

## Precipitation of Tannic Acid with Triton T-X-705

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Precipitation phenomena in aqueous solutions of the non-ionic surface-active agent Triton T-X-705 and tannic acid were examined by the light scattering method at 293 K. The shape of the precipitation diagram, as well as the micellization effects, indicate the formation of mainly associates-aquacomplexes, which can be due to the mutual interaction of two macromolecules. There is no formation of an ionic compound.

### INTRODUCTION

The understanding of problems concerning the behavior of polymers in solutions seems to be important in science and technology. In order to investigate the precipitation of polymers we used two macromolecules: tannic acid and Triton T-X-705.

Tannins are extracts of polyphenolic composition. Some of them form condensates, some exhibit hydrolytic activity<sup>1,2</sup>. The use of tannins is important in nutrition<sup>3,4</sup>, anticorrosion<sup>1</sup>, paper, textile, wood and leather industries<sup>5,6,7</sup>, and medical research<sup>8</sup>. The oldest classification of tannins was made by Berzelius<sup>2</sup>. On the basis of the hydrolytic decomposition of gallotannins<sup>2,9</sup> it was concluded that the amorphous Chinese gallotannin was a mixture of isomers, whose average composition corresponds to  $\beta$ -penta-*m*-digalloyl-D-glucose. Many authors have proved the structural variety of natural tannins. Fischer<sup>10</sup> suggested, and other authors<sup>9,11,12,13</sup> have found, that natural tannins are galloylated glucoses, contrary to the suggestion of King and White<sup>14</sup> and Grassman<sup>15</sup>.

The precipitation of blood proteins with tannic acid was examined spectrophotometrically by Bate-Smith<sup>16</sup>, who found a linear relationship between precipitation effect and tannic acid concentration. A high reproducibility of results was achieved by using freshly prepared solutions of tannic acid.

The other macromolecule used in our experiments was the non-ionic surface-active agent Triton T-X-705 (octylphenoxyethanol  $C_{18}H_{17}-C_6H_4-(OCH_2CH_2)_{70}$ ). Tritons are principally used in industrial and household detergents and petrochemical and medical research, and as detergents can combine with natural materials such as tannins.

The systematic identification of precipitation phenomena in the two-component system (plus water as solvent) is of primary importance (1) as a basic approach in theoretical examinations of model systems for construction of phase diagrams<sup>17</sup> and precipitation bodies<sup>18</sup>, (2) as an analytically important investigation in polymer determination by the nephelometric method, and (3) because of the possibility of removing tannins from waste waters.

Some authors have used the spectrophotometric method<sup>3,21</sup> for quantitative determination of tannins, while Attia and Rubio<sup>22</sup> applied the nephelometric method for determine small amounts of polyacrylamide and polyethyleneoxide in dilute solutions of tannic acid. Our nephelometric investigations of precipitation phenomena in the system of T-X-705 and tannic acid were motivated by their<sup>22</sup> experience. We used this model system in order to explain the nature of precipitation processes, and to characterize the kind of ionic or non-ionic species that would appear in such solutions.

Such precipitation systems could be much more useful for analytical purposes if the whole precipitation diagram was known.

#### EXPERIMENTAL

Aqueous solutions of tannic acid (puriss. Kemika, Zagreb) and commercial Triton T-X-705 (Rohm and Haas Co.) were prepared with double distilled water. Throughout this research, the tannic acid and the Triton T-X-705 have been assumed to have molecular weights 1701,25 and 3286, respectively. Since both are in fact mixtures, these figures are to be understood as nominal values.

The light scattering method was used (Zeiss Tyndallometer connected to a Pulfrich photometer, and Virtis Brice Phoenix universal photometer model DU 2000) to identify the appearance of solid phase from homogeneous solutions. Measurements were performed at three wave lengths: 470, 546 and 636 nm at 293 K (Hoeppler ultrathermostat) and gave information about the turbidity (measurements at 546 nm, and at angles of 90° and 0°). The ratio  $I_{90}/I_0$  is related to turbidity. Particle sizes were determined by the DQT method (measurements at 470 and 636 nm)<sup>19,20</sup>.

pH-measurements were performed on an Iskra pH-meter (Iskra, Kranj, model MA 5701) using a glass and calomel electrode.

