THE EFFECT OF SODIUM PYROPHOSPHATE IN CERTAIN CASES OF DEMINERALIZATION

V. Lesichkov, D. Mitev

It is well known from the comparatively scarce literature data available that the synthetic ionogenic, superficially active substances, unlike fatty saponins, form adsorptional layers which are endowed with weakly pronounced protective properties. To manifest their stabilizing effect, they should be applied to the various cases in the form of composite mixtures, mainly with electrolytes and with a variety of protective colloids. In the presence of similar supplements, the aggregative stability of the eliminated particles is strongly enhanced. According to Schwartz H. M. and co-workers (7), this occurs as a result of the increased surface activity of the superficially active substances. K. Lindner (6) and H. Stupel (8) point out that under the conditions outlined mycelium formation in the solutions of superficially active substances is relieved, whilst in the opinion of V. Clayton (5), the tensile strength and viscosity of their adsorption layers are being established.

As regards colloid solutions of superficially active substances, it is stated that particular importance in their capacity of activying electrolytes should be attributed to the polyphosphates with common formula $Na_{n+2}P_nO_{3n+1}$. These polyphosphates, mainly by way of complex-formation, rise the peptization of the particles eliminated and thus lower the possibility for joining the surfaces of the hard phases. However, such a regularity has merely qualitative character.

In a previous work by the authors (1), the influence of the superficially active substance sapogenate T-130 was studied, as well as the demineralization effect of 0.1 M solution of complexon III, exerted upon simple biological structures in ultrasound environment. In the present studies, we made it our aim to trace up the influence of $Na_4P_2O_7$ on demineralization under identical conditions.

Materials and Method

1. 0.1 M solution of complexon III.
2. Sapogenate T-130.
3. $Na_4P_2O_7 . 10\ H_2O$.
4. Shells of Donax venustus, Gibula divaricata and Helix nemoralis.
5. Apparatus for investigating the surface pressure of liquids.
6. Sonotherm — ultrasound generator.

The samples are prepared for work according to the method already described (1). The complexon III solutions are supplemented with 1% sapogenate T-130 and 0.5% $Na_4P_2O_7$ 10 H_2O. At the percentage of sapogenate T-130 indicated, the pH of the medium is maintained unaltered and the surface tension is readily recorded.

To determine the coefficient of surface tension, we chose the method of maximal pressure within the vesicle. In the latter instance, it was proceeded from the formula submitted by R. S. Laplas (4).

The working samples thus prepared are dried at 110° C and weighed till constant weight is recorded. A set of three samples undergo treatment over periods of 30, 60, 90 and 120 min with 0.1 M solution of complexon III in ultrasound environment. After the treatment, the samples are washed out in distilled water, dried and weighed till constant weight is established. Δ p is determined on the basis of weight differences. Another set undergoes treatment with 0.1 M solution of complexon III, with addition of 1% sapogenate T-130 in ultrasound environment. The third set, likewise in ultrasound environment, is treated with 0.1 M solution of complexon III with addition of 1% sapogenate T-130 and 0.5% $Na_4P_2O_7$. 10. H_2O.

Sonotherm — ultrasound generator was used for ultrasound treatment, with due consideration to all technical requirements (2, 3). Ultrasound was used at frequency 800 kHz±20%, vibrating area — 8 cm^2, power of ultrasound — 1 W/cm^2. All determinations were performed at room temperature, about 17° C.

Results

In the course of surface tension of 0.1 M solution of complexon III determination, the above solution after addition of 1% sapogenate T-130 and 1% sapogenate T-130+0.5% $Na_4P_2O_7$.10 H_2O disclosed the following results:

0.1 M complexon III

№	$H \cdot 10^{-3}$ m	$\Delta H \cdot 10^{-3}$ m	$\Delta H^2 \cdot 10^{-6}$ m
1	42	−0.1	0.01
2	42	−0.1	0.01
3	41	+0.9	0.81
4	42	−0.1	0.01
5	43	−1.1	1.21
6	41	+0.9	0.81
7	42	−0.1	0.01
8	42	−0.1	0.01
9	41	+0.9	0.81
10	43	−1.1	1.21
mean	41.9		$\Sigma \Delta H^2 = 4.90 \times 10^{-6}$ m

$\sigma_1 = H . a = 41.9 \times 10^{-3} \times 1.6 = 0.06704$ N/m

$$F = \pm\sqrt{\frac{\Sigma \Delta H^2}{n(n-1)}} = \pm\sqrt{\frac{4.90 \times 10^{-6}}{10 \times 9}} = \pm 0.234 \times 10^{-3}$$

$\sigma_1 = (0.06704 + 0.000234)$ N/m

0.1 M complexon III+1% sapogenate T-130

№	$H \times 10^{-3}$ m	$\Delta H \times 10^{-3}$ m	$\Delta H^2 \times 10^{-6}$ m
1	22	—1.4	1.96
2	21	—0.4	0.16
3	22	—1.4	1.96
4	20	+0 6	0.36
5	19	+1.6	2.56
6	19	+1.6	2.56
7	20	+0.6	0.36
8	21	—0.4	0.16
9	20	+0.6	0.36
10	22	—1,4	1.96
Mean	20.6		$\Sigma \Delta H^2 = 12.0 \times 10^{-6}$ m

