Saturated Ternary Systems. I.
Some Physico-chemical Properties of Solutions of 1,1,1-Trichloro-2,2-bis-(*p*-chlorophenyl)-ethane and of Gamma-1,2,3,4,5,6-Hexachlorocyclohexane in the Systems Water-Acetone and Water-1,4-Dioxane

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Investigations have been carried out of the solubility of 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane (*p,p'*-isomer od DDT) and of gamma-1,2,3,4,5,6-hexachlorocyclohexane (lindane) in the systems water-dimethylketone (acetone) and water-1,4-diethyl-dioxide (dioxane). In addition the physical properties of these saturated ternary systems were examined such as: density, viscosity, surface tension and refractive index.

The more or less sudden changes of physical properties of the investigated saturated systems in the region of about 20—25 mole per cent of the organic solvent might be explained by assuming the existance of tri - or tetrahydrates of acetone and dioxane respectively. Similar changes of physical properties were also observed in solutions of about 50—60 mole per cent of the organic solvent. This was explained by supposing a desintegration of the hydrate of the organic solvents.

In the case of the system water-dioxane-DDT it was found that two mutually non-intermiscible layers were built in the region of 30—62 mole per cent of dioxane. In the system water-dioxane-lindane the only distinct characteristic points exist in the same region of concentrations. The changes of physical properties of ternary saturated systems show a functional dependence of the changes of the same properties in binary systems.

The question of the solubility of a substance in binary mixtures has been a subject of research by many authors both from the theoretical as well as from the experimental point of view. In an endeavour to obtain new arguments for a theoretical discussion we investigated the solubility of 1,1,1,-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane (*p,p'*-isomer of DDT) and of gamma-1,2,3,4,5,6-hexachlorocyclohexane (lindane) in the systems water-dimethyl ketone and water-1,4-diethyl-dioxide. In addition to the solubility other physical properties of these ternary systems were also examined such as density, viscosity, surface tension and the refractive index in order to obtain informations on the structure of such solutions.

EXPERIMENTAL

Substances used

1. The dimethylketone was »Acetone, B.R. Elk Co. Inc. Garfield, U.S.A., Spec. 4. 1052 A«. It was taken from packages unsealed on the spot. Its physical properties were found to agree with the data of pure dimethylketone.[1]

2. 1,4-diethyl-dioxide was obtained by purifying the technical product (of unknown origin). The purified liquid revealed physical properties corresponding to pure dioxane[2].

3. The water used was twice distilled and boiled before use in order to free it from dissolved gases.

4. The 1,1,1-trichloro-2,2-bis-(p-chlorophenyl) ethane (i. e. p,p'-isomer of DDT) was isolated from the technical product by the method of Cook and Cook.[3] The purified product had a melting point of 110° C (uncorrected).
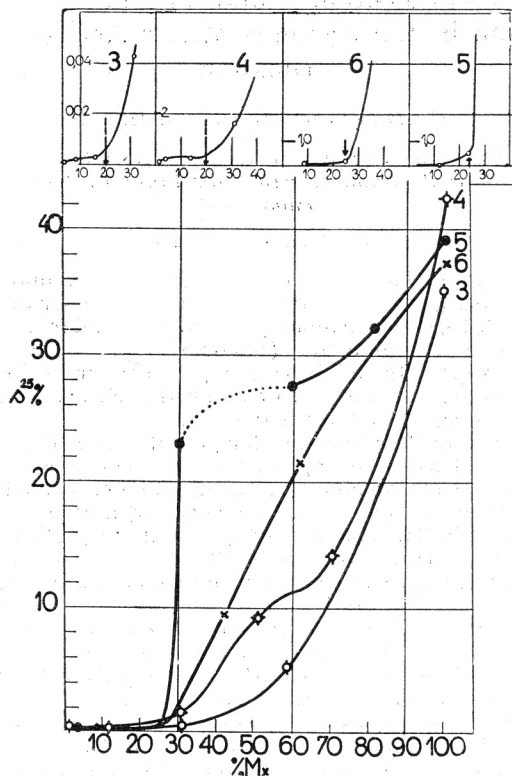

Fig. 1. Solubility of the p,p'-isomer of DDT (3) or lindane resp. (4) in the system water-acetone and of the former (5) and the latter (6) in the system water-dioxane; t = 25 ± 0,02°C.