The sign of the charge of colloid particles was determined in the field of a Zeiss ultramicroscope with a double electrophoresis cuvette.

Colloid systems were prepared by the method of B. Težak<sup>19,23</sup>, i.e. by mixing two different solutions of equal volumes, where the concentration of each of the precipitation components presented in the graphs is calculated to a final volume; turbidity measurements were made 1, 10, 60 and 1500 minutes after mixing the components.

#### RESULTS AND DISCUSSION

It is well known that aqueous solutions of macromolecules show effects of aggregation. We can define these phenomena by the critical micellization concentration (c.m.c.) or some other critical relationships depending on dimer, trimer or polymer formation, which result in a sudden change in colligative properties of aqueous solutions (osmotic pressure, surface tension, viscosity, turbidity, refractive index, etc.).

Debye<sup>24</sup> has shown that the light scattering method is appropriately sensitive to the beginning of aggregate formation.

The aggregation phenomena in aqueous solutions of tannic acid or T-X-705, at various concentrations were followed by the light scattering and surface tension methods, and results presented in Figure 1 show the agreement of the obtained critical concentrations. We may observe three characteristic regions in the graphs:

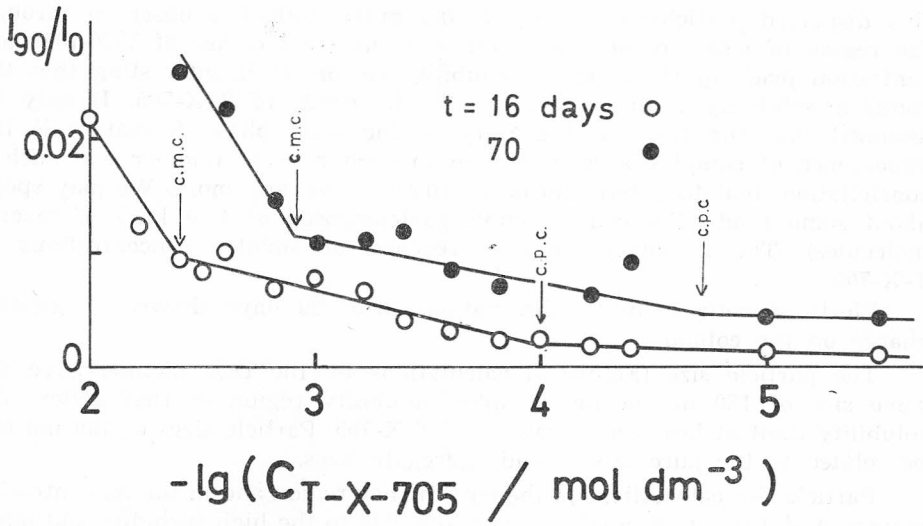
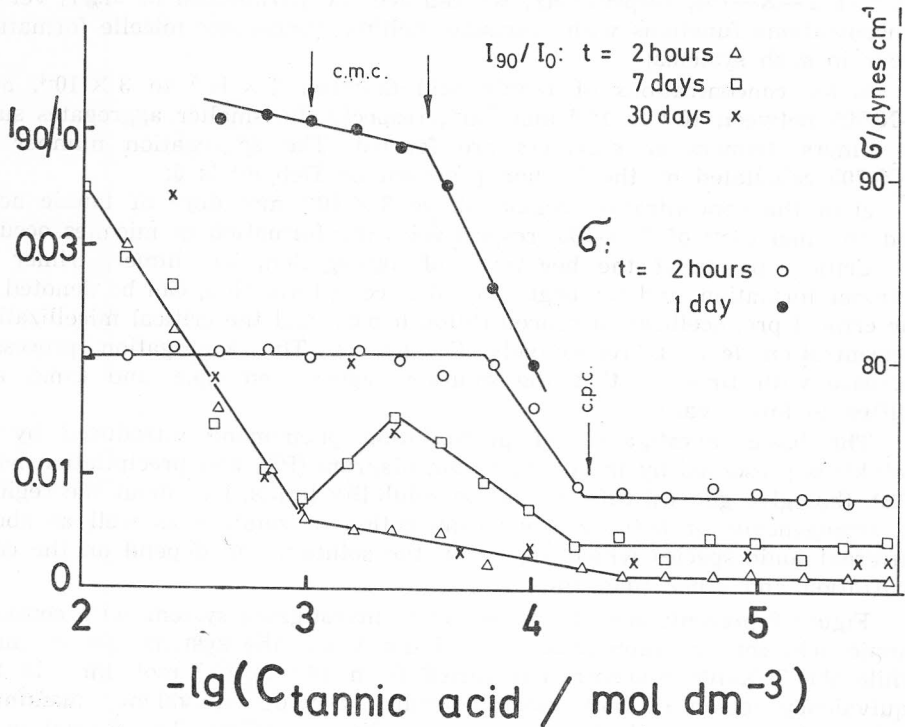


