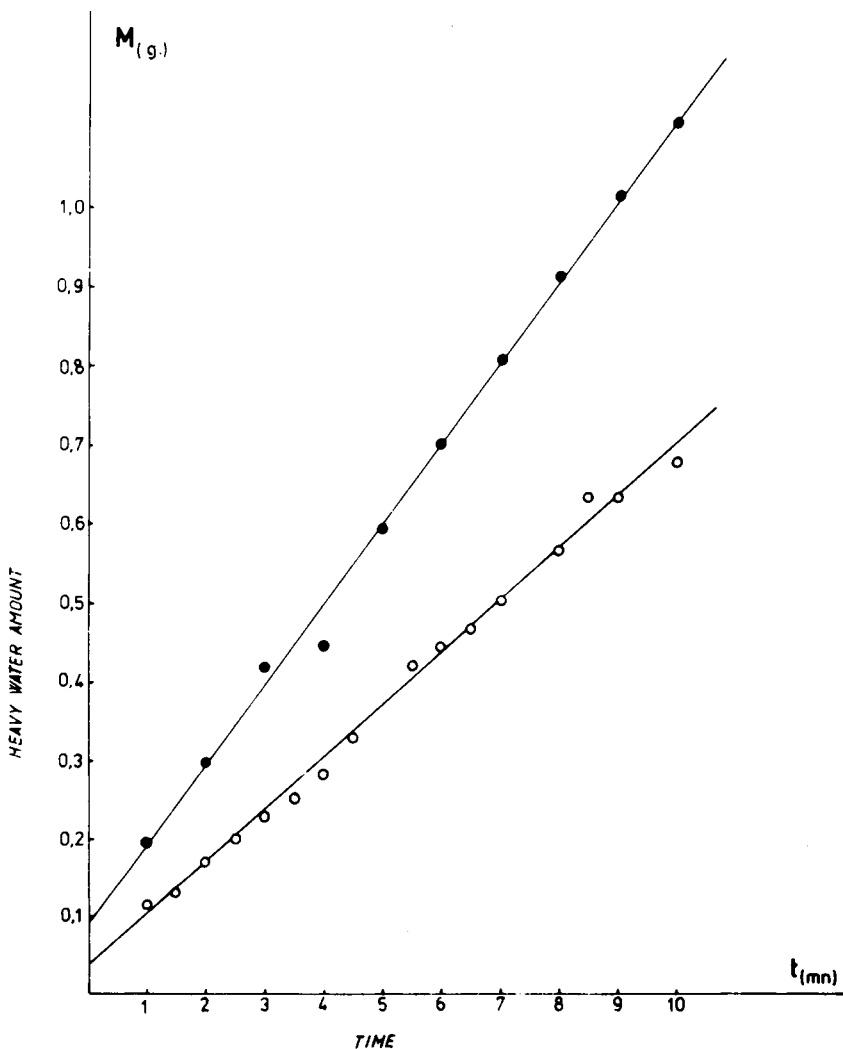


Fig. 6. Amount of heavy water crossing through alkylated poly(vinyl alcohol) membranes vs time. Reference membrane: PVA 18-6, thickness 13×10^{-4} cm, surface 12.56 cm^2 . (●) Initial concentration of feed solution in D_2O , 0.41 g/cm^3 ; permeability, 4.73×10^{-7} cm^2/sec . (○) Initial concentration of feed solution in D_2O , 0.25 g/cm^3 ; permeability, 4.65×10^{-7} cm^2/sec .

membranes. In the particular case of these derivatives of poly(vinyl alcohol), containing numerous hydroxylic groups and in similar cases, it eliminates the perturbations due to the fast isotopic exchange, in contrast to the radioactive tracer methods. One can use the densimeter as detector in diffusion processes for all species and when others detection techniques (spectroscopy, refractometry, etc.) fail.

Measurement of Apparent Specific Volume of Polystyrenes in Very Dilute Solutions

We are concerned with apparent specific volume ϕ_2 of polystyrene¹³ and particularly with the influence of the concentration; ϕ_2 is defined by the classical relationship

$$\phi_2 = V_1 + \frac{V_{12} - V_1}{\omega_2}$$

where $v_{12} = 1/d_{12}$, d_{12} being the solution density; $v_1 = 1/d_1$, d_1 being the solvent density; and ω_2 the weight concentration of the polymer.

The accuracy on the determination of the apparent specific volume depends on the concentration precision. In order to avoid the preparation of too important quantities of solutions, for the very small concentrations and to keep a relative concentration precision of 10^{-3} , we have set up a device schematized in Figure 7, in which we have combined densitometric and refractometric measurements.

