Chemistry. — *The interfacial tension of gum arabic-gelatine complex-caocervates and their equilibrium liquids.* By L. DE RUITER and H. G. BUNGENBERG DE JONG.

(Communicated at the meeting of September 27, 1947.)

1. *Introduction.*

Drops of complex caocervates, suspended in their equilibrium liquids, show motory an desintegration phenomena on application of a direct current field. [1])

It may be supposed that local changes of the interfacial tension coacervate equilibrium liquid will be of essential importance for the explanation of the motory phenomena. Here a serious lack of information exists as no interfacial tension coacervate/equilibrium liquid had ever been measured and thus the desired knowledge of the influence of variables on it in the special case of complex coacervates was not available.

We therefore have measured this interfacial tension (σ) for gum arabic (A)-gelatine (G) coacervates at various mixing proportions of the colloids at 40° C. and constant pH and the influence of some salt concentrations on it. The results of these measurements are given in the present article. Their application in the explanation of the phenomena mentioned above will be discussed in a following communication.

2. *Measuring methods.*

In some introductory experiments we found that the order of magnitude of the interfacial tensions discussed here was extraordinarily small:

1. With DU NOUY's ringmethod we could not measure any interfacial tension at all. Evidently the sensibility of this method was insufficient.

2. Determination of the height (h) to which the caocervate rises in narrow capillary tubes, brought into the phase boundary, gave h values ($\pm$ 0.1 mm) lying close to the margin of error (0.05 mm) of the kathetometer we used for these experiments. These values corresponded with $\sigma = \pm 2 \times 10^{-3}$ dynes/cm.

3. Determination of σ with the drop weight method (calculated from specific weights and microscopical dimensions of the just detaching coacervate drop) proved to be impossible, as the viscosity of the coacervate is relatively high : no well defined drops are formed, as every drop falling draws out a long thread of coacervate, which afterwards resolves into small separate droplets. Nevertheless some experiments with this method gave σ values in the above order of magnitude.

[1]) H. G. BUNGENBERG DE JONG and E. G. HOSKAM. Proc. Ned. Akad. v. Wetensch., Amsterdam, **44**, 1099 (1941).

4. The "method of pendant drops" [2]) proved impracticable, as it was nearly impossible to form sufficiently small droplets (about 100 μ in diameter) of a constant volume. Only one determination was done in this way, which again came in the expected order of magnitude ($1{,}81 \times 10^{-3}$ dynes/cm at 20° C.) in a coacervate (50 % A-sol + 50 % G-sol) in which gelation had been prevented by means of addition of urea and resorcinol [3]).

Finally a method was developed based on the principle of the capillary rise method. Initially we applied this method in its simplest form: In a tube (fig. 1 A) containing coacervate (C) and equilibrium liquid (E) a second thin tube was brought, the end of which had been drawn out to a thin capillary. The top of this capillary tube was brought into the interface coacervate/equilibrium liquid. An opening in the narrow tube below the surface of the equilibrium liquid allowed for free contact of the latter in both tubes in order to avoid hydrostatical pressure differences. The distance from the coacervate meniscus in the capillary tube to the surface of the surrounding coacervate was measured by means of a horizontal microscope (ocular-micrometer) placed just before the glaswindow of the thermostate (40° C.). Just behind the glaswindow a brass frame dipping into the thermostate allowed for the mounting of four tube combinations as described above and provided means to center the capillaries and to alter their depth of immersion in the interface.

The results obtained with this method were very unsatisfactory, for which fact several causes were responsible:

a. accurate determination of h is difficult, as the coacervate surface in the wide tube is seen as a broad diffuse dark band. Moreover the coacervate creeps up along the outside of the capillary tube. The zero level therefore should be read as far away from the capillary tube as is possible. This will increase the risk of making errors.

b. Alkali is secreted by the glass. This brings about changes in the properties of the coacervate and in the specific weights of the liquids in the capillary tube. As a result of the latter change the original capillary rise may diminish in a relatively short time to such an extent that a capillary depression seems to develop itself, though the meniscus of the interface still stands concave.

c. Very often the capillary tube is obstructed, as the funnal shaped narrowing of the narrow tube will conduct every sinking particle of dust into it.