$\sigma_2 = H \times a = 20.6 \times 10^{-3} \times 1.6 = 0.03296$ N/m

$$F = \pm\sqrt{\frac{\Sigma \Delta H^2}{n(n-1)}} = \pm\sqrt{\frac{12 \times 10^{-6}}{10 \times 9}} = \pm 0.366 \times 10^{-3}$$

$\sigma_2 = (0.03296 \pm 0.000366)$ N/m

0.1 M complexon III+1% sapogenate T-130+0.5% $Na_4P_2O_7 \times 10H_2O$

№	$H \times 10^{-3}$ m	$\Delta H \times 10^{-3}$ m	$\Delta H^2 \times 10^{-6}$ m
1	15	+0.2	0.04
2	17	—1.8	3.24
3	14	+1.2	1.44
4	16	—0.8	0.64
5	16	—0.8	0.64
6	15	—0.2	0.04
7	14	+1.2	1.44
8	14	+1.2	1.44
9	15	+0.2	0.04
10	16	—0.8	0.64
mean	15.2		$\Delta \Sigma H^2 = 9.60 \times 10^{-6}$ m

$\sigma_3 = H \times a = 15.2 \times 10^{-3} \times 1.6 = 0.02432$ N/m

$$F = \pm\sqrt{\frac{\Sigma \Delta H^2}{n(n-1)}} = \pm\sqrt{\frac{9.60 \times 10^{-6}}{10 \times 9}} = \pm 0.338 \times 10^{-3}$$

$\sigma_3 = (0.02432 \pm 0.000338)$ N/m

It is evident from the results submitted that in this particular case the addition of 1% sapogenate T-130 to 0.1 M complexon III solution brings about a reduction of the surface tension practically to one half. The supplement of 0.5% $Na_4P_2O_7 \times 10\ H_2O$ reduces the surface tension to 34.71% of the initial one.

The results obtained in the above investigation are shown in Tables 1, 2 and 3.

Table 1

0.1 M complexon III in ultrasound environment

Objects	30 min	60 min	90 min	120 min
Donax venustus	8.00	19.04	29.84	36.22
Gib. divaricata	10.56	22.48	31.00	40.02
H. nemoralis	14.00	24.10	37.66	46.00

Table 2

0.1 M complexon III+1% sapogenate T-130 in ultrasound environment

Objects	30 min	60 min	90 min	120 min
Donax venustus	14.70	25.00	42.00	58.88
Gib. divaricata	17.54	27.40	47.80	62.08
H. nemoralis	19.60	29.92	49.30	63.00

Table 3

0.1 M complexon III+1% sapogenate T-130+0.5% $Na_4P_2O_7$ in ultrasound environment

Objects	30 min	60 min	90 min	120 min
Donax venustus	17.00	28.32	44.90	62.84
Gib. divaricata	20.04	29.80	50.00	65.40
H. nemoralis	22.00	33.40	52.00	65.66

The kinetics of the process in the three sets is expressed graphically in figures 1, 2 and 3. The numbering along the curves corresponds to the data of the three tables.