5. Gamma-1,2,3,4,5,6-hexachlorocyclohexane or lindane was a completely pure product. (»Duphar Lindane Kristale«, Philips-Roxane, Amsterdam). Its melting point was 112° C (uncorrected).

The working method

1. The density ϱ was determined by a gauged pycnometer of 50 ml. and the results were expressed in four decimals.

2. The refractive index n was determined by Abbe's refractometer (c. Zeiss, Jena). Three decimals were read precisely while the fourth was estimated approximately. The refractive index was determined in sodium light.

3. The viscosity η was determined by Höppler's viscosimeter (industrial type) and expressed in millipoises since the chronometer used enabled such precision.

4. The surface tension σ was determined by a tensiometer according to Compte du Noüy. Because of the volatility of the organic solvents, the precision usually

obtained with this instrument, was not achieved. In spite of the greatest speed in work and several repetitions of the same measurement, the error made amounted up to two units of the first decimal place. However, the precision achieved was still greater than that achieved by any other laboratory instrument (Traube's stalagmometer, ordinary capilary, standing waves, etc). The reading was done directly in dyn/cm.
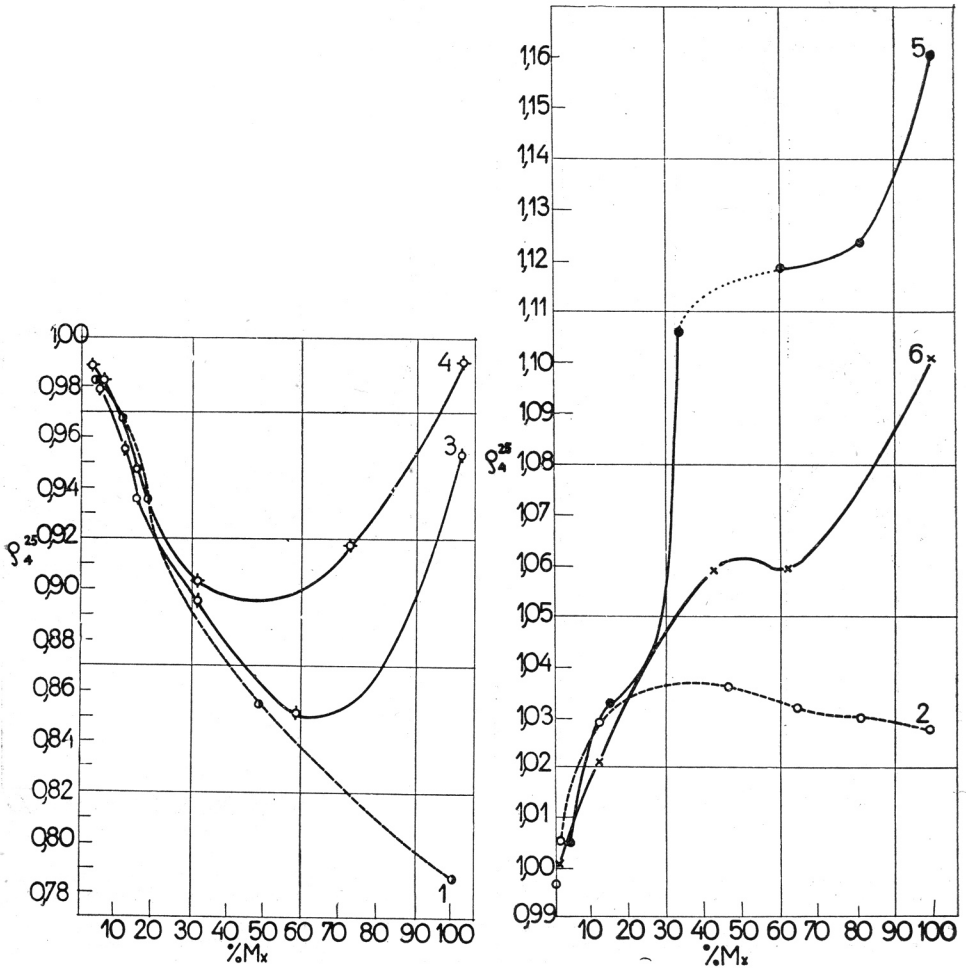

