

Chemistry. — *Extension of the theory of complex coacervation to ionic disperse systems.* By H. R. KRUYT and H. G. BUNGENBERG DE JONG.

(Communicated at the meeting of June 29, 1935).

When some years ago we started the discussion of the phenomena of partial miscibility in colloid systems¹⁾, we chose the name coacervation on the ground of the mechanical picture which in our opinion we had to introduce for the phenomenon and in contradistinction to a phenomenologically corresponding phenomenon in systems with purely true solubility.

A long series of papers have been published²⁾ since, dealing in particular with complex coacervation, i.e. the separation of a liquid phase from a mixture of two oppositely charged hydrophilic colloid sols, as well as with the essentially connected auto-complex coacervation. All results obtained in case of complex coacervation are intelligible from the following point of view. The relative viscosity of colloid mixtures with identical polarity is an additive magnitude; in case of opposite polarity a curve occurs with a minimum, while at the same time coacervation phenomena arise (ultramicro-, micro-, macro-coacervation); the position of the minimum is determined by compensation of the opposition in polarity, the intensity of the dehydration in the minimum by the density of the charge on the surface of the colloids (weak and strong coacervators).

The mechanical picture, suggested by these experiences, is the following (see fig. 1): owing to their opposite polarity the particles attract each

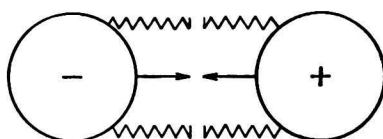


Fig. 1

other, owing to their hydration they are kept apart³⁾: an equilibrium is formed between an attracting and a repelling factor.

Meanwhile, what is this hydration and why does it decrease by opposite polarity? Hydration is the orientation of the water-dipoles in the electric field on the surface of the colloids. This hydration gradually decreases with the distance from the surface (fig. 2); the whole atmosphere of the

¹⁾ H. G. BUNGENBERG DE JONG and H. R. KRUYT, Proc. 32, 849 (1929).

²⁾ H. G. BUNGENBERG DE JONG and collaborators. Bioch. Z. 212, 318 (1929); 221, 182, 392, 403 (1930); 232, 338, 234, 367, 235, 185 (1931); 248, 115, 131, 309, 336, 254, 15, 35 (1932); 257, 62, 259, 436, 442; 260, 161; 262, 161, 390, 263, 33 (1933). These articles will further be cited in Roman figures.

³⁾ In fig. 1 the arrows represent the attraction, while the springs indicate repulsive buffers.

oriented dipoles contributes to the viscosity. In case of a mixture of

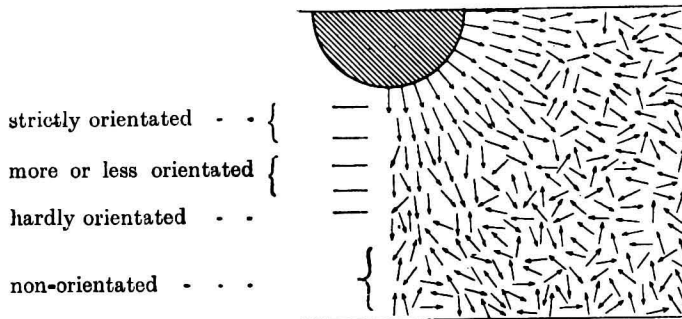


Fig. 2.

oppositely charged colloids a condition sets in which is represented by fig. 3.

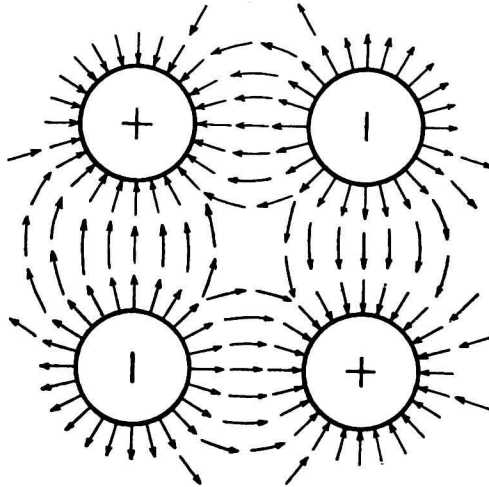


Fig 3.