The first and third of these 3 difficulties could be met by determining directly the difference between the heights to which the menisci rose in

[2]) J. M. ANDREAS, E. A. HAUSER and W. B. TUCKER. J. Phys. Chem. **42**, 585 (1938).

[3]) H. G. BUNGENBERG DE JONG and E. G. HOSKAM, Proc. Ned. Akad. v. Wetensch., Amsterdam, **45**, 3 (1942).

2 short capillary tubes of different radii (fig. 1 B). The interfacial tension then may be found by means of the formula

$$\sigma = \tfrac{1}{2}(d_c - d_e)\, g\, (h_1 - h_2)\, \frac{r_1 \cdot r_2}{r_2 - r_1}$$

where $(d_c - d_e)$ stands for the difference of specific weights of coacervate and equilibrium liquid.

Because of the small values of h_1 and especially of h_2 the application of meniscus corrections could not be neglected.

In a first approximation this correction is equal to 1/3 b, when b is the "height" of the meniscus (as an accurate determination of b was not well practicable because of optical dificulties, we have refrained from more exact correction). As b is greater for wide capillary tubes than for narrow ones, the total correction $+ \frac{b_1 - b_2}{3}$ on the difference in capillary rise is negative.

In order to meet the second of the difficulties mentioned above the 2 capillary tubes used in this method should be very short. They were fixed by means of KHOTINSKY cement to the end of a glass rod which had been drawn out into a thin thread (fig. 1 B). It proved impracticable to do this

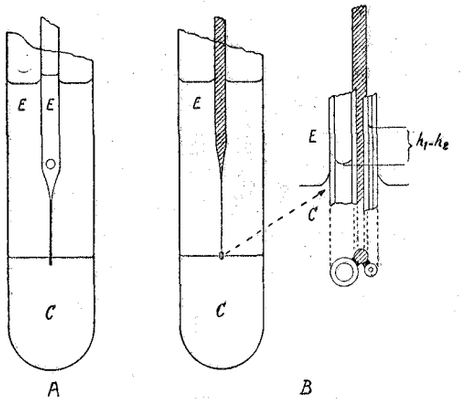

Fig. 1.

by means of paraffin. A very small droplet KHOTINSKY cement was brought on the end of the glass thread by dipping it into a molten piece of this substance. Then the 2 very small pieces (see under) of capillary tube, lying on a heated object glass were picked up by touching them with this small droplet. Usually they are all at once parallel to one another, or else can be brought easily into the right position which of course is of some importance in view of the exactness of the measurement.

It might be objected that soluble parts of KHOTINSKY cement might perhaps influence the properties of the coacervate. However, we never found evidence of such an influence in spite of the special attention we paid

to this question. Moreover the capillary tubes were always extracted in equilibrium liquid before the beginning of the experiment.

This bi-capillary method gave more or less satisfactory results only after the alkali production by the glass had been much reduced by working exclusively with Jena glass. As even this will probably produce some alkali we worked with the shortest capillary tubes we just could manipulate (about 2 mm) and extracted and washed them with equilibrium liquid before the beginning of every experiment.

We soon found that when we used the same capillary set more than once, we often obtained irregular results. Probably this is due to the fact that glass is not only dangerous on account of its alkali production, but that the silicate ions also have some influence on the coacervate that is left behind in the capillary tubes after the experiment. Initially we therefore tried to remove every remnant of coacervate from the capillary tubes by washing with concentrated salt solutions. As this did not satisfy, however, we used in the definitive experiments always a new set of capillary tubes for every single observation.

For the calibration of the capillary tubes we used an optical method given by KOHLRAUSCH [4].

The radii of the capillary tubes were usually in the order of $\pm$ 180 μ for the wide one and $\pm$ 30 μ for the narrow one.

For the calculation of σ (see formula) data were wanted concerning the specific weights of the coacervate and equilibrium liquid studied. These were not yet available. We therefore determined these specific weights by means of small pycnometers (contents about 5 cc), which gave a sufficient accuracy for the present purpose.

In order to be able to work with systems of reproducible composition all definitive experiments were carried out on one set of stock sols. These contained 2 % colloid (A, resp. G) and were buffered with an acetic acid — sodium acetate mixture (pH $\pm$ 3.7) [5].

