

Velocity of Dissociation and Viscosity of Alkaline Polymetaphosphates

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The investigations of Lamm and Malmgren^{1,2} into the relationships between alkaline metaphosphates in aqueous or in rhodanide solution respectively have proved that these substances are highly polymerized and that they very quickly dissociate, according to their composition and the solvent. Experiments with the ultracentrifuge showed that the solutions become polydispersed very soon, assuming that this has not already taken place during production; but it was impossible to get definite quantitative results.

Attempts were therefore made to follow the course of dissociation by measuring the viscosity. Here — as with every total characteristic of a solution — only summary effects are obtained; but since the viscosity can be measured accurately and changes considerably in the present instance, it might be expected that the theoretical analysis of the time curve would yield some information.

EXPERIMENTAL WORK

Measurements were taken at a temperature of 20° C with the Ostwald viscosimeter. This had a water outflow time of about 200 seconds in the case of table 1, so that the outflow times of these solutions fell from about 800 to about 340 seconds; they are therefore accurate at least initially to within less than 1‰. The surface tension correction³ could be ignored since it is very small and practically constant for the given total concentration.

For the purpose of the experiments the mixed salt $K_2Na(PO_3)_3$ was employed. It dissolves only very slowly in water, and before its complete dissolution noticeable dissociation may already have occurred. Therefore in the first experiments at different concentrations the zero point of dissociation time and consequently the particularly important changes in the early stage were uncertain. On that account no details are given here. The following conclusions could be deduced.

The increment of viscosity * $\varrho = \frac{\eta - \eta_0}{\eta_0}$ changes almost uniformly as a function

of the time at different total concentrations a (gram per kilogram solution). The reactions of dissociation are therefore analogous. The intrinsic viscosities $Wa = \varrho_0/a$ at $\tau = 0$ depend only to a small degree on the total concentration; therefore ϱ is the sum of the partial values of the dissociation products. As an example some typical values are given below.

a	ϱ_0	ϱ_0/a
1.58	9.26	5.9**
0.790	5.10	6.5
0.343	2.21	6.4
0.201	1.26	6.3
0.040	0.26	6.5

In taking the more exact measurements of table 1 the solution was filtered after a quarter of an hour, without waiting until the substances had been dissolved completely, and the concentration was then tested. The result of the phosphate analysis *** showed that the proportion between sodium and potassium changes slightly when fractionally dissolved, but this circumstance is of no particular importance.

The duration τ of the experiment was counted in hours from the moment of adding the water to the solid substance, and as a starting point for each measurement the average value between the beginning and end of the outflow was selected. By this means the important initial values are accurately determined to within 1 to 2 minutes.

Table 1 gives the time values τ and the increments of viscosity ϱ as they were determined. ϱ is deduced from the relative outflow time and the specific gravity of the solution. ($a = 0.660$, $^0/_{00} s/s_0 = 1.00465$).

Table 1. Change of the increment of viscosity (ϱ) with age (τ hours) of a solution of $K_2Na(PO_3)_3$.

τ	ϱ	τ	ϱ
0.76	3.046	24.08	2.456
1.02	3.037	24.30	2.451
1.27	3.031	24.51	2.448
1.77	3.018	25.62	2.426
2.68	2.988	27.10	2.399
3.50	2.963	28.10	2.378
4.20	2.939	29.10	2.362
5.20	2.911	48.58	2.063

* We avoid the expression «specific viscosity» used in scientific literature, because the term specific values is understood to mean such values which refer to the unit of the quantity of substance.

