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Compressibility of Colloids: II. Compressibility Studies of Tri-block Non-ionic Polymers in Toluene and Water Solutions

by

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**COMPRESSIBILITY OF COLLOIDS: II. COMPRESSIBILITY STUDIES OF TRI-BLOCK NON-IONIC POLYMERS IN TOLUENE AND WATER SOLUTIONS**

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**ABSTRACT**
Ultrasonic velocity measurements were made on a series of Pluronics i.e. tri-block non-ionic co-polymers of poly(ethylene oxide) poly(propylene oxide) poly(ethylene oxide) in solvents showing near ideal and non-ideal behavior. Aqueous solutions of the Pluronics studied show non-ideal behavior, namely non-linear apparent compressibility as a function of Pluronic concentration. This non-ideality is thought to arise from aggregate formation. This is confirmed by laser light scattering measurements. Those polymers...
that dissolved in toluene showed near ideal behavior enabling us to determine intrinsic compressibilities of hydrophobic and hydrophilic blocks as $4.9 \times 10^{-11}$ dyn/cm$^2$ and $3.9 \times 10^{-11}$ dyn/cm$^2$ respectively. The volume fraction of the bound water per segment of poly (ethylene oxide) is estimated and found to be dependent on the segment population. The mathematical treatment presented in this paper stems from that of Shiio, but goes further to define possible limits to the true compressibility, volume and density of bound water rather than making the assumption that no contraction of the water occurs.
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I. Introduction

In part I of this series we have shown that an association-dissociation type chemical reaction between colloid and counter ion may give rise to an additional dispersive contribution to the adiabatic compressibility of a colloidal dispersion. Coating the particle-electrolyte interface with an amphiphilic polymer decreased this excess compressibility presumably by suppression of an association-dissociation type chemical reaction due to dipole-ion interactions between polar moieties of the absorbed block co-polymer and the ionic end groups of the polymer colloid. However, the decrease may also be explained on the basis that the amphiphilic polymer is strongly adsorbed on the basically hydrophobic particle surface with its hydrophobic segments anchored to the surface, resulting in a more rigid structure. The use of an interface with net ion charge should be avoided for such studies if one wishes to determine the compressibility of adsorbed polymers unambiguously.

A liquid-liquid interface may be considered an ideal substrate for such studies. Emulsions with high surface area of oil-in-water (o/w) or water-in-oil (w/o) of various immiscible liquids can be prepared with amphiphilic polymers to be studied as emulsifiers. Selection of a stable (in the sense of colloidal stability) model system for a high surface area liquid-liquid interface is not simple.

Micro-emulsions and macro-emulsions prepared with mixed surface active and ionic surface active agents were excluded as
model systems. Ionic surface active agents may exhibit a chemical relaxation between counter-ions and polar heads and hence complicate the measured compressibility.

In the study to be reported in part III of this series of studies, non-ionic block co-polymers of poly(ethylene oxide) - poly(propylene oxide) - poly(ethylene oxide), A - B - A tri-block type (the hydrophobic portion in the center and the hydrophilic portions at both ends) were used as emulsifier for toluene in water emulsions. Their ample solubility in both toluene and water facilitates acoustic study of their behavior (compressibilities) in either medium. At the present time, knowledge concerning the conformation of non-ionic copolymers at the oil/water interface is very limited.

However it is generally assumed\textsuperscript{2,3} that interactions between the hydrophilic and hydrophobic portions of the emulsifying molecule not only determines the radius of curvature of the oil/water dispersion, it also determines the stability of it. Therefore, it will be very informative to study the interaction between oil and water soluble segments of the emulsifier by measuring their compressibilities in both liquids as a function of concentration. These results are presented here as part II of this series.