For the preparation of the stock sols we started from:

60	g	A or G (air dry).
300	cc	0,1 n. sodium acetate.
150	cc	2 n. acetic acid.
2490	cc	dest. water.

When in the following pages we are speaking of a "33 % A" mixture, a system is meant consisting for 33 % of stock sol 2 % A and for 67 % of stock sol 2 % G.

After its preparation the gum arabic stock sol was filtered through an about 1 cm thick layer of filterpaper fibres, obtained by cooking pieces of

[4]) F. KOHLRAUSCH, Lehrbuch der praktischen Physik, B. G. Teubner, Berlin, 13e Auflage (1921) p. 97.

[5]) H. G. BUNGENBERG DE JONG and E. G. HOSKAM, Proc. Ned. Akad. v. Wetensch., Amsterdam, 45, 3 (1942).

filter paper. The gelatine stock sol was kept in the refrigerator in six separate flasks, of which only one at a time was molten in order to prevent repeated thermolytic effects. To both stock sols a drop of carbon tetrachloride was added against fungi.

For the investigation of the influence of the salt concentration on σ we added to 600 cc stock sol A 1,879 gr. KCl (i.e. about 42 m. aeq. p. l.). By mixing this solution with normal stock sol A we prepared such concentrations as were wanted for the experiments (7 and 10,5 m. aeq. KCl in 50 % A mixtures).

All glass used in the experiments was freed from fat by means of acetone. No other measures were taken to prevent errors caused by "capillary active" substances, as the stock sols themselves are already a source of impurities. Moreover there seems to be some justification for the expectation, that the interface we studied here will not be very much influenced by such substances, as it separates 2 media of only slightly different polarity.

The systems which we examined were prepared by mixing the stock sols in the desired proportion at 40° C., shaken in order to mix more thoroughly and kept over during one night at 40° C., during which time the coacervate sedimented. Next day coacervate and equilibrium liquid were separated by cooling below the gelating point (8 min. at 20° C.) and decanting, and separately heated to 40° C. again. Then the coacervate was brought into the tubes for σ-determination and once more gelated; some warm equilibrium liquid was then brought on the gelled coacervate and the tube immediately placed in the thermostate (40° C.) in which the observations were carried out. Before the experiment the capillary tubes were extracted in equilibrium liquid (40° C.) during 30 minutes, then washed with equilibrium liquid, and afterwards brought deeply into the coacervate, so that their inner surface was completely wetted with the latter (which took about 20 min.). Then they were half drawn out and fixed in that position until the menisci had fallen to their ultimate positions, which they usually had reached after 80 minutes. Then the capillary tubes were brought once more deeper into the coacervate. We then waited until the menisci had risen to their new positions again. We always followed the movements of the menisci as function of the time in order to detect possible irregularities. The definitive value of the height difference of the menisci in each case was found by taking the average of 4 separate measurings of this difference. The mean value of the 2 average height differences found after the falling and rising of the menisci was taken as the definitive value for the calculation of σ.

The method we used for the determination of the specific weights has an absolute error margin of about 0,0003 in the specific weights (i.e. a relative one of about 2 % in the differences of spec. w. between coac. and eq. liq.). The error margin of the σ-determination is about 15 % for the extreme mixing proportions (only about 7 % for the equivalent mixing proportion).

3. *Specific Weights.*

The results of these measurements have been summarized in table I. The values mentioned sub A have been obtained with the same mixtures which were used for σ-determination, those sub B from another set of stock sols of the same composition (each of the latter is the average of 2 or 3 separate determinations).

With d_{coac} and $d_{eq.liq.}$ is indicated the quotient of the masses of one cc coacervate (or equilibrium liquid) and one cc of destilled water at 40° C.

TABLE I.