** Probably too small because dissociation had already advanced too far.

*** For this information the author is indebted to fil.mag. H. Malmgren.

τ	ρ	τ	ρ
50.37	2.037	143.4	1.290
51.82	2.022	146.0	1.276
52.92	2.008	148.9	1.259
73.92	1.780	167.5	1.160
74.17	1.778	171.6	1.140
75.83	1.761	172.8	1.135
95.80	1.596	192.0	1.038
97.37	1.586	197.9	1.006
98.90	1.576	217.0	0.918
101.12	1.557	220.9	0.900
119.83	1.429	244.1	0.793
122.98	1.412	263.9	0.714
125.0	1.398		

THEORY

According to the above mentioned results the increment of viscosity ρ at the time τ is expressed as an algebraic sum of the products of the intrinsic viscosities $W_a, W_b \dots$ of the components and their concentrations respectively. If the substance dissociates in several stages and if the part x of the initial concentration a has dissociated after τ hours — and furthermore in the same time the part y of x has dissociated etc., — then the following equations will apply if three stages only are considered:

$$\begin{aligned}
 \text{a) } \rho &= W_a (a - x) + W_b (x - y) + W_c (y - z) + W_d \cdot z \\
 &= W_a \cdot a - (W_a - W_b) x - (W_b - W_c) y - (W_c - W_d) z \\
 &= \rho_0 - \Delta_1 x - \Delta_2 y - \Delta_3 z \\
 \text{b) } \frac{d\rho}{d\tau} &= -\Delta_1 \frac{dx}{d\tau} - \Delta_2 \frac{dy}{d\tau} - \Delta_3 \frac{dz}{d\tau}
 \end{aligned}$$

As a second fundamental assumption which needs hardly to be verified, it may be assumed that any dissociation whatever progresses as a first class reaction without any inverse reaction.

The following relations for different schemes of dissociation are thus obtained.

First case. The originally homogeneous polymeric substance A may dissociate into a stable product B which for its part may consist of particles of the same or different size*.

* If the particles vary in size, the coefficient W_b for stage B is expressed as a sum of several terms, which is indivisible but does not need to be divided. The same applies to all subsequent stages.

The velocity equation will then be

$$1a) \frac{dx}{d\tau} = k_a (a - x) \text{ with the integral } 1c) x = a - a \cdot e^{-k_a \tau}$$

and the viscosity may be written

$$1b) \varrho = \varrho_0 - \Delta_1 x$$

From the differentiation of 1b follows *

$$1d) - \frac{d^2 \varrho}{d\tau^2} / \frac{d\varrho}{d\tau} = k_a$$

Second case. A may dissociate in two parallel processes into two stable products B₁ and B₂. Each of them may be composed either of equal or unequal parts.

Instead of one velocity equation the two following are obtained:

$$2a) \frac{dx_1}{d\tau} = k_1 \cdot (a - x) \quad \frac{dx_2}{d\tau} = k_2 (a - x)$$

where $x_1 + x_2 = x$. If $x_1 = n \cdot x$ and $x_2 = (1 - n) x$, it follows that $k_1 : k_2 = n : (1 - n)$; but as n is unknown, it is impossible to separate the two constants, and only their sum $k_0 = k_1 + k_2 = \frac{1}{a-x} \cdot \frac{dx}{d\tau}$ can be obtained as in the first case.

The friction is expressed by the term

$$2b) \varrho = W_a (a - x) + W_{b_1} n x + W_{b_2} (1 - n) x = \varrho_0 - \Delta_1 x$$

also as above. ($\Delta_1 = W_a - W_{b_1} n - W_{b_2} + W_{b_2} n$)

Therefore this case and every subsequent analogous case can be treated as if there were only one dissociation process.

Third case. A may dissociate first into B and B into a stable product C. It is preliminary assumed that B consists of equal parts. For the first dissociation equation 1a applies; for the second

$$3a) \frac{dy}{d\tau} = k_b (x - y)$$

* If therefore ϱ can be expressed by an empirical series

$$\varrho = \varrho_0 + \alpha \tau + \beta \tau^2 + \gamma \tau^3 + \delta \tau^4$$

then case 1 requires that

$$k_a = -\frac{2\beta}{\alpha} = -\frac{3\gamma}{\beta} = -\frac{4\delta}{\gamma}$$

and the friction equation will be

$$3b) \quad \rho = W_a (a - x) + W_b (x - y) + W_c y = \rho_0 - \Delta_1 x - \Delta_2 y$$