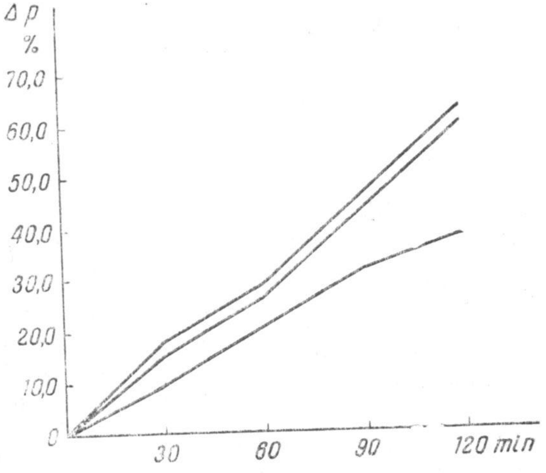

Fig. 1

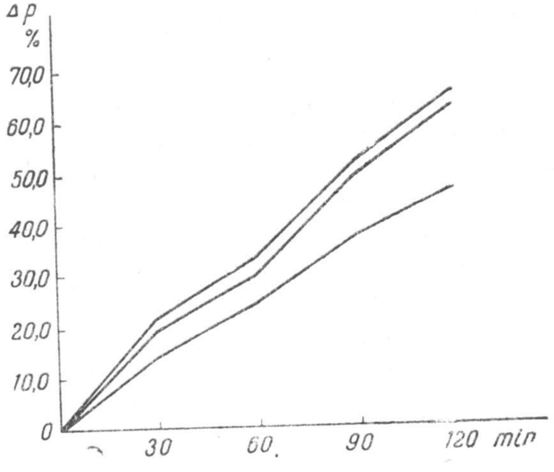

Fig. 2

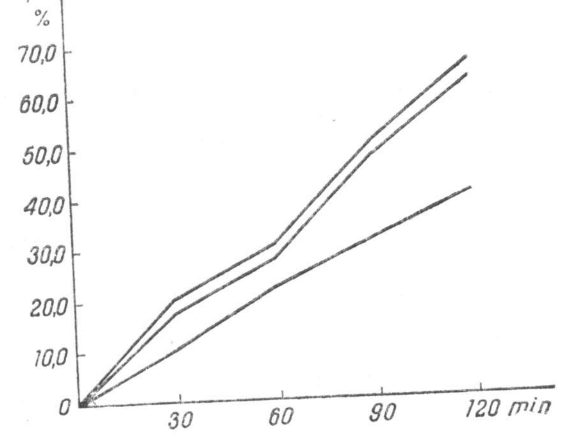

Fig. 3

Discussion

It is obvious that, on the whole, demineralization in this particular case runs a course of strictly linear regularity. The differences between the various representatives of simple biostructures, made up by $CaCO_2$ mainly, are by no means substantial. Of course, the latter fact should be related to the similarities in their structural build up.

In this instance, of particular importance appears to be the influence exerted by pyrophosphate upon the surface tension of the complexon III solution, to which a superficially active substance is added. A single, insignificant $Na_4P_2O_7 \times 10\ H_2O$ addition of the order of 0.5% causes lowering of the superficial tension of the solution with about 19 per cent. As a result of the latter, the effect of demineralization is increased with several per cents. It should be assumed that in this case, the pyrophosphate ions exert a favourable effect on complex formation and most probably, take part in the formation of complex phosphate-containing calcium chelate complexes. They favour the peptization of the salt ions, eliminated by the attacked surfaces and thus exert an overall favourable effect on the disintegration process. In compliance with the general theoretical principles, it should be recognized that at sufficient concentration of the surface substance, the sodium pyrophosphate contributes to the obtaining of optimal colloid-chemical properties by the solutions. Such a colloidization should be manifested by the fact that in the solutions proper mycelium formation is accomplished at the participation of the powerful electrolyte, whereas the adsorptional layers of the dividing surface assume particular stability, in accordance with the general thermodynamical principle of the free superficial energy minimum.

Unfortunately, at the present stage of scientific research, many of the regularities in the phenomena involved, conditioning the action of superficially active substances, bear a qualitative nature. Hence, it is impossible to establish the simple relationship existing between the effectiveness of their action and the numerous factors involved, the presence of polyphosphates inclusive.

REFERENCES

1. Лесичков, Вл., Д. Митев, Цв. Обретенов. Относно деминерализацията на просто построени биоструктури с комплексон III в присъствие на сапогенат Т-130 в ултразвукова среда, под печат в Годишните научни трудове на ВМИ — Варна
2. Бергман, Л. Ультразвук и его применение в науке и технике. Изд. Иностр. лит., Москва, 1956.
3. Бражников, Н. И. Ультразвуковые методы. Год. изд. Энергия, 19 М, 1955 Л.
4. Горский, Ф. Физический практикум. ИВШ, Минск, 1969.
5. Клейтон, В. Эмульсии. Изд. Иностр. Лит., Москва, 1950.
6. Lindner, K. Textilhilfsmittel und Waschrohstoffe. Stuttgart, 1954.
7. Schwartz, A. M., I. W. Perry, I. Berch. Surface active agents. vol. 1—2, N. Y.—L., 1949—58.
8. Stupel, H. Synthetische Wash- und Reinigungsmittel. Stuttgart, 1954.

ВЛИЯНИЕ ПИРОФОСФАТА НАТРИЯ В НЕКОТОРЫХ СЛУЧАЯХ ДЕМИНЕРАЛИЗАЦИИ

Вл. Лесичков, Д. Митев

РЕЗЮМЕ

В работе изучено влияние пирофосфата натрия на поверхностное натяжение 0,1 М раствора комплексона III с 1%-ным сапогенатом Т-130 в целях улучшения деминерализующих свойств этого реагента.

Было установлено, что добавка 0,5% $Na_4P_2O_7.10\ H_2O$ вызывает снижение поверхностного натяжения 0,1 М раствор комплексона III с 1%-ным сапогенатом Т-130 на 34,71% по сравнению с первоначальным. Поверхностное натяжение определяли методом продавливания пузырька.

Деминерализационный эффект определяли в ультразвуковой среде с частотой ультразвука 800 кгц — 20% и интенсивностью 1 вт/см^2 на раковинах Donax venustus, Gibula divaricata и Helix nemoralis.

Авторы считают, что ионы пирофосфата благоприятствуют комплексообразованию, участвуя, по всей вероятности, в составе сложных содержащих фосфор хелаткомплексов кальция. Последние благоприятствуют пептизации солей, отделяемых с подвергшихся обработке поверхностей, способствуя таким образом расщеплению.