CONTENTS

Biochemistry. — *Distribution of the complexcomponent which is present in excess, between Complexcoacervate and Equilibrium liquid.* By H. G. BUNGENBERG DE JONG.

(Communicated at the meeting of April 26, 1947.)

1. Introduction.

At a definite mixing proportion of the two equally concentrated (2 %) isohydric Gelatin and Gum Arabic Sols, complexcoacervation is a maximum [1]). At this mixing proportion the Gelatin-cations and Arabinate-anions unite in aequivalent proportions. As the (apparent) aequivalent weights of both colloids are functions of pH, this "aequivalent" mixing proportion shifts to other values if the pH is changed.

From previous publications it was already known in which direction the compositions of the coacervate and of the equilibrium liquid are altered, if at constant pH the mixing proportion is changed [1]), respectively if at constant mixing proportion the pH is changed [2]).

Below it will be shown, that both changes can be summarized from one simple point of view.

2. Variation of the mixing ratio of the sols at constant pH.

The following table contains the analytical results for pH 3.51 [3]). The mixing proportion of the isohydric 2 % sols (column 1) is here varied. The colloid contents (G = Gelatin, A = gum arabic) of the coacervate layer and of the equilibrium-liquid are represented in the columns 2 and 3, respectively in 4 and 5.

The "colloidcompositions", i.e. $100 \, A/A + G$, to be found in the last two columns, were calculated from the data of columns 2, 3, 4 and 5.

These colloid compositions as function of the mixing ratio are represented

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[1]) H. G. BUNGENBERG DE JONG and W. A. L. DEKKER, Kolloid Beih. **43**, 213 (1936). The analytical results, which will serve as a base for what follows, are to be found on p. 222—223. For a discussion of the changes in composition of coacervate and equilibrium liquid, see p. 233 and fig. 11.

[2]) H. G. BUNGENBERG DE JONG and B. KOK, Proc. Ned. Akad. v. Wetensch., Amsterdam, **45**, 51 (1942).

[3]) It has been recognized since a few years, that in the calculating the pH from E.M.F. measurements with the H electrode, a systematic error was introduced. All pH values in the publication mentioned in note [1]) must be increased with 0.33. The isohydric mixing series thus actually was not pH 3.51 but 3.84. In the same way all pH values in table 2 must be increased with 0.33. As also the I.E.P. of the gelatin used must be increased with the same amount and as in the discussion of the experimental result only pH differences and not the absolute values of the pH play a rôle, general conclusions rest the same. In the aim not to cause confusion the originally given pH values have been maintained in this publication.

in fig. 1 by curve C (coacervate, column 6) and curve E (equilibrium liquid, column 7).

Mixing ratio of sols $100\frac{A}{A+G}$	Composition coacervate		Composition equilibrium liquid		$100\frac{A}{A+G}$	
	$\%$ G	$\%$ A	$\%$ G	$\%$ A	in coacervate	in equilibrium liquid
33.6	7.69	6.11	0.686	0.234	44.3	25.4
40.4	7.86	6.60	0.419	0.151	45.6	26.5
45.4	7.55	6.77	0.256	0.154	47.3	37.6
50.4	7.01	6.93	0.170	0.200	49.7	54.1
55.4	6.15	7.30	0.162	0.318	54.3	66.3
60.4	5.88	7.38	0.195	0.535	55.7	73.3
65.3	5.41	7.15	0.261	0.839	56.9	76.3

These curves intersect each other at the aequivalent mixing proportion (colloid composition of coacervate = colloid composition of the equilibrium liquid). At this or very near to this mixing ratio lays also the electro-
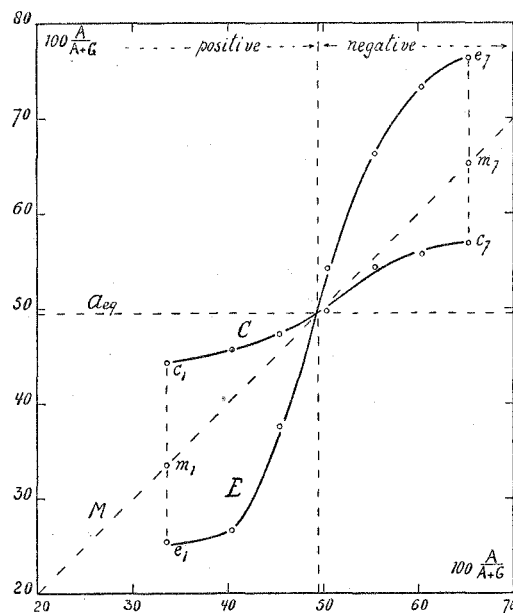

Fig. 1.

phoretic reversal of charge of the boundary coacervate drops/equilibrium liquid.

The figure further contains three dotted lines, all three going through the intersecting point of the curves C and E. The vertical one divides the plane of the figure into a left half, in which the coacervate is positively charged, and a right half, in which the coacervate is negatively charged. The horizontal dotted line ("Aeq") gives the colloidcomposition of the coacervate (and equilibrium liquid) at the aequivalent mixing ratio.

The third dotted line ("M"), drawn at an angle of 45° represents the colloid compositions of the total mixtures (as they were prepared by mixing equally concentrated Gelatin and Gum Arabic Sols).

As at the aequivalent mixing proportion, the colloid composition of the coacervate and of the equilibrium liquid are equal, these colloid compositions are of cause here also equal to that of the total solmixture. Therefore the intersecting point of the curves C and E must lay on the dotted line "M".

We must now draw our attention to the relative positions of the curves C, E and of the dotted lines "Aeq" and M.

From the relative position of C, E and "Aeq" follows, that if one of the colloid components is present in excess, this component distributes itself in such a way, that the colloid composition of the equilibrium liquid is much more changed than that of the coacervate.

