CORRECTION OF FLOTATION COEFFICIENTS, 
DERIVED FROM ULTRACENTRIFUGATION, FOR 
PRESSURE AND CONCENTRATION

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Abstract—Flotation coefficients are usually determined from data obtained under high pressure (cell 
bottom) conditions. A power series expansion is proposed for correction to atmospheric pressure 
(meniscus) conditions. The same expansion may be applied to the concentration correction of flotation 
coefficients.

From sedimentation experiments with polymer sol-
solutions in the analytical ultracentrifuge, we can derive 
sedimentation coefficients of the polymeric com-
ponent. A widely applied procedure is to identify the 
sedimentation coefficient with the slope of the best 
straight line through the data points In x* and 
2ω²t 
(where ω = angular speed in radians per second, 
t = time in sec, x* = r*/r, r* = distance of the top 
of the Schlieren peak to the centre of rotation, 
r m = distance of the meniscus to the centre of rota-
tion).

This procedure leads to sedimentation coefficients 
which depend on the concentration, and are not cor-
corrected to the pressure at the meniscus (where 
p = 1 atm.). We will denote such an uncorrected sedi-
mentation coefficient by s. Several procedures have 
been developed to obtain "true" sedimentation coeffi-
cients, corrected for pressure and concentration [1-4]. 
These procedures apply to dilute solutions.

When the solvent is heavier than the polymer, flota-
tion occurs. Now the boundary layer travels from the 
high pressure region (where the pressure is of the 
order of 100 atm.) at the cell's bottom towards the low 
pressure region near the meniscus. The procedures for 
correction for pressure which apply to sedimentation 
do not hold for flotation. The reason is that correc-
tions for pressure have to be carried out for a region 
in the cell where the boundary layer has not pro-
ceeded "too far" away from its starting point (the 
meniscus, for sedimentation; the bottom for flotation). 
This is connected with the requirement that the time 
parameter τ = 2ω²t (where k = the "true" sedimen-
tation coefficient) should not be "too far" from zero 
[1]. As for t → 0 in the flotation case, the boundary 
is still in the high pressure region; in contrast with the 
sedimentation case, we cannot use the correction pro-
cedures of sedimentation for flotation without appro-
propriate modification.

As far as we are aware, no proposals for the correc-
tion of flotation coefficients (needed for a study on 
permeability [6]) have been published. Pouyet and 
Dayantis [5] suppose for their semi-dilute solutions 
(concentration > say 2%) that the pressure effect 
affects all flotation coefficients to the same extent, i.e. 
as if all the concentrations were multiplied by the 
same (compression) factor. In a plot of log|s| vs log c 
this would result in a shift to the right of the whole 
plot, without any influence on the slope of the straight 
line which is characteristic for the dependence of log 
s on log c in the semi-dilute region. In this paper we 
consider in more detail if the latter conclusions can be 
justified by a less qualitative reasoning. We start from 
the correction procedure of Dishon et al. [1] for sedi-
mentation coefficients obtained in dilute solution.

Dishon et al. [1] wrote the solution of the (diffusion 
free) differential equation describing the sedimentation 
process (the so-called Lamm equation) as a series 
expansion in powers of the time parameter τ. It holds 
only for τ → 0:

\[ \ln x^* = \tau/(\tau + 1) - \frac{(2τ + 1)m - \tau}{2(τ + 1)^3} τ^2 + O(τ^3) \] (1)

where

\[ τ = 2ω²t \]

\[ x = k_s c \ (k_s = \text{concentration effect parameter}) \]

\[ m = \text{pressure effect parameter} \]

(We have not written out the clumsy third power term 
in full; it should not be neglected however.)