The compressibilities of water and oil soluble portions of the emulsifier can then be compared with the three dimensional surface compressibilities of the emulsion globules prepared with the same emulsifier.
II. Theoretical

The apparent molar compressibility (adiabatic) of a solute \( \phi_K \) is defined as:

\[
\phi_K \, CV' = \beta V' - \beta_0 V'_0
\]  

(1)

where \( C \) is the concentration of the solute as moles/liter, \( \beta \) is the compressibility of the solution, \( V' \) is the volume of the solution, \( \beta_0 \) is the compressibility of the pure solvent and \( V'_0 \) is the volume of the solvent if its density were that of the pure state. This is related to the specific apparent compressibility \( \phi_k \) by:

\[
\phi_K C = \phi_k \, c
\]  

(2)

where \( c \) is the concentration of the solute in grams/cm\(^3\). We can write

\[
V' \phi_K \, c + V' \beta_0 = \beta V'
\]  

(3)

Dividing the above equation by the total volume of solution and substituting \( \beta_{app} \cdot \phi_V \) for \( \phi_K \), where \( \beta_{app} \) is the apparent compressibility of the solute, we obtain:

\[
c \beta_{app} \phi_V + V_0 \beta_0 = \beta
\]  

(4)
$V_0$ is the volume fraction of solvent and can be determined from $V_0 = (\rho - c)/\rho_0$, while $\beta$ can be determined from the velocity $U$ and density measurements by means of $\beta = 1/(\rho U^2)$.

Following Shiio's model considering the compressibility of the bound water $\beta_2$ and true compressibility $\beta_1$ and true volume $V_1$ of solute, the total volume $V'$ of the solution can be written as:

$$V' = V'_0 + V'_1 + V'_2 - V_0$$  \hspace{1cm} (5)

A portion of the solvent of volume $V'_0$ will be attached to the solute and compressed to a smaller volume $V'_2$. Using the same line of thought for the corresponding compressibilities, and again converting volumes (primed quantities) to volume fractions, eq (4) can be written as:

$$\beta_{\text{app}} = \phi_V + \beta_0 V_0 = \beta = V_1 \beta_1 + V_0 \beta_0 + V_2 \beta_2 - V_0 \beta_0$$  \hspace{1cm} (6)

The left hand side of the above equation expresses the total compressibility of the solution in terms of normal solvent, while the right hand side expresses it in terms of bound and unbound solvent as well as true compressibility and volume fraction $V_1$ of the solute.

In Shiio's treatment, the solute molecule was treated as a whole. However, in our case, the solute consists of an A - 3 - A type, tri-block co-polymer. The A type block is poly
ethylene oxide. There is considerable evidence in the literature\textsuperscript{5,6} that the interaction between ethylene oxide groups and the water molecules causes a complete conformation change from zig-zag shaped linear polymer strands to what is referred to as "meandering form". The equilibrium angles between the bonds are retained, but the overall length of the strand is considerably contracted (by about 50\%). This contraction probably has associated with it a decrease in volume of the molecule. Therefore the meandering structure may show smaller compressibility.

![Zig Zag Form and Meandering Form](image)

Although Rosch\textsuperscript{5} or Schonfeldt\textsuperscript{6}, in their description of the two conformations, did not discuss compressibility, it is anticipated that the bound water molecules associated with this "meandering structure" will exhibit a smaller compressibility than the unbound and weakly associated water.

If the polymer solution shows ideal behavior when dissolved in a solvent, such as toluene, the apparent molar compressibility of the polymer can be considered the intrinsic compressibility of the substance. If the subscripts $A$ and $B$ refer to poly(ethylene oxide) and poly(propylene oxide) respectively, the volume fractions $V_A$, $V_B$ and compressibilities
$\beta_A$, $\beta_B$ of the blocks can be determined by velocity and density measurements on solutions of a series of polymers with varying proportions of poly(ethylene oxide) content. A value for $\beta_B$ can be obtained by extrapolating the measured compressibility value to 0% POE content. Similarly, the $\beta_A$ value is determined by extrapolating the compressibilities to 100% POE content.

The total specific apparent compressibility of the above mentioned "zig-zag structure" can be expressed as:

$$\phi_k \text{ (zig-zag)} = (V_A\beta_A + V_B\beta_B) \quad (7)$$

As we will show in the results section, solutions of these polymers in toluene fulfilled the conditions of a nearly ideal solution, and the intrinsic compressibility of the polymer was thereby determined.

This treatment of data is not valid for aqueous solutions of these polymers. Attempts to obtain $V_A$ and $\beta_A$ similarly by extrapolating to 100% POE suffers from the complication of the change of form; zig-zag structure to meandering. The meandering structure appears to be more compact than the zig-zag structure and may have a lower compressibility. It is impossible, however, to decide just how much of the change in volume and compressibility is associated with the polymer as compared with that caused by the change in the water structure surrounding the polymer.