Mixture No.	% A	m. aeq. p.l. KCl added	$d \cdot \frac{40}{40}$ coac.	$d \cdot \frac{40}{40}$ eq. liq.	$d_c - d_e$	average difference
A 1	33	0	1.0417	1.0052	0.0365	0.0366
2			1.0417	1.0050	0.0367	
3	40	0	1.0422	1.0044	0.0378	0.0378
4			1.0420	1.0042	0.0378	
5	50	0	1.0431	1.0038	0.0393	0.0393
6			1.0431	1.0039	0.0392	
7	60	0	1.0427	1.0047	0.0380	0.0381
8			1.0428	1.0046	0.0382	
9	67	0	1.0423	1.0057	0.0366	0.0366
10			1.0424	1.0059	0.0365	
11	50	7	1.0383	1.0054	0.0329	0.0326
12			1.0379	1.0057	0.0322	
13		10.5	1.0353	1.0065	0.0288	0.0288
14			1.0354	1.0066	0.0288	
B	0	0	—	1.0064		—
	33	0	1.0411	1.0052		0.0359
	40	0	1.0418	1.0044		0.0374
	50	0	1.0426	1.0039		0.0387
	60	0	1.0423	1.0047		0.0376
	67	0	1.0420	1.0057		0.0363
	100	0	—	1.0081		—

The agreement between the two series of different mixing proportions A and B is sufficient. The differences hardly surpass the error margin of the method. That the values sub B are systematically lower than sub A is no doubt due to the fact that we started from different stock sols.

Figure 2 gives the relation between mixing proportions and specific weights of coavervates and equilibrium liquids respectively.

The specific weight of the solmixtures if no coacervation had occurred is represented by a dotted nearly horizontal line, drawn between 1.0064 for the gelatin stock sol and 1.0081 for the gum arabic stock sol. From an earlier investigation it was known that the mixing proportion for optimal coacervation under the prevailing circumstances lies at 50 % A (see in fig. 5 the position of the reversal of charge point and the maximum of the

volume of the coacervate separated from 20 cc sol mixtures). Fig. 2 shows conform expectation a maximum for the specific weight of the coacervate and a minimum for the specific weight of the equilibrium liquid at the same

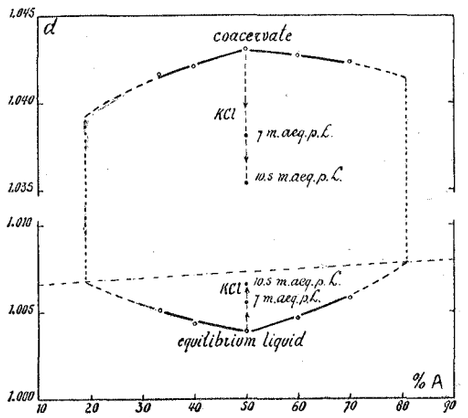

Fig. 2.

mixing proportion. Still more pronounced is the maximum at 50 % *A* for the difference in specific weight of coacervate and equilibrium liquid (see last column of table I).

The results show that the more one of the colloids is in excess the more the specific weights of coacervate and equilibrium liquid will come nearer to one another. By trying to extrapolate the specific weight curve of the equilibrium liquid to those values of the mixing proportion at which just no longer coacervation occurs (19 % *A* and 81 % *A*, see fig. 5) no improbable course is obtained (see fig. 2).

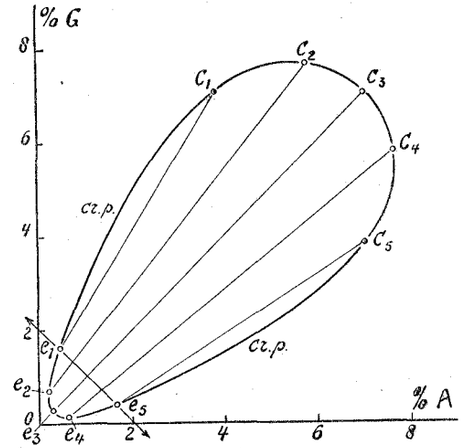

Fig. 3.

TABLE II.

Influence of mixing proportion.

33 % A		40 % A		50 % A		60 % A		67 % A	
Mixt no.	σ in dyne/cm × 10^3	Mixt no.	σ in dyne/cm × 10^3	Mixt no.	σ in dyne/cm × 10^3	Mixt no.	σ in dyne/cm × 10^3	Mixt no.	σ in dyne/cm × 10^3
1	1.42	3	1.88	20	2.55	28	1.78	9	1.56
	1.45		2.14		2.39		2.25		1.65
2	1.49	4	1.93	21	2.51	29	2.21	10	1.60
	1.39		2.24		2.62		2.16	32	1.51
15	1.55	18	1.92	22	2.19	30	2.14		1.64
16	1.42		1.90		2.28		2.20	33	1.65
17	1.51	19	1.97	23	2.40	31	2.44		
			1.91		2.07				
				24	2.37				
					2.00				
				25	2.35				
					2.28				
				26	2.38				
					2.29				
				27	2.15				
					2.05				
1.46 ± 0.022		1.99 ± 0.046		2.31 ± 0.045		2.17 ± 0.075		1.60 ± 0.023	

TABLE III.