The essential point in the derivation of (1) is the 
assumption

\[ s = s(p, c) = \frac{s_0}{(1 + k_c c)(1 - m + m x^*)} \]

\[ = \frac{s(p, 0)}{1 + k_c c} = \frac{s(1, c)}{1 - m + m x^*} \] (2)

where the effects of pressure and concentration are 
separated; s(p, 0) being the pressure dependent sedi-
mentation coefficient corrected to zero concentration, 
and s(1, c) being concentration dependent, but cor-
corrected to meniscus conditions were p = 1 atm.

From equation (1) we can see that correction for 
pressure and concentration can be carried out inde-
pendently. An easy correction for pressure for 
instance is to identify s(1, c) with the initial 
slope of the plot of ln x* vs 2ω²t. The thus obtained s(1, c) can 
be corrected further for the effect of concentration by
plotting \(1/s(1, c)\) vs \(c\). The intercept is \(1/s_0\) and from the slope we can calculate the concentration dependence parameter \(k_s\):

\[
1/s(1, c) = (1/s_0)(1 + k_s c).
\]

(3)

A more precise procedure would be to calculate the coefficients of a cubic polynomial in \((2\omega^2 t)\) by a least squares approximation; the time \(t\) should be taken with respect to a starting time \(t_0\). A good approximation for \(t_0\) is the abscissa intercept of the straight line through \((r^* - r_m)\) plotted vs \(t_i\) (= the time of the \(i\)-th photographed Schlieren peak with respect to the moment when the first peak was photographed).

We applied the method of Dishon et al., with the assumption (2), to flotation essentially by writing the value of their function

\[
h(x^*) = x^*/(1 - m + mq)
\]

where

\[
h = h_{x=0} = q/(1 - m + mq),
\]

and from

\[
1 + m(q - 1)\text{(intercept)}
\]

so from the first and the second coefficient of the cubic polynomial through \(\ln x'\) and \((2\omega^2 t)\). Then we plotted the reciprocals of the first coefficients of the other concentrations vs \(c\) and calculated \(k_s\) and the true flotation coefficient \(s_0\) from:

\[
k_s = \frac{q}{1 + m(q - 1)}\text{(slope)}
\]

(6)

\[
s_0 = \frac{1 + m(q - 1)}{\text{(intercept)}}.
\]

(7)

The use of this procedure presupposes that \(m\) has been determined accurately enough for the most dilute solution, and that it remains constant over the whole concentration region. As we were only interested in an order of magnitude of the corrections for \(s\) and \(k_s\), we did not construct a more accurate iterative procedure. Experimental details have been given [6].

For the floating system poly(2,6-dimethyl-1,4-phenylene oxide) of \(M_n\ 87,000\) in trichloroethylene at \(25^\circ\), we thus calculated \(s(p, 0) = 2.29\) (Svedberg) and \(s_0 = 2.70\), with \(m = 0.5\). For the same system at \(35^\circ\) we find \(s(p, 0) = 2.58\) and \(s_0 = 3.20\), with \(m = 1.1\). At both temperatures, the correction for pressure adds about \(20\%\) to \(s(p, 0)\). The difference found for \(m\) is not a consequence of the temperature difference, but of the poor reproducibility of the assessment of the first and the second coefficients of Eqn (3).

The values obtained for this system for \(m\) are in accordance with values for \(m\), determined by others for other polymers in chlorinated hydrocarbon solvents [4]. From equation (1) we found for the above mentioned polymer in toluene solution at \(25^\circ\) (where sedimentation occurs) \(s(p, 0) = 3.12\) (Svedberg) and \(s_0 = 3.23\), with \(m = 0.7\) (in agreement with findings for other polymers in toluene [2, 3]).

For the flotation case we found \(k_s = 117\) (ml/g) at \(25^\circ\) by means of the procedure outlined above, whereas for uncorrected \(s\) it was 111 (ml/g). This difference is not significant, however; it depends strongly on the experimental uncertainty in \(m\) [cf. Eqn (6)].

Thus, at \(35^\circ\) we found \(k_s = 89\) (ml/g) from Eqn (6) and \(k_s = 118\) (ml/g) from uncorrected \(s\) values.

REFERENCES