The dipoles are sucked into the lines of electric force, since this means a decrease of the free energy of the system.

If (as is commonly done) *dilute* solutions of the colloids are put together, a system as represented in fig. 3 will give rise to the separation of a phase rich in colloids. In equilibrium with this phase rich in colloids there is then a phase rich in water, the so-called "equilibrium liquid" ¹⁾.

The opposition in polarity disappears if, e.g. by means of neutral salts, the ζ potential of one of the components is annihilated. Since this is dominated for negative colloids by the valency of the cations, for positive ones by the valency of the anions (rule of SCHULZE-HARDY), the prevention of coacervation by neutral salts (and the compensation of an

¹⁾ H. G. BUNGENBERG DE JONG, L. W. J. HOLLEMAN and B. S. Tj. MODDERMAN, Koll. Beih. **39**, 334 (1934).

already present coacervation respectively) takes place according to two rules of valency, viz. 1—1, 1—2, 1—3, etc. and 1—1, 2—1, 3—1, etc.

The conception of complex coacervation briefly stated here is founded on the above-cited researches: the viscosimetrical experiences are found in the treatises I, II, III, those on the constitution¹⁾ of the coacervate drops in IV and V (electrical disintegration), VI and XI (amount of water in the coacervate drops), those on the influence of neutral salts in I, II, III, VI, and XX.

The form of the coacervate will depend on various factors. In the first place the amount of water will decide whether the coacervate is drop-liquid or rigidly solid (cf. VI) and the amount of water, we only just mentioned it, is a function of the mutual attraction. It is also possible that the micelles are arranged according to an ordered pattern, which however in case of colloids occurs so rarely that GRAHAM felt justified to regard the ideas colloid and crystalloid as complete contrasts.

On closer consideration of the view that opposition of potential decreases the hydration but does not annihilate it completely, because the sucking in of the oriented water-dipoles may yet bring about a stabler condition than that of the separated components, it is clear that no specifically colloid-chemical datum is discussed here, but it is suspected that in *every* system with oppositely charged particles, dispersed in water, the same phenomena will be possible and under wellchosen conditions even probable. Immediately, therefore, the question rises whether complex coacervation (or — if desired — unmixing) consequently must generally occur in *electrolyte*-solutions, for in the solution of a strong electrolyte in water the very same conditions are found: oppositely charged ions, surrounded by oriented water-dipoles.

In this direction already points the existence of the so-called *auto-complex coacervation* (e.g. gum arabic + Hexol nitrate), where the formed coacervate possesses all typical properties of the complex coacervates, in spite of the fact that only one colloid component is present here and the other is replaced by an oppositely charged crystalloid ion (cf. VII—XX). The representation used thus far, viz. that the crystalloid ion is adsorbed to the colloid particle, which causes a mosaic of charge to be formed on the surface of the colloid particles, may have been a fertile work hypothesis for the exploration of this type of coacervation, but after all it only represents the condition of the particles before their union to the coacervate and it only has reason of existence for the description of the coacervation mechanism.

The fact, however, that the disintegration phenomena also are completely identical to those of the complex coacervates rather indicates that in the formed coacervate itself the oppositely charged crystalloid ion may not be considered more bound to one special colloid particle than to the surrounding particles. This signifies, therefore, that in auto-complex coacervates the crystalloid ions are in a position perfectly equivalent to that of the "colloid ions".

Owing to this fact it may also be expected that these colloid ions likewise may be

1) More elaborate analyses will be published later in the *Kolloid Beihefte*.

replaced by well-chosen crystalloid ions, with the preservation of the "coacervation phenomenon", while the unmixed electrolyte-containing liquid will display the same characteristic properties of the "complex coacervates".