Influence of saltconcentration.

50 % A					
0 maeq KCl		7 maeq KCl		10.5 maeq KCl	
mixt no.	σ in dyne/cm × 10^3	mixt no.	σ in dyne/cm × 10^3	mixt no.	σ in dyne/cm × 10^3
See Table II		11	0.75	13	0.34
		12	0.83		0.53
			0.78	14	0.39
		34	0.87		0.54
			0.85	36	0.41
		35	0.87		0.57
			0.98	37	0.51
					0.57
2.31 ± 0.045		0.85 ± 0.028		0.48 ± 0.031	

If this however is tried with the coacervate curve in fig. 2, it seems very unlikely that at 19 or 81 % *A* the specific weight should have become identical with the equilibrium liquid. It seems more probable that this coacervate curve takes a course as indicated in fig. 2. Such a course can even be foreseen, using a schematic phase diagram simplifying the coacerv-

ation as an unmixing in a ternary system $G + A +$ Water (see the schematic isotherm drawn in fig. 3).

On mixing 2 % A and 2 % G sols we enter and leave the area in which coacervation occurs in points so situated, that the two phases c_1 and e_1 and also c_5 and e_5, belonging to those points do not coincide. The equilibrium liquids (e_1 and e_5) have here the composition of the total sol mixture, the coacervates (c_1 and c_5), though infinitesimal small in volume, have compositions widely different from the equilibrium liquids.

The few data concerning the influence of the salt concentration on the specific weights indicate that with increasing KCl concentration the differences of composition between coacervate and equilibrium fluid decrease. (See fig. 2). This is just what might be expected, as an added indifferent salt increases the mutual solubility of coacervate and equilibrium liquid.

4. *Interfacial tension.*

In tables II and III the values found for σ in our experiments have been summarised.

At the bottom of tables II and III the mean value of σ for each series and its standard error are given.

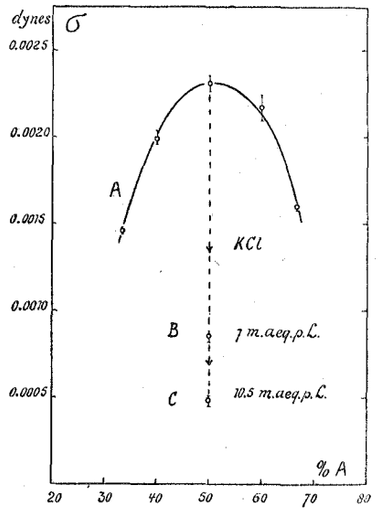

Fig. 4.

In fig. 4 the mean values for σ have been plotted against the percentage gum-arabic. (Moreover the mean values for σ in a 50 % A system to which 7 and 10,5 m. aeq. KCl resp. have been added have been indicated.)

To give some idea in how far these experiments can be reproduced

we may mention that with another set of stock sols we obtained (for 50 % A)

$\sigma = (2{,}49 \pm 0.08) \times 10^{-3}$ dyne/cm ($2{,}31 \pm 0.04 \times 10^{-3}$ dyne/cm in table II)

and with another set again

$\sigma = (3{,}13 \pm 0.08) \times 10^{-3}$ dyne/cm.

Latter value seems rather different from the other two. This may be due to the fact that in this series we did not keep the coacervate during one night at 40° C., but brought about sedimentation immediately by centrifugating during 30 min. at 38° C. and determined σ immediately afterwards. (Prevention of the slow hydrolysis of the gelatin component at 40° during some 16 hours.)

As always we again found in these experiments, especially in the determination of specific weights of the coacervate, that a very rigorous uniformity of treatment of the coacervate was a conditio sine qua non to obtain agreeing results.

As every complication in the experimental procedure involves a danger for uniformity of treatment, and this uniformity is highly desired as theoretically a maximum σ value was to be expected at a certain mixing proportion (see below), we preferred in the definitive experiments to bring about the separation into two clear liquid layers by spontaneous sedimentation during a fixed time and not by centrifugation.