The total specific apparent compressibility of the meandering structure can be expressed as;
\[ \phi_k (\text{meandering form}) = V_A \beta_A + V_3 \beta_3 + v_2 \beta_2 - v_0 \beta_0 \quad (8) \]

In this case \( \beta_A \) and \( V_A \) values are not necessarily the same as in the previous case (polymer dissolved in toluene). Rearranging eq. (6) and dividing by \( \beta_0 \) the following equation is obtained.

\[ \frac{1}{\beta_0} (\beta-\beta_0 V_0 - \beta_1 V_1) = v_0 (1 - \frac{v_2 \beta_2}{v_0 \beta_0}) \quad (9) \]

Although it is not possible to determine uniquely the volume fraction and compressibility of all the components, a great deal of further qualitative information can be derived. We may suppose \( V_A \) and \( \beta_A \) retain the values found in toluene and all the bound water (strongly and loosely bound) is considered together. The measurements then give a value for \( v_0 (1 - \frac{v_2 \beta_2}{v_0 \beta_0}) \) through eq. (9). In his treatment Sniio assumed \( \beta_2 \) to be the same as ice \((1.8 \times 10^{-11} \text{ dyn/cm}^2)\). In fact definite upper and lower limits can be set for \( \beta_2 \) in that it must be greater than 0, and second, as \( \beta_2 \) is assumed to approach \( \beta_0 \), the resulting calculated \( v_2 \) and \( v_0 \) increased to infinity. Since no volume fraction can be greater than 1, this effectively sets the upper limit as: \( \beta_2 \leq \beta_0 + (V_0 - v_0 + v_2) \beta_0 + V_1 \beta_1 - \beta \). The value of \( \beta_2 \) also determines the value of the density of the bound water through the relationship expressing volume average of the densities.

\[ v_0 = v_1 \rho_1 + V_0 \rho_0 + v_2 \rho_2 - v_0 \rho_0 \quad (10) \]
where \( \rho, \rho_0, \rho_1, \rho_2 \) are the densities of the solution, pure water, solute, and bound water respectively.

III. Experimental

Sound velocity measurements were made at 2 MHz with a Schall interferometer. All velocity measurements were performed at 25\(^\circ\)C. The temperature was kept constant during measurements within \( \pm 0.02\)^\circ C. Description of the interferometer and the measurements can be found in part I of this series. The velocity results were obtained in the polymer solutions with the accuracy of 0.001% for toluene, and 0.01% for water when used as solvents. The density of polymer solutions as a function of polymer concentration were measured with a Mohr balance to 0.1%. A series of tri-block type non-ionic block co-polymer of poly(ethylene oxide) were obtained from BASF Wyandotte Corporation U.S.A., under the commercial name of Pluronic\textsuperscript{®} polyols. The Pluronics of the code, P103, P104, P105, P75 and P108, P68, P38 and L62 were used during this study. The first letters P, F and L denote paste, flakes and liquid respectively. The last digit of every Pluronic multiplied by 10, gives its approximate % poly(ethylene oxide) in the total molecule, while the preceeding digits are a code for the molecular weight of the poly(oxypropylene). The average molecular weights range from 2,000 to 14,000 was studied. The manufacturer did not provide any information about the distribution around the average molecular weight of a given Pluronic.
Commercial ethylene oxide condensation products may show either a narrow or wide distribution of molecular weights for each block depending on the conditions of manufacturing. It was found during the solution preparation of Pluronics in water and toluene that while some Pluronics contain toluene insoluble fractions, some others contain water insoluble materials. For example, P103 yields complete solution in water, while it left an estimated 2% of the total weight insoluble residue in toluene. We attribute this behavior to a distribution of molecular weight of these samples. All Pluronics were used without further purification or fractionation.

IV. Results and Discussion

Solutions of various Pluronics were made using toluene and water as solvents, each in a range of concentrations generally from 1 g Pluronic/liter to 200 g/liter. The densities of these solutions were measured at a constant temperature. Within the accuracy of our measurements, (±0.001 g cm\(^{-3}\)) the density of polymer solutions in both water and toluene varied linearly with concentration. However, a comparison of the density measurements in the two solvents yield significantly different apparent specific volumes. The density values given by the manufacturer for the pure Pluronics are in reasonable agreement with those determined in toluene. The results are given in Table I. The smaller specific volume in water reflects the fact that either there is water in compressed state associated with the
hydrophilic portion of the molecule or the "meandering structure" takes up a smaller volume. In the zig-zag structure the former is likely to be the main contributor to this effect.