Figure 1. Light scattering and surface tension versus a) tannic acid concentration, b) T-X-705 concentration. The arrows denote critical concentrations of premicelle and micelle formation.

a) below a concentration  $4 \times 10^{-5}$  mol dm<sup>-3</sup> of tannic acid, and  $10^{-5}$  mol dm<sup>-3</sup> of T—X—705, respectively, we can see the parallelism of » $I_{90}/I_0$  versus concentration« functions with abscissae; neither dimers nor micelle formation occur in such systems;

b) for concentrations of tannic acid between  $4 \times 10^{-5}$  to  $3 \times 10^{-4}$ , and T-X-705 between  $10^{-5}$  to  $10^{-3}$  mol dm<sup>-3</sup>, respectively, smaller aggregates such as dimers, trimers or polymers are formed. The aggregation number of T-X-705 calculated by the method proposed by Debye<sup>24</sup> is 6;

c) in the concentration region above  $3 \times 10^{-4}$  mol dm<sup>-3</sup> of tannic acid, and  $10^{-3}$  mol dm<sup>-3</sup> of T-X-705, respectively, the formation of micelles occurs.

Critical points of the beginning of aggregation, i.e. dimer, trimer or polymer formation, and the beginning of micelle formation, can be denoted as the critical premicellization concentration (c.p.c.), and the critical micellization concentration (c.m.c.), respectively (Figure 1). The aggregation processes increase with time, so that the solution »ages«, and c.p.c. and c.m.c. are shifted to lower values.

The basic investigation of precipitation phenomena introduced by B. Težak<sup>25</sup> is presented by the precipitation diagram (PD) and precipitation body (PB), that give general information on solubility limits, i.e. about the regions of homogeneous or heterogeneous composition of solution as well as about different ionic species which appear in the solution and depend on the concentration and other conditions.

Figure 2 presents one of systematically investigated system, with constant tannic acid concentration ( $2 \times 10^{-3}$  mol dm<sup>-3</sup>), i.e. the systems above c.m.c., while the T-X-705 concentration varied from  $10^{-2}$  to  $10^{-7}$  mol dm<sup>-3</sup>. In the equivalency region of both macromolecules, a wide equivalency maximum is formed as a mutual flocculation neutralization effect. The formation of fine dispersed particles in a very turbid milky colloid is observed through the region of wide spread maximum, and further increase of T-X-705 concentration leads to the complex solubility region. It is interesting that the complex solubility limit coincides with the c.m.c. of T-X-705. It may be assumed that the first heterogeneity in the solid phase formation is the appearance of complex species formed in such a great number and such a constellation, that they have no possibility to grow any more. We may speak about some kind of micellar complexes (composed of two kind of macromolecules). The solubility limit is reached at smaller concentrations of T-X-705.

Electrophoretic mobility observations after 20 days showed a negative charge on the colloid.

The particle size (Figure 3) calculations by the DQ<sub>T</sub> method gave the same size of 180 nm in the complex solubility region as that bellow the solubility limit at low concentrations of T-X-705. Particle sizes of 180 nm can be related to the pure tannic acid aggregate sizes.