The integral of 3a is

$$3c) \quad y = a + a \cdot \frac{k_b}{k_a - k_b} \cdot e^{-k_a \tau} - a \frac{k_a}{k_a - k_b} \cdot e^{-k_b \tau}$$

If we differentiate 3b repeatedly and substitute x and y (according to 1c and

3c), we get in abridged form $\frac{d\rho}{d\tau} = d_1$ and $\frac{d^2\rho}{d\tau^2} = d_2 \dots$

$$3d) \quad -k_b = \frac{d_3 + k_a d_2}{d_2 + k_a d_1}$$

Fourth case. A may dissociate in one reaction into two unequal parts B_1 and B_2 , which in turn change into stable final products, $B_1 \rightarrow C_1$ and $B_2 \rightarrow C_2$. The equation 1a applies as before, but 3a is split into two formulae

$$4a) \quad \frac{dy_1}{d\tau} = k_{b1} (x_1 - y_1) \quad \frac{dy_2}{d\tau} = k_{b2} (x_2 - y_2)$$

If we put $x_1 = n \cdot x$, $x_2 = (1 - n) x$, as above, the integrals will be

$$4c) \quad y_1 = n \left(a + a \cdot \frac{k_{b1}}{k_a - k_{b1}} e^{-k_a \tau} - a \frac{k_a}{k_a - k_{b1}} e^{-k_{b1} \tau} \right)$$

$$y_2 = (1 - n) \left(a + a \cdot \frac{k_{b2}}{k_a - k_{b2}} e^{-k_a \tau} - a \frac{k_a}{k_a - k_{b2}} e^{-k_{b2} \tau} \right)$$

where n remains unknown as before. The friction equation is

$$4b) \quad \rho = \rho_0 - \Delta_1 x - \Delta_2 y_1 - \Delta_3 y_2$$

where $\Delta_1 = W_a - W_{b1} n - W_{b2} (1 - n)$, $\Delta_2 = W_{b1} - W_{c1}$, $\Delta_3 = W_{b2} - W_{c2}$ and after repeated differentiation as above it is found that *

$$4d) \quad -k_{b2} = \frac{d_4 + (k_a + k_{b1}) d_3 + k_a \cdot k_{b1} d_2}{d_3 + (k_a + k_{b1}) d_2 + k_a \cdot k_{b1} d_1}$$

* If one of the two first dissociation products should be stable, case 4 is reduced to the foregoing case 3.

Fifth case. A may dissociate only into equal parts B, these further into C and C, finally, into a stable product D.

Besides the velocity equations 1a and 3a we have here

$$5a) \quad \frac{dz}{d\tau} = k_c (y - z)$$

with the integral

$$5c) \quad z = a - a \cdot \frac{k_b \cdot k_c}{(k_b - k_c)(k_c - k_a)} e^{-k_a \tau} + a \frac{k_a \cdot k_c}{(k_b - k_a)(k_c - k_b)} e^{-k_b \cdot \tau} - a \cdot \frac{k_a \cdot k_b}{(k_c - k_a)(k_c - k_b)} e^{-k_c \tau}$$

If we introduce this into the friction equation

$$5b) \quad \rho = \rho_0 - \Delta_1 x - \Delta_2 y - \Delta_3 z$$

(here again $\Delta_1 = W_a - W_b$, $\Delta_2 = W_b - W_c$, $\Delta_3 = W_c - W_a$)

and then differentiate as above, it follows that

$$5d) \quad -k_c = \frac{d_4 + (k_a + k_b) d_3 + k_a \cdot k_b \cdot d_2}{d_3 + (k_a + k_b) d_2 + k_a \cdot k_b \cdot d_1}$$

From the foregoing five examples, the number of which could be increased indefinitely, the relation between the differential quotient of ρ and the velocity constants becomes quite clear. The greater the number of separate reactions, the more time terms will be needed for the calculation, and consequently the more accurate the measurements must be. A formula including the fourth differential quotient of ρ as in case 4 and 5 would seem to be the limit of what is obtainable by viscosity measurements at the present time.