TABLE I

The apparent specific volumes, $\phi_v$ (cm$^3$/g) of various Pluronics in water and toluene and in pure form. Unless otherwise stated these are for 25°C.

<table>
<thead>
<tr>
<th>Pluronics molecular wt</th>
<th>% POE</th>
<th>$\phi_v$(water)</th>
<th>$\phi_v$(toluene)</th>
<th>$\phi_v$(pure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P103 4950</td>
<td>30</td>
<td>0.932</td>
<td>0.957</td>
<td>0.96*</td>
</tr>
<tr>
<td>P104 5850</td>
<td>40</td>
<td>0.913</td>
<td>0.948</td>
<td>0.96*</td>
</tr>
<tr>
<td>P105 6500</td>
<td>50</td>
<td>0.914</td>
<td>0.940</td>
<td>0.95*</td>
</tr>
<tr>
<td>F108 14000</td>
<td>80</td>
<td>0.866</td>
<td>-----</td>
<td>0.94**</td>
</tr>
<tr>
<td>F38 5000</td>
<td>80</td>
<td>0.860</td>
<td>-----</td>
<td>0.93**</td>
</tr>
<tr>
<td>F68 8350</td>
<td>80</td>
<td>0.866</td>
<td>-----</td>
<td>0.94**</td>
</tr>
<tr>
<td>P75 4150</td>
<td>50</td>
<td>-----</td>
<td>0.942</td>
<td>0.94*</td>
</tr>
</tbody>
</table>

* calculated from density values given at 60°C
** calculated from density values given at 77°C

Taking a series of Pluronics with varying fractions of poly(ethylene oxide), (or POE) we can extrapolate the reciprocal specific volume results to obtain the apparent specific volumes of pure POE and pure poly(oxypropylene) (POP) as shown in Fig. 1
Fig. 1. Reciprocal apparent specific volume, $1/\rho_v$, of various Pluronics in water (upper curve) and toluene (lower curve) as a function of poly(oxyethylene) fraction in the polymer.
for both water and toluene. The extrapolated values representing the pure POP should ideally be the same in both toluene and water, no interaction is expected between POP and toluene. However, velocity measurements on solutions of Pluronics in toluene have shown that there is a small but observable interaction between toluene and Pluronics. The extrapolated values of $1/\phi_v$ from toluene and water solutions, or "apparent density", of POP are 1.0168 and 1.0243 g/cm$^3$, or in terms of apparent specific volume, 0.9834 and 0.9763 cm$^3$/g respectively. Likewise extrapolating to pure POE we find densities of 1.1108 and 1.1843 g/cm$^3$ for toluene and water respectively, or 0.9003 and 0.8444 cm$^3$/g respectively.

The velocity of sound at 2 MHz as a function of concentration of P105 and P75 in toluene are given in Fig. 2, along with the theoretical curve assuming ideal behavior; i.e. taking volume average densities and compressibilities. It can be seen that the fit of the experimental data to the theoretical curve are good, but not perfect. All the other Pluronics dissolved in toluene used in this study gave similar curves.

The data can also be represented by plots of apparent compressibility $\beta_{\text{app}}$ as a function of concentration, as in Fig. 3. The scatter of points at the low concentrations is due to the fact that small errors in density or velocity measurements are magnified in such compressibility plots. The apparent compressibilities of the solutes are essentially constant at concentrations up to 250 g/liter, indicating near ideal behavior.
Fig. 2. The velocity of sound at 2 MHz as a function of concentration of P105 and P75 in toluene, along with the theoretical curves assuming ideal behavior. Calculations were made taking volume average densities and compressibilities. Solid line: theoretical curve for P105, dashed curve for P75. Experimental points: □ - P105, X - P75.
Fig. 3. Apparent compressibility, $\beta_{app}$ of various Pluronics in solutions of toluene as a function of concentration.