The fact that unmixing is not known in salt solutions seems to refute this view. However, it should be considered *where* there is a chance to meet with this phenomenon.

1. The condition of unmixing is regulated by the dipoles passing in and out the electric field. The higher the kinetic energy of the dipoles, the more unfavourable is the chance to realize a phenomenon of unmixing of the type discussed above. It is necessary to remain below a certain critical consolute temperature and consequently to make researches at a *low* temperature.

2. Moreover, we should not investigate the concentrations below those of the "equilibrium liquids"; the higher the salt concentration, the greater is the chance of getting within the heterogeneous area.

Consequently 1 and 2 lead the investigation to a *high* salt concentration and *low* temperature.

3. It has been stated above that the condition of coacervation may be one of less free energy than that of homogeneity. It should, however, be considered that a condition of *still* lower energy is possible, viz. that where the electrolyte separates out in the form of solid crystals (with or without water of crystallization). The rivalry between lattice energy and hydration energy dominate this problem. The condition of unmixing may consequently be an energetic intermediate stage between homogeneous distribution and saturated solution with Bodenkörper. At a low temperature and high concentration, however, the limit of solubility is generally far surpassed. The preceding considerations consequently lead the investigation to the *supersaturated* solutions.

These now may be attained by causing the electrolyte, which has to lead to "complex coacervation", to be formed in homogeneous solution, i.e. by e.g. double decomposition.

If we wish to obtain AB in supersaturated solution, we mix the solutions of the soluble combinations AC and DB; but then generally DC is formed as a neutral electrolyte with its detrimental consequences for the complex coacervation which have been described above.

Considering all these difficulties, it is not surprising that these phenomena have "never" been found accidentally. A purposeful investigation, however, has indeed demonstrated the existence of the phenomena of unmixing in salt solutions.

A number of examined cases follow below.

UNMIXING IN MIXTURES OF TWO AQUEOUS SALT SOLUTIONS.

*Luteo-cobalt chloride — Antimonyl potassium tartrate*¹⁾).

We start from a 0.1 N solution of luteo-cobalt chloride and a 0.1 mol.

¹⁾ These first two examples of unmixing were already found in 1932 in collaboration with F. A. MENALDA.

solution of antimonyl potassium tartrate, further indicated below by L and A. At room-temperature the mixtures 10 L + 90 A, 14 L + 86 A and 80 L + 20 A remain clear. In the intermediate range of mixture proportions a strong turbidity sets in, which has altogether the character of unmixing, viz. in a system with an upper consolute temperature: When slightly heated, the strongly turbid mixtures become clear and once more show turbidity on cooling, while retardation phenomena (such as may play a part in crystallization) are out of the question. Microscopically very small globules are observed.

After a shorter or longer time, however, the turbidity does not disappear any more on heating; microscopically it is seen that the original merely present very small globules have been replaced by crystals. The crystals, therefore, have a smaller solubility than the globules and this can be beautifully observed in the microscopic preparation: In the original field full of small droplets crystals originate somewhere radially from one single point. These crystal-rosettes now are always surrounded by a clear space, i.e. the globules are dissolved and the luteo-antimonyl tartrate is crystallized.

The unmixing, however, disappears at room temperature, on shaking with a little solid KCl or K_2SO_4 . It is observed here that K_2SO_4 has a stronger action in this respect than NaCl.

However, these clear mixtures are also supersaturated with regard to the crystalline Luteo-cobalt antimonyl tartrate: Frequently it is crystallized soon after it has become clear by means of a neutral salt.

The phenomenon of unmixing described above soon does not appear any longer in more dilute solutions: The limit is found at about 0.04 N L and 0.04 mol. A.

Hexol nitrate — Antimonyl potassium tartrate.