Particle size calculations in the equivalency region and in the concentration maximum did not give satisfactory results, due to the high turbidity and inner absorption of light in the very turbid medium. In the system of constant concentration of T-X-705 ( $10^{-5}$  mol dm<sup>-3</sup>) (Figure 4) and systematic variation of tannic acid concentration, the equivalency concentration maximum is limited by the solubility limit region at a lower concentration, and by com-



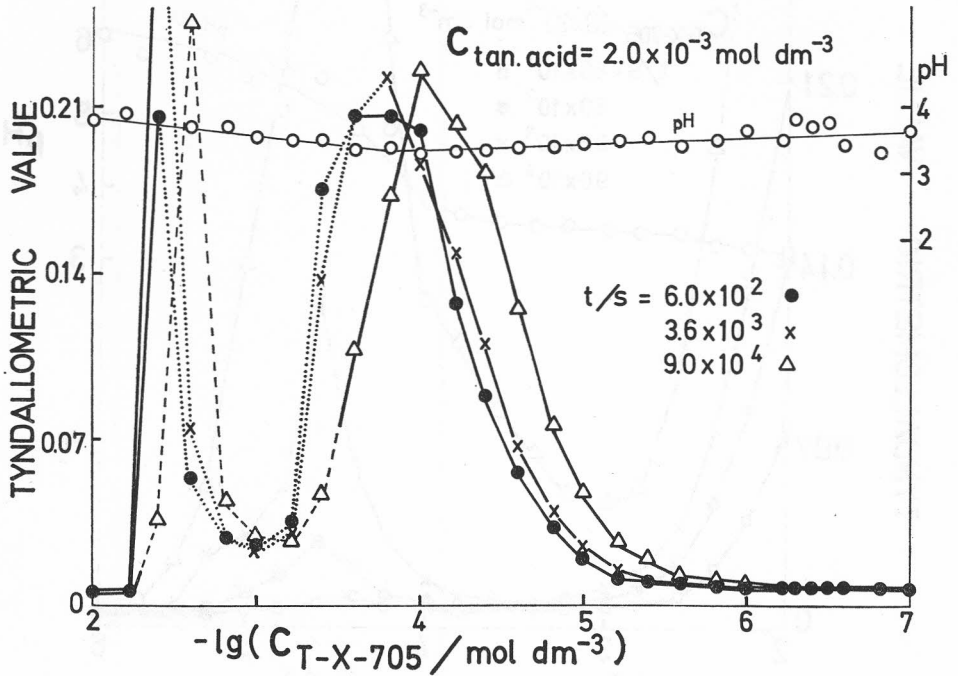


Figure 2. Tyndalometric values in a system of constant concentration of tannic acid, and varying concentrations of T-X-705.