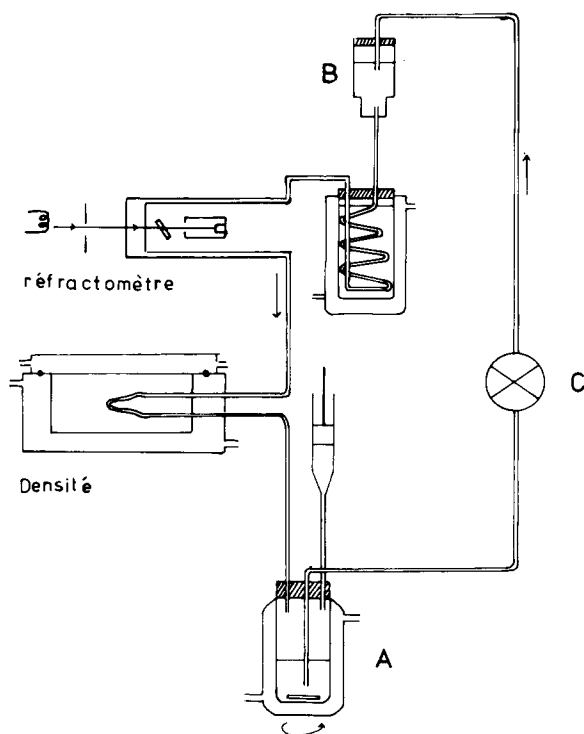


Fig. 7. Design of the device for measurements of flow.

Experimental Device

The liquid introduced in A located in the lowest level circulates through the densimeter and the refractometer Waters-Waters by gravitation from B supplied at a constant level with a gear pump. The studied solution passes through a coil of metal tube immersed in a thermostated liquid before entering the density cell which used the same thermostat circuit as A and B. We start the measurement with pure solvent (20 ml) and successively add finite volumes of polymeric solution determined within an accuracy of 10^{-4} ml.

Preliminary Results

A previous work¹³ has shown the influence of the intramolecular concentration inside the macromolecular coil on the apparent specific volume of polystyrenes of various molecular weights and structures. It is in good agreement with others studies concerning the thermodynamic properties of polymers in solution. However, all the measurements of ϕ_2 have been carried out for a range of concentrations between 0.2% and 2%. It is clear that this range does not correspond to the same concentration range for polymers of molecular weights varying between 5×10^3 and 10^7 , and it is consequently difficult to determine the relative participation of the intramolecular and intermolecular contacts.

It was thus of interest to study the variation of ϕ_2 in the whole range of concentrations, and we shall give here some preliminary results concerning the dilute solutions. Our polystyrene samples were prepared by anionic polymerization and their molecular weights are, respectively, 1.4×10^6 – 1.4×10^4 and 5×10^3 for samples 1749–1770 and 1903.

In Figure 8, we have reported the variation in density of the polymeric solution versus the concentration expressed in g/g, for PS 1770 and 1903 in benzene at 25°C. These plots are only linear V for concentrations larger than 0.2%, and this corresponds to the variation of ϕ_2 versus ω_2 , which is represented in Figure

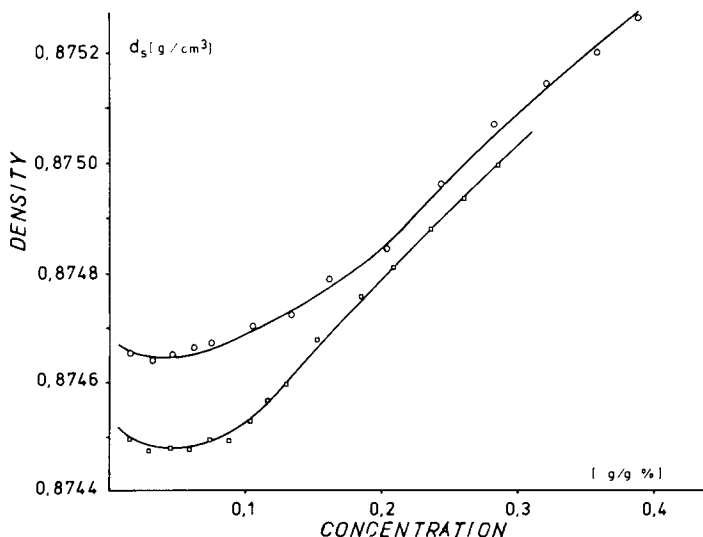


Fig. 8. Solution density vs concentration ω_2 for two polystyrene samples: (○) PS 1770; (□) PS 1903.

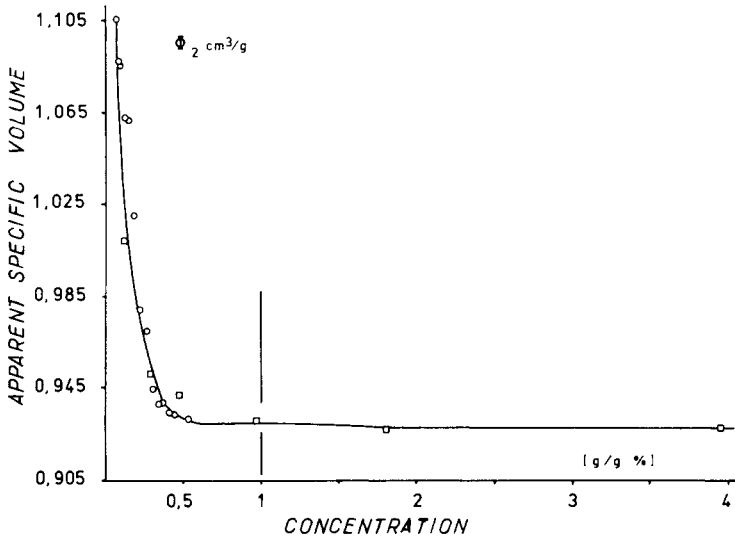


Fig. 9. Apparent specific volume vs concentration: (O) flow measurements (dn/dc); (□) static measurements (ϕ_2) PS 1770.