In principle the same unmixing-phenomenon is found here as has been described above (remixing by neutral salts, crystallization). However, the turbidity in 0.1 N Hexol nitrate and 0.1 mol. antimonyl potassium tartrate does not clear up altogether on heating. The main mass of the sediment sticks to the glass as a viscous lump. Since this unmixing salt, which arises by double transmutation, has a hexavalent cation (to a trivalent cation above) it may be understood that the effective attraction is more powerful, which becomes manifest in the greater viscosity, the higher consolute temperature, and at room-temperature the lower limit of concentration at which unmixing still takes place. The latter lies below 0.01 N and 0.01 mol. respectively.

Hexol nitrate — $K_3Co(CN)_6$.

Here also the unmixing is still found in fairly low concentrations, e.g. still in 2 m. equiv. solution. This system was elaborately investigated by K. C. WINKLER, who found a complete analogy with the complex coacervation. For example, the separating droplets electrophoretically have

a positive and negative charge respectively, according as the one component or the other is present in excess.

Further the unmixing is removed according to the two rules of valency: $3-1 > 2-1 > 1-1$ and $1-3 > 1-2 > 1-1$ respectively.

Hexol nitrate — Sodium amyl sulphate (iso).

In this combination also unmixing occurs, but the required concentrations are considerably higher.

The unmixing-phenomena mentioned above are by no means exclusively bound to the complex Luteo or Hexol cations. They are, for example, also met with in the following combinations, containing salts in which bivalent cations of the principal or secondary series of the periodical system are present.

$\text{Cd}(\text{NO}_3)_2$ — Sodium tartrate

$\text{Cd}(\text{NO}_3)_2$ — Sodium benzoate

$\text{Pb}(\text{NO}_3)_2$ — Sodium succinate

Here we may with advantage proceed as follows:

We put 2 drops of the two fairly concentrated salt solutions (e.g. of 1—2 N) by the side of each other on an object-glass (without their touching each other) and cover this with a cover-glass. By diffusion, automatically obtained, all sorts of mixing-proportions are formed closely around the line of contact, and the unmixing into droplets may now be observed. With respect to the Cd tartrate it should be remarked that it may with advantage be slightly heated, the "coavervate" at room-temperature being very poor in water. It is at the same time favourably distinguished by the fact that here the spontaneous crystallization does not easily set in.

All phenomena of unmixing occurring here disappear again if a sufficient amount of neutral salt is added.

BaCl_2 — Ammonium molybdate

SrCl_2 — Ammonium molybdate

Here again concentrated solutions are used and now the formation of truly liquid drops may be observed under the cover-glass.

Particularly the combination with SrCl_2 is very well suited for demonstration, as at room-temperature it yields a very slightly viscous "coacervate", which soon separates out in the test-tube as a completely clear, mobile macro-liquid layer.

As in all cases of unmixing described above, the mixing-proportion here also plays an important part. Compare the following table, where the effect is stated of increasing addition of a solution (prepared in the cold) of 25 gr. Ammonium molybdate in 85 gr. water (solution A) to a SrCl_2 solution 2 N.

5 cc SrCl ₂ 2 N +	1 cc A	} no unmixing	
"	2 "		
"	3 "		
"	4 "		
"	5 "		
"	6 "		small unmixed layer
"	7 "		larger unmixed layer
"	8 "		still larger layer
"	10 "		max. large layer
"	15 "		layer smaller than with 8 cc A
"	20 "	no unmixing.	

The A solution being about 1 N (the Ammonium molybdate regarded as $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ 4 aq.), the maximal unmixing takes place at about the equivalent proportion.

After a short while the unmixed layer is crystallized, which is accompanied by the rising of liquid bubbles (= upper layer) originating from the surface of the crystals. Although in the tubes with $A=5$ and $A=20$ no unmixing occurred, soon crystals are formed here also.

Unmixing in the binary system salt-water.

In the examples of unmixing described above we still have to do with 4 kinds of ions. It was remarked before that the salt DC, formed by double decomposition, should not be ascribed an active part in the formation of the ionic unmixing in the system AB-water. It should rather be considered as detrimental.