More important than the velocity factors discussed in the above mentioned deductions are the intrinsic viscosities W_b , W_c etc. (see equation a). From the velocity formulae (see equation b) it follows that in the limit case $\tau = 0$ all the first differential quotients of the concentrations become zero, except $dx/d\tau$, which acquires the value $a \cdot k_a$. Thus irrespective of the number of stages, the following will always apply:

$$6) \frac{1}{\rho_0} \cdot \lim_{\tau=0} \frac{d\rho}{d\tau} = -\Delta_1 \cdot \frac{a}{\rho_0} \cdot k_a$$

In the second derivation all the terms for $\tau = 0$ are eliminated, except $d^2x/d\tau^2$ and $d^2y/d\tau^2$, and the following limit value is obtained:

$$7) \frac{1}{\rho_0} \cdot \lim_{\tau=0} \frac{d^2\rho}{d\tau^2} = \Delta_1 \frac{a}{\rho_0} \cdot k_a^2 - \Delta_2 \frac{\pi}{\rho_0} \cdot k_a \cdot k_b$$

likewise independent of all that follows the second stage. If k_a and Δ_1 are known, we get from this relation a value for $\Delta_2 = W_b - W_c$ (see case 3), irrespective of whether the dissociation product C is stable or dissociates further*.

RESULTS

According to formula 1d the same value for **) $k_a = -\frac{d_2}{d_1} = -\frac{d_3}{d_2} \dots$ should be obtained all along the curve, if only the single dissociation $A \rightarrow B$ were to take place. Calculations of the differential quotients for different lengths of the curve show that this is not the case. At most the subsequent reactions approximately can be neglected up to $\tau = 50$. For longer times they must be taken into consideration, but here only case 3, $A \rightarrow B \rightarrow C$, is discussed in detail.

Up to $\tau = 100$, ρ can be expressed by the empirical series $\rho = 3.065 - 3.11_9 \cdot 10^{-2} \cdot \tau + 2.95_5 \cdot 10^{-4} \cdot \tau^2 - 1.88 \cdot 10^{-6} \cdot \tau^3 + 0.548 \cdot 10^{-8} \cdot \tau^4$ wherefrom the differential quotients d_1, d_2 etc. can be easily deduced for each time; thus — according to formula 6 —

* Given case 5, the relation

$$8) \lim_{\tau=0} \frac{d^2\rho}{d\tau^2} = -\Delta_1 a k_a^3 + \Delta_2 a \cdot k_a \cdot k_b (k_a + k_b) - \Delta_3 a \cdot k_a \cdot k_b \cdot k_c$$

would be formed, where k_c and $\Delta_3 = W_c - W_d$ also appear. Given case 3 only, ($k_c = 0$), the last term in formula 8 disappears.

** If the fundamental assumption stated above is not fulfilled, namely that at the time $\tau = 0$ only one homogeneous highly polymerized substance A is present, but if in consequence of a very quick reaction at the given time a part b of the total concentration a is already transformed, we have to substitute in all relations for the term a the constant but unknown term $a - b$. This does not entail any alteration in the formulae, but in the limit value $\rho_0 = W_a \cdot a$ and in the differential quotients of ρ .

Incidentally though perhaps unnecessarily, it may be mentioned that there is no change in all these considerations if the molecular concentrations are introduced in place of the weight concentrations employed here. The molecular weights will then appear everywhere as constant but unknown factors.

$$\frac{1}{\varrho_0} \cdot \lim_{\tau=0} \frac{d\varrho}{d\tau} = -\Delta_1 \frac{a}{\varrho_0} \cdot k_a = -1.02 \cdot 10^{-2}$$

Since $\Delta_1 = W_a - W_b$ cannot be greater than $W_a = \frac{\varrho_0}{a} \frac{3.065}{0.660} = 4.65$, k_a must be greater than $1.02 \cdot 10^{-2}$. According to formula 3d the second velocity constant k_b is calculated by some selected values for k_a $1.02 \cdot 10^{-2}$, further

according to formula 6, $\Delta_1 = \frac{1.02 \cdot 10^{-2} \cdot 4.65}{k_a}$ from which follows $W_b = W_a - \Delta_1$ and finally Δ_2 according to formula 7. Thus the following table is obtained*.