- $\square$ - P105, $\Delta$ - P104, $\triangledown$ - P103, $\times$ - P75.
The velocity data for solutions of Pluronics in water are treated similarly. An example of velocity versus concentration of P105 is shown in Fig. 4. Unlike the toluene data, deviation from ideal behavior is very pronounced. The shape of the velocity curve is typical for molecules showing solute-solute and solute-solvent interactions, such as solutions forming micelles.

The plots of apparent compressibilities of P103, P104, P105 and P103 are given in Fig. 5. Excluding P108, the others show a steep rise with concentration up to about 40 g/liter, which tailed off at high concentrations. In the high concentration region there is a trend towards higher compressibility with decreasing POE content in the molecule. Laser light scattering results on a sample of P105 at a concentration of 40 g/liter in water indicated formation of monodisperse aggregates of 250 Å diameter. As polymer containing POE comes in contact with water it immediately converts from zig-zag form to "meandering structure", incorporating strongly bound water of reduced compressibility. This behavior is unique to POE with the minimum polymerization number of 9. The Pluronics which have been investigated all have at least 15 contiguous segments. In addition to this tightly bound water it is reasonable to assume the presence of more loosely bound water. It is also assumed that POP interacts much less with water since Pluronics with less than 20% POE do not dissolve in water. As the concentration of polymer is increased, the POP portions of the molecules will associate. This results in micelle-like
Fig. 4. The velocity of sound at 2 MHz as a function of P105 concentration in water, along with the theoretical curve assuming ideal behavior. Calculations were made taking volume average densities and compressibilities.
Fig. 5. Apparent compressibility, $\beta_{app}$ of various Pluronics in solutions of water as a function of concentration. Compressibility values obtained at 2MHz, 25°C.
aggregates, with the POP's inside and POE segments protruding out into the water phases.

There has been some conflicting evidence reported in the literature\(^7,8\) as to whether micelles form in aqueous solutions of the Pluronics, including those involved in this present study. Schmola\(^7\) has concluded, mainly on the basis of dye absorption experiments, that micelles form, with the CMC (critical micelle concentration) at around 0.3 g/l. Pluronics containing 80% POE (such as F38, F68 and F108) only form dimers\(^9\). In this work, velocity measurements were made on aqueous solutions of these polymers as a function of concentration and the \(\theta_{app}\) curve vs. concentration (see Fig. 6) showed no evidence for aggregate formation. At very high concentrations, X-ray diffraction studies show that water molecules contribute to an interaction between POE chains, forming lamellar or cylindrical structures\(^10,11\). The viscosity reaches a maximum when the ratio of water molecules to oxygen of the POE segments is approximately 2 to 1 \(^12\). During the aggregation process much of the loosely bound water is squeezed out, but tightly bound water incorporated in the meander structure will remain. As is normal for micellar solutions, increasing the concentration of polymer molecules beyond the critical micelle concentration increases the number of aggregates but not their size or structure, while the concentration of unassociated polymer molecules remains virtually constant and becomes insignificant compared to aggregates. Thus the proportion of tightly bound to loosely
Fig. 6. Apparent compressibility $B_{app}$ of several Pluronic containing 80% POE, in aqueous solutions as a function of concentration.
bound water increases and levels off at higher concentrations.

F108 differs from the others due to the fact that 80% of the polymer consists of POE. At concentrations above 100 g/liter it forms gels and meaningful measurements cannot be performed. From Fig. 5 there appears to be less interaction between F108 molecules within the concentration range in which velocity measurements were performed. Other Pluronics with 80% POE (F38 and F68) were found to be similar in this respect (Fig. 6) reinforcing the conclusion of Cowie\textsuperscript{9}.