From this we may draw the conclusion:

a) It must be possible also to realize the unmixing directly in the binary system: salt AB-water.

b) Cases may be found where we do not observe unmixing, if we try to obtain it by the usual method of double decomposition, whereas it may be found in the binary system AB-water itself.

ad a) After a while the Sr molybdate mentioned above is crystallized and now it may be sucked off, washed and then made into a saturated solution. If a drop of this solution is observed microscopically *without cover-glass*, the phenomenon of unmixing is soon perceived on the periphery of the solution, for here the evaporation of the water brings about relatively the largest rise in concentration. After a shorter or longer time here also crystallization sets in. Beautiful pictures are likewise obtained with crystals of Luteo-cobalt antimonyl tartrate. Owing to the easy formation of germs it is advisable first to filter the saturated solution and then slightly heat it.

ad b) In mixtures of Luteo-cobalt chloride and Sodium thiosulphate we did not observe unmixing at room-temperature. From concentrated solutions the *Luteo-cobalt thiosulphate* soon separates out in crystalline form. However, the saturated solution of these crystals by the method described above does indeed show the phenomenon of unmixing on the periphery of

the liquid. The neutralizing action of the NaCl, formed by double transmutation, consequently prevents us to observe the existence of an area of unmixing in the system Luteo-cobalt chloride + Sodium thiosulphate + H₂O¹⁾.

Discussion.

Unmixing in supersaturated solutions of electrolytes is consequently a frequently occurring phenomenon, exactly as our premises led us to expect. That yet in many cases it cannot be demonstrated may certainly be partly ascribed to the fact that research at really low temperatures is excluded, owing to the nature of the solvent water. There is besides another consideration which makes it understood that in many cases the realization of the intermediate state of unmixing is exceedingly hard to attain. We need only ask: why does in the above-mentioned cases the coacervation (accumulation) of ions take place, but not the arrangement to a solid crystalline phase? That is the well-known question, raised by HABER in 1921, about Häufungs- and Ordnungsgeschwindigkeit. On the ground of his researches he concludes that for dipoles the Ordnungsgeschwindigkeit is great with regard to the Häufungsgeschwindigkeit, for multipoles however small; in the first case, namely, the correct state of order is highly probable, in the latter case it is far less so. In anhydrous 1—1 valent electrolytes the observation of the Häufung, of the "coacervation", will be mostly impossible, because it is immediately covered by Ordnung (in the crystal lattice). It is, therefore, not accidental that the above-described cases always contain at least one multivalent ion.

We do not want to omit remarking that VAN LAAR²⁾ already 30 years ago discussed the existence of hidden areas of unmixing in systems with "abnormal" components.

The results described here show the unusual fact that a phenomenon was sooner discovered and understood in the field of the hydrosols than in that of the largely examined electrolyte solutions in water. This is due to the fact that in this special case the conditions in the hydrosols are much more favourable than in the true solutions. In the colloids the density of charge is smaller than with ions, consequently the effective attraction less strong, the permanent dipole orientation of the water greater, the tendency to lattice formation smaller. The separation into two stable liquid phases is consequently much more easily obtained, but this does not affect the fundamental similarity of the two kinds of systems.

Utrecht,
Leiden, } June 1935.

¹⁾ It is to be expected that, if the double decomposition is led in such a way that CD also is insoluble, the unmixing of AB may yet take place, although it fails to occur when the ions C and D are chosen in such a manner that the salt CD remains in dissolved condition. Cf. the observation mentioned in Abegg Vol. II, 2 p. 481: Durch Umsatz von CdSO₄ mit Ba₂S₂O₃ oder SrS₂O₃ in konzentrierter Lösung erhält man ein dickes Öl, das kristallinisch zu CdS₂O₃ · 2H₂O erstarrt.

²⁾ J. J. VAN LAAR, These Proc. 1905, p. 517.