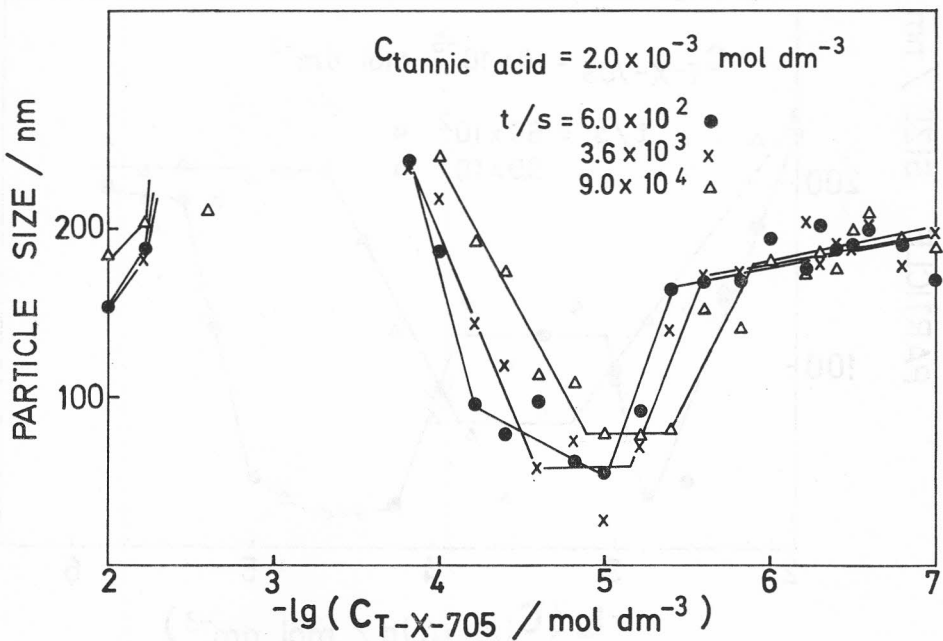


Figure 3. Particle sizes of corresponding systems from Figure 2.

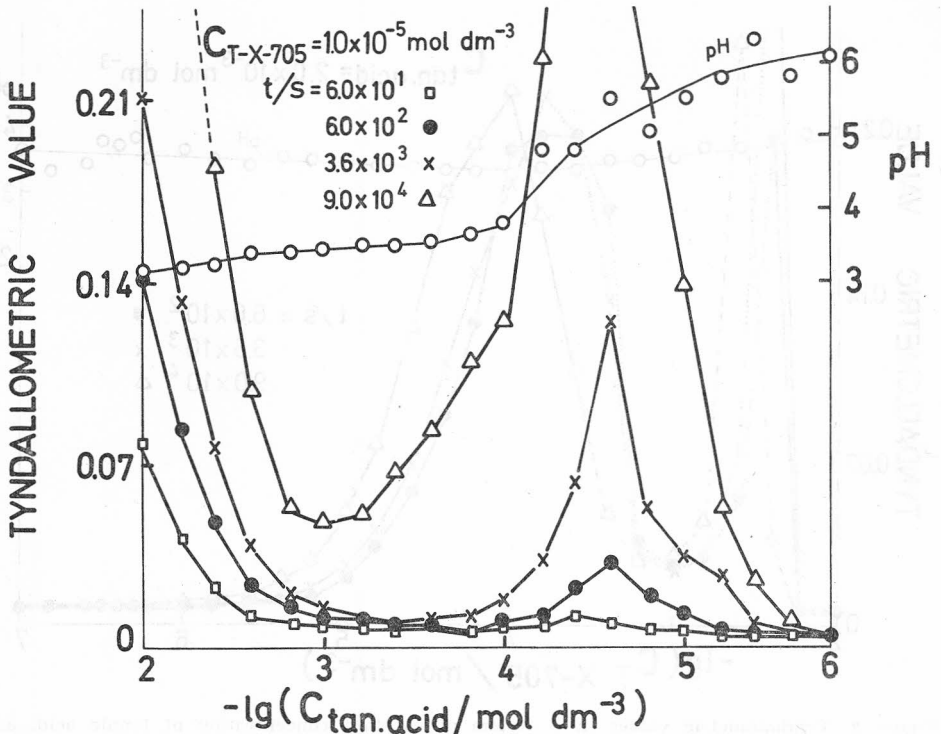


Figure 4. Tyndallometric values in a system of constant concentration of T-X-705, and varying concentration of tannic acid.