For P103, P104 and P105 polymers, the high concentration apparent compressibility values are extrapolated to infinitive dilution using the data of Fig. 3 and Fig. 5. This is done so that one can eliminate the contribution due to the aggregate-aggregate interaction. This is a minor effect in toluene. Along with these values, the intercepted compressibilities for all three polymers from toluene solutions data are plotted as a function of POE percentage. Results are given in Fig. 7. Both sets of points fall on straight lines. For zero percent POE block, both lines merge at the same intercept of $4.9 \times 10^{-11}$ dyn/cm$^2$ of apparent compressibility. The compressibility value for POE segments can be obtained in principle from the intercept of the toluene data line to 100% POE, which yields $3.9 \times 10^{-11}$ dyn/cm$^2$. We believe that this value represents the compressibility of the zig-zag formed POE, in the absence of water molecules. The volume average of these compressibilities yield the intrinsic compressibility of the POE-POP-POE tri-block co-polymer. The interpretation of the intercept of the line at
Fig. 7. High polymer concentration compressibility values extrapolated to infinite dilution for Pluronics with various poly(ethylene oxide) POE, fractions. X and □ represents toluene and water solutions respectively. The data point + is for another Pluronic L62 which, being in the liquid state, could be measured in pure form.
the 100% POE for water solutions is not so clear cut, but can be
considered to give the value of the apparent compressibility of
the meander structure of POE which includes its tightly bound
water, along with the amount of loosely bound water associated
with aggregates. On the assumption that there is no alteration
of volume and intrinsic compressibility on conversion to the
meander form, the quantity \( v_0\left(1 - \frac{v_2}{\beta_0 v_0}\right) \) was calculated for
all the aqueous solutions from the measurements. If we assume
that the bound water has the compressibility of ice, i.e. \(1.8 \times \)
\(10^{-11}\) dyn/cm\(^2\), corresponding values of \(v_2\) can be estimated per
segment of POE. These are plotted in Fig. 8. Ideally the \(v_2\)
values for various Pluronics might be expected to coincide. The
fact that the Pluronics with higher percentage of POE will have
the longest chain length protruding in the water, i.e, in a
configuration less densely packed results in it retaining more
loosely bound water.

The possible range of \(\beta_2\) is from 0 to \(4.2 \times 10^{-11}\) dyn/cm\(^2\)
as explained in the previous section leading to a possible range
of \(v_2\) from \(3.97 \times 10^6\) to \(7 \times 10^{-2}\) cm\(^3\) per segment. This further
defines a possible range of densities, \(\rho_2\), for the total bound
water, from 1.0025 to 1.090 g/cm\(^3\).

V. Conclusion

Ultrasonic compressibility measurements are very sensitive
to the molecular configurations of the tri-block non-ionic
copolymers in solvents showing ideal and non ideal behavior.
Fig. 8. Volume of bound water per gram of poly(ethylene oxide) as a function of concentration of various Pluronics, assuming the bound water has the compressibility of, $1.8 \times 10^{-11}$ dyn/cm$^2$. 
The Pluronics studied in this work showed a very pronounced non-ideal behavior in aqueous solutions indicating aggregate formation. This is confirmed by laser light scattering measurements. Those polymers that dissolve in toluene showed near ideal behavior enabling us to determine intrinsic compressibilities of hydrophobic and hydrophilic blocks. The volume fraction of the bound water per segment of poly(ethylene oxide) is estimated and found to be dependent on the segment population. The treatment presented in this paper stems from that of Snijio, but goes further to define possible limits to the true compressibility, volume and density of bound water rather than making the assumption that no contraction of the water occurs.
LIST OF SYMBOLS

C = Concentration of the solute as moles/liter

c = Concentration of the solute as grams/cm³

U = Velocity of sound in the solution

V' = Volume of the solution

V'₀ = Volume that would be taken up by equal amount of pure solvent

V₀ = Volume fraction of V₀

V₁ = True volume of solute

V₁ = True volume fraction of the solute

V₂ = True average volume of the bound water

V₂ = True average volume fraction of the bound water

V'₀ = Volume of the same amount of unbound water

V₀ = Volume fraction of V₀

Vₐₐ = Volume fraction of poly(ethyleneoxide)

V₃ = Volume fraction of poly(propylene oxide)

βₐₐₚ = Apparent compressibility of solute

β₁ = True adiabatic compressibility of the polymer

β₀ = Compressibility of the pure solvent

β₂ = Volume average compressibility of the strongly and loosely bound water

βₐₐ = True compressibility of poly(ethylene oxide)

β₃ = True compressibility of poly(propylene oxide)

ρ = Density of solution

ρ₀ = Density of solvent

ρ₁ = Density of the solute

φₖ = Apparent molar compressibility of the solute

φᵥ = \( \frac{(\rho₀ - \rho - c)}{(c \rho₀)} \) apparent specific volume, cm³/g

φₖ = Specific apparent compressibility of solute
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12- Rosch, M., Kolloid-Z. 147, 78 (1956).
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