Fig. 2a. Density of the systems water-acetone (1) water-acetone-DDT (3) and water-acetone-lindane (4); t = 25 ± 0.02⁰C.

Fig. 2b. Density of the systems water-dioxane (2), water-dioxane-DDT (5) and water-dioxane-lindane (6); t = 25 ± 0,02⁰C.

5. The solubility s was determined as follows: a quantity of 25 ml was taken from the thermally equilibrated solution with a gauged pipette. The aperture of the pipette was provided with a small tube filled with glass wool in order to prevent minute particles of the unsolved substance to enter the solution withdrawn.

In the case of the DDT-solution the quantity of the liquid thus taken was transferred into crucibles and weighed. The solutions were evaporated to dryness on a water bath and then further dried at 110⁰ C to constant weight. The results were expressed in per cent (s^{25}%).

In the case of lindane the procedure mentioned could not be applied because lindane is very volatile. Therefore the dissolved substance was determined by analysing chlorine: hydrochloric acid was extracted at an increased temperature from the dissolved lindane using an alcoholic solution of sodium hydroxide; chloride was precipitated as AgCl and the excess of $AgNO_3$ was then re-titrated with ammonium sulphocyanide. The result was also expressed in per cent.
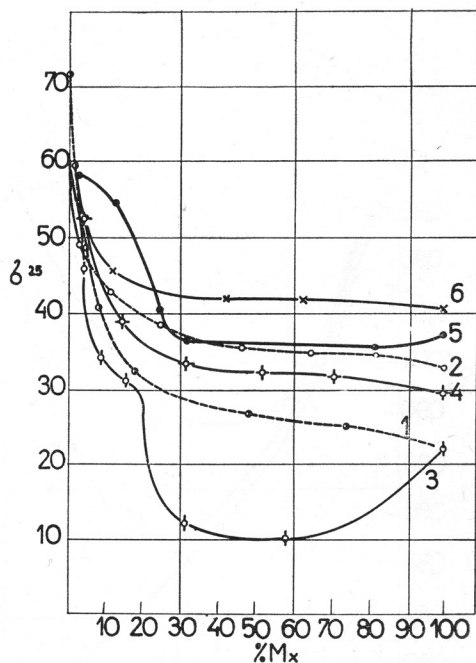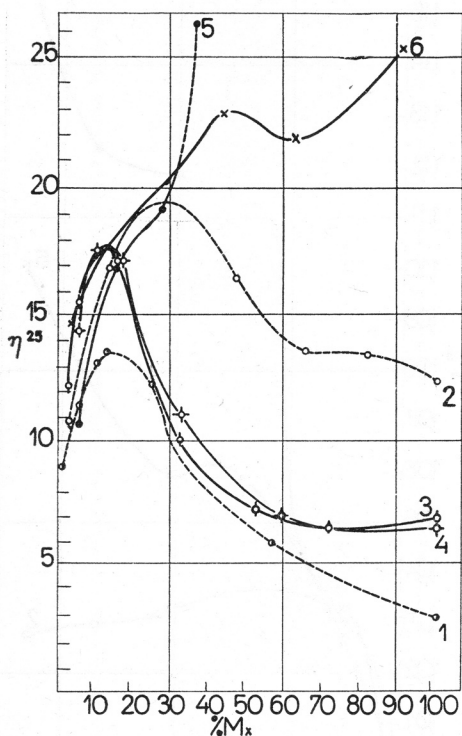

Fig. 3. Viscosity of the systems water-acetone (1), water-dioxane (2), water-acetone-DDT (3), water-acetone-lindane (4), water-dioxane-DDT (5) and water-dioxane-lindane (6); t = 25 ± 0,02⁰C.