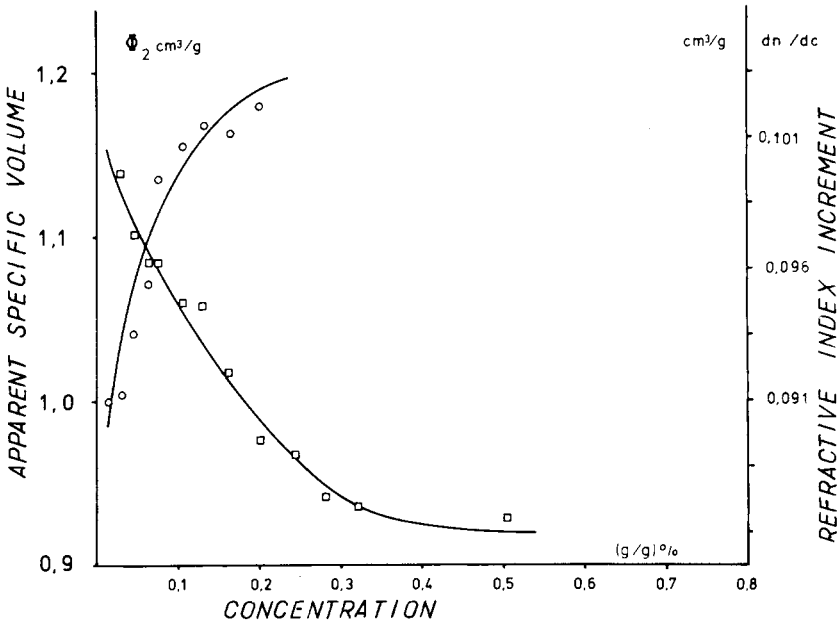


Fig. 10. (□) Apparent specific volume and (O) refractive index increment vs concentration ω_2 . PS 1770.

9. We can note the very good agreement between two experiments carried out with polystyrene 1770.

For concentration lower than 0.5%, the apparent specific volume increases when ϕ_2 tends to 0, and the magnitude of this effect is very surprising. Nevertheless, the measurements of the refractive index increment in the same range of concentrations are in good agreement with density determinations, as shown in Figure 10.

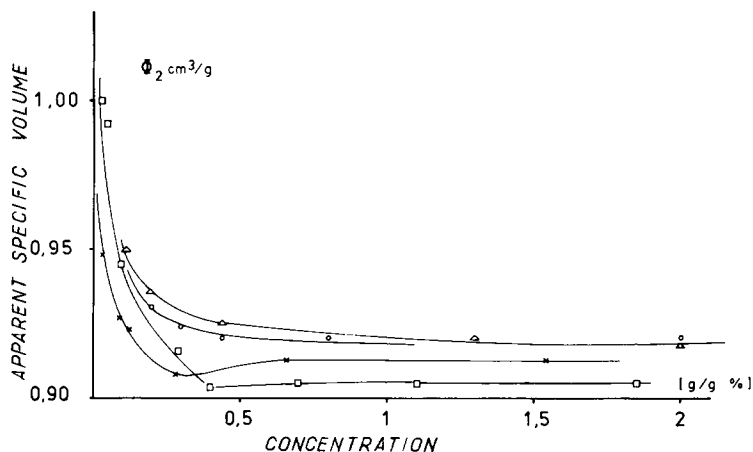


Fig. 11. Comparison between Rosen's¹⁴ results and ours. Rosen: PS 9.55 10^5 (Δ) chloroform; (O) toluene. Polystyrene 1749: (\square) benzene; (\times) toluene.

For polystyrene 1749, in solution in benzene and toluene, we have obtained the same results than Rosen,¹⁴ who studied a polystyrene sample of 9.55×10^5 molecular weight in chloroform and toluene (Fig. 11). These results are discussed elsewhere from a thermodynamic point of view.¹⁵

CONCLUSIONS

This density cell, adapted to the Kratky apparatus, let us obtain the same accuracy (2×10^{-6} g/cm³) for density determination than the flow densimeter conceived by Picker et al.³ It still retains the advantages of the original Kratky cell, its volume requirement being only 1.2 ml liquid and the glass oscillator being inert to almost all chemical systems. Our systematic investigations of its performance have shown that its design confers a great stability with respect to all temperature and time variations.

This instrument opens the door to numerous studies either as concentration detector in kinetic processes (diffusion, GPC, chemical reactions) or for the thermodynamic measurements of volumes changes.

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