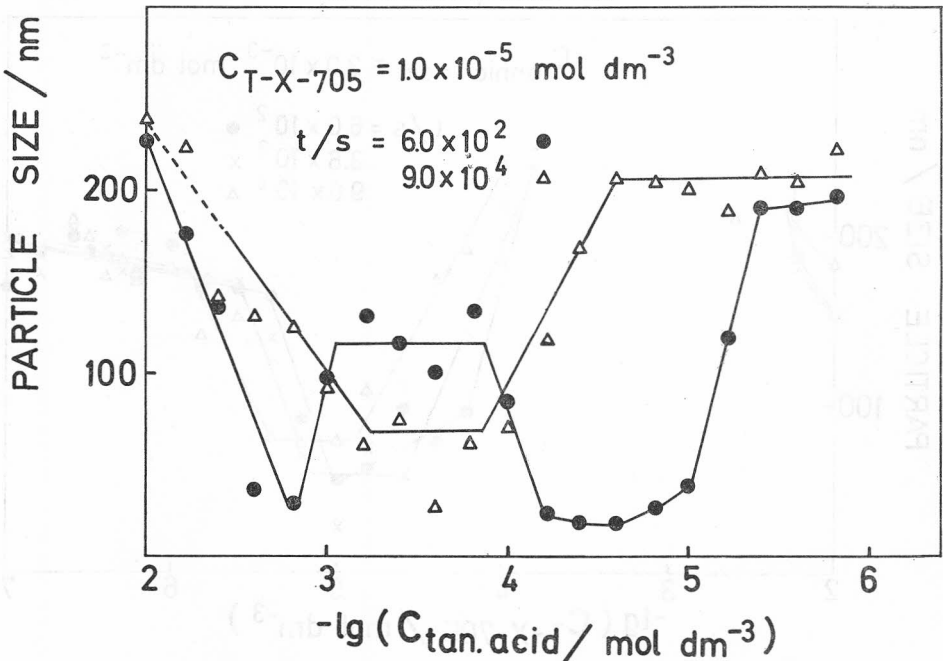


Figure 5. Particle sizes of corresponding systems from Figure 4.

plex solubility at a higher concentration of tannic acid. Above the c.m.c. of tannic acid the turbidity is very marked.

Particle sizes (Figure 5) below the solubility limit are constant, i. e. about 200 nm; in the complex solubility region 110—150 nm, and they grow in the c.m.c. region of tannic acid towards 200 nm. The sign of particle charges is always negative.

On comparing Figure 3 and Figure 5 we can see the constant value of particle sizes below the solubility limit, while these values grow towards the concentration maximum.

It can be assumed that the aggregation or disaggregation character of the precipitation processes at the maximum is based on the stereospecificity of these mutual neutralization effects, because between the two reactants, according to surface tension measurements, there is no formation of chemical compound. This is in agreement with the presumption that can be done on the basis of the shape of the precipitation diagram in Figure 6. The aggregation and micellization character can be correlated with the mutual precipitation phenomena, i. e. mutual neutralization and complex species formation. There is competition between the formation of aqua-complexes — associates in the narrow concentration region, as the segments parallel with the axes in PD show, and complex species formation in the region of higher concentrations of both of the reacting components. The precipitation follows the neutralization type<sup>25</sup>, while solubility product conditions do not exist. It can be concluded that there is no formation of an ionic compound, but an aggregation process occurs as a mutual interaction between the macromolecules caused by steric forces, while the particle sizes and the number of particles are related to the concentration conditions. The shift of precipitation boundaries with time to smaller concentrations of the precipitation components shows the micellar character of these precipitation processes. The complex solubility region corresponding to the micellization ability of both components (above the c.m.c.) shows a high rate of complex species formation, and no further growth of particles. Complex formation occurs in the region above the c.m.c. of T-X-705. Above the c.m.c. of both the reacting components the appearance of a very thick colloid is observed. Almost all precipitation phenomena occur in the concentration region above the existence of molecular solutions of both components.

The relation T-X-705 : tannic acid = 2 : 1 (determined by a graphical method<sup>26</sup>) is valid for complex formation in excess of T-X-705. In excess of tannic acid the complex tannic acid : T-X-705 = 2 : 1 is formed, but it is unstable, and it appears for only a short time after preparation of the precipitation system, while in a longer time period (1 day) the formation of associates is the dominant process. The question arises what are the structures of complexes, of micelles, and the composition of associates. Generally these polymers are hydrophilic colloids<sup>27</sup>. The solubility of polar groups is strong enough to break the van der Waals cohesion forces between the non-polar segments. The configuration of polymer in solution is dependent on the interaction energy polymer — solvent, which is generally related to the dipole interaction, hydrogen bonding and ionic interactions.