5. *Discussion.*

a. *σ as function of the mixing proportion.*

Fig. 4 shows that in the isohydric mixing series (pH 3.7) the interfacial tension is not independent of the mixing proportion and that at a certain mixing proportion σ reaches a maximum value. From general considerations such a maximum curve of course can already be expected, as somewhere in the coacervation region the difference in composition of the two liquid layers will be maximal and this difference will become smaller in nearing the coacervation limits.

If we try to extrapolate both branches of the σ curve in fig. 4 (and 5) up to the coacervation limits (19 % and 81 % A) is seems probable that σ falls regularly to zero. We might however expect by a similar reasoning as given in 3a) that the interfacial tension will keep a finite value up to the coacervation limits. Evidently these finite values of σ are here very small.

b. *The postion of the σ maximum.*

Fig. 5 contains besides the σ curve from fig. 4 also results from an earlier investigation, in which the circumstances (2 % sols from the same colloid-preparations, same concentration of the acetate buffer) were exactly the same.

We may conclude that the interfacial tension reaches its maximum at

practically the same mixing proportion, at which the coacervate volume curve (coacervate volume separated from 20 cc sol mixtures) shows its maximum.

Of much importance is the fact that at this mixing proportion also the electrophoretic reversal of charge point is situated. Theoretically it should just be expected that an uncharged interface has a maximum interfacial tension, and that the acquisition of a positive (towards smaller % A) or of a negative (towards higher % A) capillary electric charge would lower the interfacial tension.

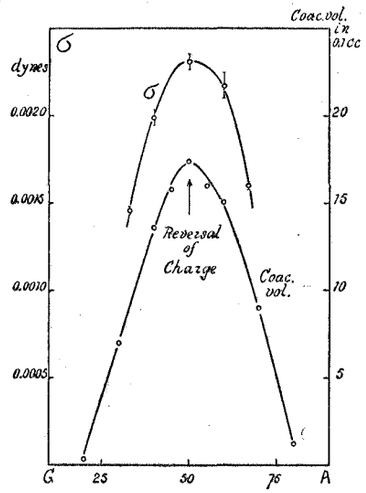

Fig. 5.

It seems possible that the above discussed (see a) strong decrease of σ up to only a very small definite value at the coacervation limits, is mainly due to this effect of the still increasing capillary electric charge of the interface.

c. *The influence of an added indifferent salt.*

Fig. 4 shows that 7 and 10.5 m. aeq. KCl diminishes considerably the interfacial tension of coacervate and equilibrium liquid. This result is in accordance with expectation as an indifferent salt increases the mutual solubility of the complex coacervate and the equilibrium liquid, thus diminishing considerably the original difference in composition of the two phases, which also expresses itself in a strong decrease of the original difference in specific weight of the two phases, see fig. 2.

d. *The order of magnitude of the interfacial tension.*

Most interesting is the very low order of magnitude of the interfacial tension, this even at its maximum value amounting to only a few thousandths of a dyne per cm. An argument for the correctness of this value

is to be found in the fact, that with several other less precise methods we mentioned above in 1, most of which were fully independent of the present method, we obtained values in the same order of magnitude.

Undoubtedly the interfacial tension we measured in the above experiments are lower than those to be expected if for the adjustment of the pH not a diluted buffer but only HCl had been used. The buffersalt present in our experiments (10 m. aeq. p. L. Na acetate) being of the same type (1—1) as KCl will have had a decreasing influence on the maximum of the σ curve of approximately 2.10^{-3} dynes p. cm.

By using HCl instead of a buffer, the coacervated system would still contain an indifferent salt, namely $CaCl_2$, originating from the counterions of both colloids (Ca from gum arabic and Cl from gelatin).