Fig. 4. Surface tension of the systems water-acetone (1), water-dioxane (2), water-acetone-DDT (3), water-acetone-lindane (4), water-dioxane-DDT (5) and water-dioxane-lindane (6); t = 25 ± 0.02⁰C.

6. All measurements of the physical properties were carried out at constant temperature which was maintained by means of an ultra-thermostat after Höppler (model NB). Thus all measurements performed apply to a temperature of 25.00 ± 0.02⁰ C.

7. The preparation of the solutions. The weighed quantity of the substance (DDT or lindane) was placed into a volumetric flask. The calculated amount of the organic solvent (acetone or dioxane) was then added with a pipette, the flask weighed, and finally a fixed quantity of water added, and then the volumetric

flask weighed again. At the same time care was taken to prevent evaporation of the organic solvent and to secure that always a small quantity of the solid substance remained in the flask to ensure saturations.

In order to achieve an equilibrium between the sold and the liquid phases and to ensure saturation the solutions thus prepared were kept seven days in an ultra-thermostat and mechanicaly stirred. Controls have shown that seven days stirring was sufficient to achieve a saturation of the solutions.

RESULTS

The obtained results are shown in Fig. 1—5 as follows: the solubility s of DDT or lindane respectively, in the system water-acetone and in the system water-dioxane (Fig. 1); the density ϱ of these ternary systems (Fig. 2a and 2b); viscosity η (Fig. 3); surface tension σ (Fig. 4); and the refractive index n (Fig. 5a and 5b). In addition to the changes of physical properties of the corresponding ternary systems the changes of the same properties of the

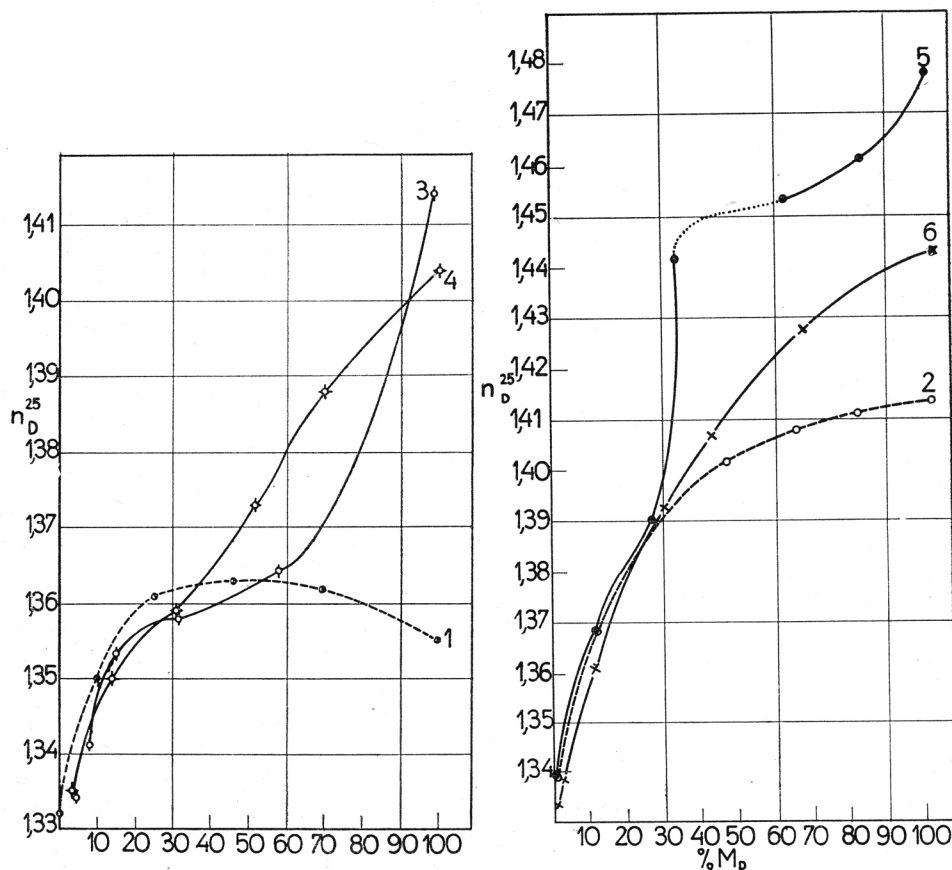Fig. 5a. Refractive index of the systems water-acetone (1), water-acetone-DDT (3) and water-acetone-lindane (4); t = 25 ± 0.02⁰C.