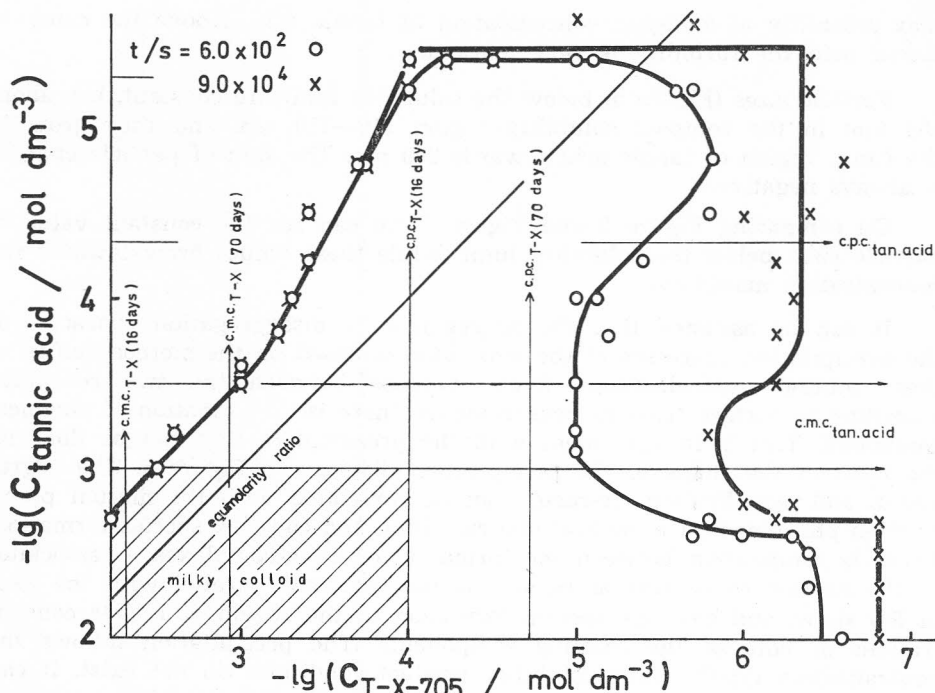


Figure 6. Precipitation diagram of anionic component (tannic acid concentration on ordinate) and non-ionic component (T-X-705 concentration on abscissae). The solubility and precipitability regions correspond to associate and complex ion formation. The arrows denote the critical concentrations of both precipitation components for various aggregate formation.

Following Kitchener's<sup>27</sup> conclusions on the formation of hydrogen bonds, in the case of two hydrophilic colloids such as T-X-705 and tannic acid interacting, we could assume that the basic mechanism is the formation of H-bonds either in complexes, or associates, or micelles, and that the appearance of various types of species in the solution is due to the concentration relationships of reacting component concentrations. Sensitization and flocculation as steric effects, can be related to the amphoteric nature of tannic acid. Some authors<sup>9,27,28</sup> have introduced a linking mechanism due to the possibility of »bridge linkage« resulting from the existence of specific places on the polymer molecule. Goldstein and Swan<sup>29</sup> found complex formation between  $\beta$ -glucosidase and tannic acid dependent on pH, ionic strength and concentration conditions. Destruction of the complexes was achieved by adding cationic, anionic or non-ionic tensides. These effects have been explained by authors assuming that protein and tannin possess H-bond linkages. It has also been shown by Jones and Hulme<sup>30</sup> that polyvinyl pyrrolidone acts protectively on tannic acid because of complex formation between the polymer and tannin.

In the case of non-ionic T-X-705 and negatively charged tannic acid, van der Waals forces are obviously responsible for the formation of complexes, or other aggregate-type species.

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## SAŽETAK

## Taloženje taninske kiseline s tritonom T-X-705

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Taložni fenomeni u vodenim otopinama neionskog površinski-aktivnog agensa tritona T-X-705 i taninske kiseline ispitivani su metodom raspršenja svjetla na 293 K. Oblik taložnog dijagrama, kao i pojave micelizacije, pokazuju stvaranje uglavnom asocijata — akvakompleksa, što se može pripisati međusobnoj micelarnoj interakciji dviju makromolekula. Nema stvaranja ionskog spoja.