A rough estimation (assuming the decreasing influence of $CaCl_2$ to be twice as strong as of KCl) would lead for such ideal complex coacervates, which contain besides water only the oppositely charged macromolecular ions of both colloids, to a maximal value of the interfacial tension of approximately 8.10^{-3} dynes per cm, which still is surprisingly low.

e. *Interfacial tension and effective electrostatical attraction.*

Earlier investigations have sufficiently shown that the electrostatical atraction between the oppositely charged macromolecular ions of gelatin and gum arabic is the only factor which unites these colloids in the complex coacervate. The effective attraction depends on pH, mixing proportion and salts present, and gives an explanation of the occurrence at each given pH of an optimal mixing proportion, of the coincidence with a reversal of charge point, of the changes in composition of coacervate and equilibrium liquid and of the suppressing effect of added salts on complex coacervation. It seems logical to correlate the above found changes in interfacial tension also directly with the changes in effective electrostatical attraction.

The interfacial tension is thus no longer seen as an accidental property, which is modified by changes in composition of the two adjacent phases (as above in a and c) or by electrification of the interface (as above in b), but as the direct outcome of the electrostatical attraction of the oppositely charged macromolecular ions within the coacervate, which attractions in the interface have no longer a resultant zero.

Then at once the occurrence of a maximum σ value at the reversal of charge point (optimal attraction), the large fall of σ at both sides of this optimal mixing proportion (the effective attraction becomes small), and the strong reduction of σ by added salt (decrease of the effective attraction by the screening effect of both cation and anion of the added salt) becomes evident.

This conception may also explain qualitatively the low order of magnitude of the interfacial tension.

Compared with the surface tension of molten alkalihalides (e.g. NaCl/air $= \pm$ 100 dynes per cm at 1000° C.), this interfacial tension must be very much lower because:

1. The "concentration" of the charges of both sign is relatively high in the molten salt, but relatively small in the coacervate (it contains ± 16 % colloids and 84 % water, from which the concentration of the "gelatin arabinate" expressed in aequivalent p. L. can be roughly calculated to be only 0.07 N).

2. The electrical attraction in the coacervate is diminished considerably (80 ×) because the macromolecular ions are inbedded in a medium (water) possessing a high dielectrical constant. This medium is the same as the equilibrium liquid (apart from some dissolved macromolecules in the latter), so that no contribution to the interfacial tension results from it.

Both factors would perhaps lead to even too small values for the interfacial tension of the coacervate, which may be due to the fact that we did not account for the very great difference in temperature.

Without doubt the two above points would not suffice for a quantitative theoretical treatment of the problem, and other factors (the attachment of the ionized group on flexible macromolecules) should also be taken into account.

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Biochemistry. — *Oleate systems containing potassium chloride in which the KCl concentration is still too low for coacervation. I. The viscosity-KCl curve.* By H. G. BUNGENBERG DE JONG and G. W. H. M. VAN ALPHEN.

(Communicated at the meeting of March 29, 1947.)

1. *Introduction. Technic of measurement.*

In previous research about coacervation of oleate sols by KCl, we have already mentioned that KCl concentrations still too low for coacervation, induce peculiar systems behaving as liquids of a high viscosity and showing elastic properties moreover [1]).

In this and the next communication, we discuss in principle their viscous behaviour, in the third communication follows a discussion of the elastic behaviour.

This investigation, being only of an orientating nature, does not aim in the first place, at measuring the characteristics already mentioned with a high degree of accuracy.

The purpose is rather to become acquainted with the variables which we have to deal with and especially to learn also something about the influence of non-electrolytes (in particular here the influence of primary normal alcoholes) exercising such an enormous great influence on oleate coarcervates, as shown in previous research [1]).

The expression $\frac{\eta_s - \eta_0}{\eta_0}$, in which we are interested in the first place at constant oleate concentrations, varies so enormously with increasing KCl concentrations that one has not enough of one and the same viscosimeter to record accurately the KCl curve but needs a whole set of them.

But in the circumstance that in these sols of high viscosity elastic properties are clearly present beyond a definite KCl concentration, the presented difficulties are not to overcome by increasing the accuracy of time measurement which may be obtained from the use of a set of mutually tested viscosimeters.

For our purposes we rather need to record with one viscosimeter the whole KCl curve, which necessitates the selection of a small value for the time of flow for water and KCl solutions resp.; at the same time we are limited to relatively small oleate concentrations, lest the times of flow become inpractically great in adding KCl.

But small oleate concentrations produce a relative time of flow of the sol

[1]) H. G. BUNGENBERG DE JONG, H. L. BOOY and G. G. P. SAUBERT, Protoplasma 28, 543 (1937).