Table 2. Velocity constants and intrinsic viscosities deduced from table 1.

$10^3 k_a$	$10^3 k_b$	Δ_1	W_b	Δ_2	W_c
2.00	1.62	2.36	2.29	0.16	2.13
2.20	1.82	2.15	2.50	0.36	2.14
2.50	1.86	1.89	2.76	0.61	2.15
3.00	1.88	1.58	3.08	0.92	2.16
4.00	1.88	1.18	3.47	1.32	2.15
5.00	1.89	0.95	3.70	1.56	2.14
6.00	1.89	0.79	3.86	1.71	2.15

Without placing any value on the absolute magnitude of the velocity coefficients the intrinsic viscosities obtained may be considered. They show the expected sequence $W_a > W_b > W_c$, but are of the same order of magnitude, which means that the fragments formed are not much smaller than the original substance A, *i. e.* they are still highly polymerized. This result could be extended by including case 5 in the calculation, in which case values of ϱ corresponding to longer times would be required.

Such a calculation based on formula 5d is not only very involved, but also far more liable to error than that carried out above. A satisfactory result, however, with respect to order of magnitude may be obtained by another method. Since the value of k_a is apparently very high, $(a - x)$ is reduced to such an extent about the middle of the experimental series that it can be practically ignored*.

* Values of $k_a < 2 \cdot 10^{-2}$ were not taken into consideration since it follows from them that $k_b > k_a$, which would mean that the first stage $A \rightarrow B$ does not come into question and $A \rightarrow C$ takes place directly. Further Δ_2 would also become negative, *i. e.* $W_c > W_b$, which is likewise excluded.

The curve then runs on as if A had not been present from the outset; hence the dissociation $B \rightarrow C \rightarrow D$ may be treated according to case 3, any possible subsequent stages being disregarded. Above $\tau = 160$, it is thus found that $k_b = 1.88 \cdot 10^{-2}$ (see table 2), $k_c \approx 0.5 \cdot 10^{-2}$. The concentrations of the components can be calculated according to the formulae 1c, 3c and 5c, wherefrom formula a gives the values for W_b , W_c and W_d .

By this means it was found that $\Delta_1 = 1.22$, $\Delta_2 = 1.15$, $\Delta_3 = 1.0$, thus $W_a = 4.65$, $W_b = 3.43$, $W_c = 2.3$, $W_d \approx 1.2$, approximately equal to the values in table 2.

Accordingly W_d is likewise still so large that it could belong to a very high polymer.

As already mentioned, no importance should be attached to the absolute values of the intrinsic viscosities and dissociation constants obtained. The following results, however, may be considered reliable.

SUMMARY

The theoretical analysis of the temporary change in viscosity shows that the polymerized alkaline metaphosphates dissociate in a series of successive reactions, each of which may consist of several side reactions. Two stages of this series could be definitely isolated and the third with some probability, with respect to possible further stages the experiments yield no results. The first dissociation proceeds very quickly, but in the following the velocities decrease noticeably. In the same way the intrinsic viscosities decrease, but their values show that the dissociation products are still highly polymerized.

The final state is by no means reached even at the end of a month, and a freshly prepared solution rapidly passes into a polydispersed system even if it was highly polymerized in a uniform manner at the outset.

The author again takes the opportunity of cordially thanking Professor The Svedberg for his constant friendly interest.

The author is also indebted to fil.mag. H. Malmgren, whose experiments were the starting point for the present investigation.

REFERENCES

1. Lamm, O., and Malmgren, H. *Zeitschr. Anorg. Chem.* 245 (1940) 103.
2. Lamm, O., and Malmgren, H. *Zeitschr. Anorg. Chem.* 252 (1944) 255.
3. Drucker, C. *Arkiv Kemi, Mineral. Geol.* 22 A (1946) no. 20.

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* If $k^a = 4.0 \cdot 10^{-2}$, A is dissociated to more than 99 % at $\tau = 160$.