Fig. 5b. Refractive index of the systems water-dioxane (2), water-dioxane-DDT (5) and water-dioxane-lindane (6); t = 25 ± 0,02⁰C.

corresponding binary systems are also shown. The individual systems are marked in the figures with the following numbers: 1. water-acetone; 2. water-dioxane; 3. water-acetone-DDT; 4. water-acetone-lindane; 5. water-dioxane-DDT; 6. water-dioxane-lindane. The data for the physical properties of the binary systems acetone-water were taken from literature.[4,5] The composition of the mixture of the solvents is expressed in mole per cent of acetone or dioxane resp. (% M_x).

<div align="center">DISCUSSION OF THE RESULTS</div>

Examination of the diagrams in Fig. 1—5 shows that with the change of the concentration of the components of the saturated ternary system the physical properties of these systems change in a very different manner. First of all in all four ternary systems examined (Fig. 1) the solubility of the substance in small concentrations of organic solvent is extremely small, nearly negligible, but is increasing rapidly as the concentration of the organic solvent increases over 20—25 mole per cent.

On the other diagrams representing the changes of physical properties both of binary and ternary systems, it is in many cases possible to detect some more or less characteristic points (in the form of maxima, minima or other kinds of inflections) in the neighbourhood of the mentioned values of mole per cent of organic solvent.

Considering that the characteristic points appear often both in binary and ternary systems, it can be presumed that some change of physico-chemical bonds between the water and the organic solvent takes place at these concentrations and that in the vicinity of these points tri- or tetra-hydrates (or both) of relevant organic solvent are formed in appreciable concentration. — Warenne and Godfroy[6] consider that acetone can build hydrates with 3, 4, 8 and 34 molecules of water. — Having in mind that acetone can resonate between two mesomeric structures, i. e. $R_2C::\ddot{O}:$ and $R_2C^+:\ddot{O}^-:$, and that the two structures contribute almost equally to the normal state of the molecule,[7] we can suppose that in the assumed tetrahydrates of acetone the molecules of water are connected to the acetone molecule through the hydrogen bonding or through an ion-dipole linkage.

We could not find in the literature any data about the hydrates of dioxane. — The discrepancy between the position of the maximum in the plot of viscosity of the system water-acetone *versus* mole per cent of the solvent, is comprehensible, for it is well known from experience that the maxima of viscosity often move towards the component having a greater viscosity.

The hypothesis of the formation of hydrates of acetone may explain the negligible solubility of solid matter in the region of smaller concentrations of the organic solvent. All molecules of the organic solvent are at first engaged in building the hydrate, and only when the respective hydrates are formed, the solid substance will begin to dissolve.

In ternary systems the characteristic inflections appear often also in the neighbourhood of about 50—60 mole per cent of organic solvent. In the system water-dioxane-DDT in the mentioned region the solution is divided in two layers which do not mix.

On the basis of physical changes reported above, the following assumption on the dinamics of the solubility of the systems investigated could be made:

First of all, in the binary solvent itself various products created by solvatation can exist which may be caused by a distinct dipole of water; by the partly ionic character of the organic solvent; by the ability of the solvent to facilitate hydrogen bonding etc. When a solid substance is introduced into such a binary system the substance develops a tendency towards being solved and a struggle for the solvent, i. e. for solvatation, ensues between the substance and one of the solvents. Then a conflict of the attractive inter-molecular forces takes place, and in dependence on the liberated free energy the equilibrium moves in the one or in the other direction.