A total mixture m_7 thus divides in an equilibrium liquid e_7, which is still richer in A than m_7, and in a coacervate c_7, which comparatively is but little richer in A than the aequivalent coacervate (c_7 lies not far from the horizontal dotted line "Aeq").

The same can be observed with positively charged coacervates: the equilibrium liquid e_1 is still richer in G than m_1, but the coacervate c_1 is only little richer in G than the aequivalent coacervate.

From this much smaller shift in composition of the coacervate compared with the shift in composition of the equilibrium liquid appears that the processes at work in complexcoacervation tend to the separation of the aequivalent coacervate.

The colloid component in excess mainly accumulates in the equilibrium liquid. A smaller part of it nevertheless enters the coacervate changing it in two ways:

1) the coacervate boundary assumes the electrical sign of the component in excess,
2) the reciprocal solubility of coacervate and equilibrium liquid is increased.

Fig. 1 is valid for one chosen pH; at other pH values for the isohydric mixing-series the system of intersecting curves C and E shifts in such a way that its intersecting point always lies on the dotted line "M". At higher pH this intersecting point moves to the left, at lower pH to the right. For the rest, the relative positions of the curves C, E and the lines (through the intersecting point) "Aeq" and "M" are not altered in principle, and therefore the conclusions drawn are the same as above.

3. Variation of the pH at constant mixing ratio of the sols.

Combining the analytical result for five isohydric mixing series, it is possible to survey the changes in G and A composition of the coacervate and equilibrium liquid at one constant mixing ratio and variation of the pH.

For this aim we choose the mixing ratio of 50 %, for alone this ratio occurs in all five mixing series.

We then find the colloid percentages as given in the columns 2, 3, 4 and 5 of the following table. From these figures are then calculated the "Colloidcompositions" of the coacervate and the equilibrium liquid as given in columns 6 and 7.

pH	Coacervate		Equilibrium liquid		$100 \dfrac{A}{A+G}$		Mixing ratio of aequivalent Coacervation
	% G	% A	% G	% A	Coacervate	Equilibrium liquid	
3.00	5.44	6.92	0.59	0.495	56.0	45.6	62.2
3.29	6.68	7.39	0.277	0.183	52.5	39.8	55.2
3.51	7.06	6.92	0.175	0.195	49.5	52.7	49.5
3.80	6.25	5.27	0.324	0.446	45.7	57.8	40.4
4.00	3.9	3.0	0.80	0.90	43.5	52.9	32.7

These colloid compositions as function of pH are represented in fig. 2 by the curves C (coacervate) and E (equilibrium liquid). The colloid
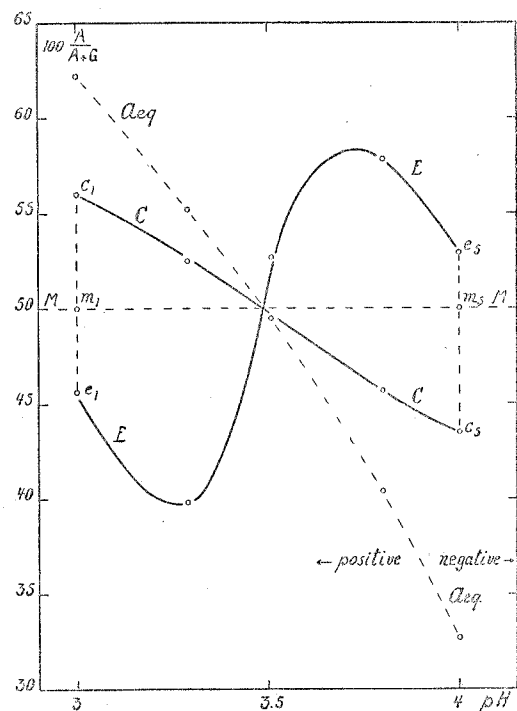

Fig. 2.

compositions of the total mixtures lie, as they all have now the same mixing ration (50 %), on the dotted horizontal line "M". Also in this fig. 2 the curves C and E intersect and the intersecting point necessarily must lie on the dotted line M.

This intersecting point lies at that pH, whereby the chosen mixing ratio of the sols, is at the same time the aequivalent mixing ratio.

Fig. 2 further contains a curve "Aeq", indicating the colloid compositions of the aequivalent coacervates at different pH values (from column 8).

As at or very near to the aequivalent mixing ratio reversal of charge is obtained, curve "Aeq" divides the plane of the figure into a positive half (to the left) and a negative half (to the right).

From the relative positions of the curves C, E, Aeq and the line M one may conclude that here once more the same tendency of the processes at work in complexcoacervation may be perceived as in fig. 1: these processes tend to the separation of the aequivalent coacervate at the prevailing pH.

As the mixing ratio is now held constant, this tendency can only be satisfied completely at one pH value. At the remaining pH values this tendency reveals itself in the fact that a total mixture (e.g. m_1 or m_5) separates into a coacervate (c_1 or c_5) the colloid composition of which is much nearer to that of the aequivalent coacervate belonging to that pH, and an equilibrium liquid (e_1 or e_5), the colloid composition of which is still farther different from that of the aequivalent coacervate as the colloid composition of the total mixture.

Summary.

1) The distribution of the complexcomponent which is in excess, between complexcoacervate and equilibrium liquid, is discussed using formerly published analytical data.

2) In both cases considered:

   a) variation of mixing ratio of sols at constant pH,

   b) variation of pH at constant mixing ratio,

the above distribution takes place in such a way, that therein a tendency can be perceived to maintain the separation of a complexcoacervate of aequivalent colloid composition, belonging to the prevailing pH.