In the systems examined it can be noticed that at first the attractive forces between the water and the organic solvent prevail so that only a small quantity of the solid matter can dissolve (the region up to 20—25 mole per cent of organic solvent). When the respective hydrate of the organic solvent is formed, the substance begins to dissolve freely in the excess of the organic solvent. As the concentration of the organic solvent increases, however the solved substance is also increasing, and in a certain critical region a splitting of the existing hydrate of the organic solvent may ensue. Namely, the attractive forces between the solved substance and the organic solvent may prevail over the linking forces between the water and the organic solvent in the hydrate. This can lead to a new change in the solving force of the solid substance or even to the formation of two layers.

In that way the more or less sudden changes of the solubility and the other physical properties in the region of about 50—60 mole per cent of organic solvent could be explained.

The system water-dioxane-DDT shows the formation of two layers in the region of approximately 30—62 mole per cent of dioxane. This system differs appreciably from other systems in so far as the solubility of DDT in the region od 25—30 mole per cent of dioxane shows an abrupt increase.

CHANGES OF PHYSICAL PROPERTIES

By carefully comparing the changes of physical properties in passing from binary to ternary saturated systems (Fig. 1—5), the following phenomena could be noticed (with the exception of the system water-dioxane-lindane):

a) the parabolic curves in a binary system taek here the form of paraboles of the third order in the ternary system (see Fig. 5a: refractive index in the systems water-acetone (1), water-acetone-DDT (3) and water-acetone-lindane (4); Fig. 5b: water-dioxane (2) and water-dioxane-DDT (5); Fig. 2b: density in the systems water-dioxane (2), water-dioxane-DDT (5) and water-dioxane-lindane (6));

b) the hyperbolic curves related to an examined binary system result, in the ternary system, in curves of parabolic form (see Fig. 2a: density in the systems water-acetone (1), water-acetone-DDT (3) and water-acetone-lindane (4); Fig. 4: surface tension in the systems water-acetone (1) and water-acetone-DDT (3), water-dioxane (2) and water-dioxane-DDT (5);

c) the form of the exponential curves does not change considerably when one of the examined binary systems turns into a ternary system (see Fig. 3:

viscosity in the systems water-acetone (1), water-acetone-DDT (3), water-acetone-lindane (4), water-dioxane (2) and water-dioxane-lindane (6)).

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IZVOD

Zasićeni ternarni sistemi. I. Neka fizikalna svojstva zasićenih otopina 1,1,1-triklor-2,2-bis-(p-klorfenil)-etana i gama-1,2,3,4,5,6-heksaklorcikloheksana u sistemima voda-aceton i voda-1,4-dioksan

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Određivana je topivost 1,1,1-triklor-2,2-bis-(p-klorfenil)-etana (p,p'-izomera DDT-a) i gama-1,2,3,4,5,6-heksaklorcikloheksana (lindana) u sistemima voda-dimetil-keton (aceton) i voda-1,4-dietil-dioksid (dioksan). Pored toga ispitivana su i neka fizikalna svojstva ovih zasićenih ternarnih sistema i to gustoća, viskozitet, površinska napetost i indeks loma.

Naglo mijenjanje fizikalnih svojstava ispitivanih sistema u području od 20—25 molskih procenata organskog otapala mogla bi se rastumačiti pretpostavkom o stvaranju tri- ili tetrahidrata acetona odn. dioksana.

Kod ispitivanih sistema često su primijećene točke nagliej mijenjanja fizikalnih svojstava i u području od 50—60 molskih procenata organskog otapala. Ova pojava mogla bi se protumačiti raspadom hidrata organskih otapala.

Kod sistema voda-dioksan-DDT pokazalo se je stvaranje dvaju međusobno odijeljenih slojeva u oblasti od 30—62 molskih postotaka dioksana, dok kod sistema voda-dioksan-lindan postoje u toj oblasti samo izrazito nagle promjene nekih svojstava.

Mijenjanje fizikalnih svojstava zasićenih ternarnih sistema pokazalo je funkcionalnu ovisnost o mijenjanju istih svojstava binarnih sistema.

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