QUATERNARY SOLUBILITY DIAGRAM FOR THE SYSTEM NaCl–NaBr–$CdCl_2$–$CdBr_2$–H_2O

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Dedicated to Professor S. Škramovský on the occasion of his 70th birthday.

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By using a modified Schreinemakers method of wet residue, the isotherm for 25°C has been determined experimentally and constructed in the quaternary solubility diagram of the reciprocal salt pair system NaCl–NaBr–$CdCl_2$–$CdBr_2$–H_2O. For a plane representation of the isotherm formed by broken area and space configurations within the square pyramid, the central projection from the apex onto the square base of the pyramid has been used. By the same experimental procedure the course of isotherms for 25°C has been verified in corresponding ternary systems NaCl–$CdCl_2$–H_2O and NaBr–$CdBr_2$–H_2O. The constructed quaternary diagram and related ternary diagrams include demonstrably the figurative points, corresponding to the compounds of the following stoichiometric composition: $Na_3Cd_4Cl_{11}.14\ H_2O$; $Na_2CdCl_4 . 3\ H_2O$; $Na_2.CdCl_3Br.3\ H_2O$; $Na_2CdCl_2Br_2.3\ H_2O$; $Na_2CdClBr_3.3\ H_2O$; $Na_2CdBr_4.3\ H_2O$; $NaCdClBr_2.\frac{5}{2}\ H_2O$; and $NaCdBr_3.\frac{5}{2}\ H_2O$. Recently, studying complex particles in solutions, an attention has been paid by some authors to the formation of complex ions resulting from the coordination of at least two kinds of anion ligands to the central ion[1–6]. In one of our works we have studied the formation of some mixed halogen complexes in aqueous and aqueous ethanolic solutions. By means of potentiometry we have proved the presence and determined the stability and conditions of existence of chloro–bromo and bromo–iodo complexes with central ions Ag^+, Cd^{2+}, Pb^{2+}, and Bi^{3+} (see[7]).

Till now, however, a question remained unanswered, whether it is possible, at least in some cases, to prepare solid phases with stoichiometric composition analogous to the composition of mixed halogen-complex particles in a solution by crystallization from the solutions. A reliable answer to this question could give only the experimental investigation of the isothermal solubility diagram of such a suitably chosen system of reciprocal salt pair in which one of both present cations is the central ion and it is coordinated to both anions present.

Our potentiometric study proving the formation of mixed halogencadmates in a solution as well as the comparison of the solubility of single components and especially hopeful results of crystallizations carried out preliminary made us in-

vestigate in detail the salt system NaCl, NaBr, $CdCl_2$, and $CdBr_2$. By means of Schreinemakers' method we determined the course of the quaternary solubility diagram at 25°C and the course of two corresponding ternary diagrams at the same temperature.

The substance of Schreinemakers' method of the construction of isotherm in a solubility diagram consists in a simple preparation of series of heterogeneous mixtures containing various amounts of single components of the system and in an accurate experimental determination of the composition of the resulted equilibrium saturated solution and of so-called wet residue. The wet residue is the solid phase wetted more or less with the saturated solution. Since in diagrams in which the straight line and lever rules hold the figurative points of composition of the saturated solution, wet residue, and dry solid phase are located on the same straight line, it is possible to determine the points of the solid phase composition in terms of points of intersection of series of connecting lines of corresponding saturated solutions and wet residues. It is indifferent whether we are treating a set of lines in a space or in a plane. Consequently Schreinemakers' method can be used not only for the solution of ternary systems, as was proposed by the author[8], but also for more-component ones[9,10].

The spatial isotherm of a quaternary diagram can be best represented by a broken area and space configurations inside the square pyramid. Figurative points of salt components of the system lie in corners of the pyramid square base, the figurative point of a solvent is in the apex of the pyramid.

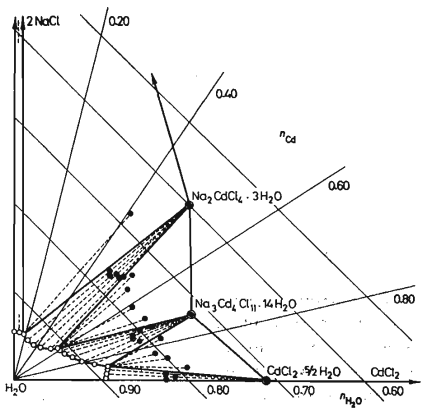

FIG. 1

The 25°C Isotherm for Ternary System 2 NaCl–$CdCl_2$–H_2O

○ Composition of saturated solution, ● composition of wet residue, ⊙ figurative point of compound.

For the representation of the isotherm in a plane, Jänecke[11] used the central projection from the apex onto the square base of the pyramid. This method of representation is suitable because in the central projection the straight line and lever rules hold and therefore the results obtained by Schreinemakers' method can be directly entered in Jänecke's diagrams. The content of solvent in the solid phase or in the solution is not, of course, evident from the central projection of the isotherm. This lack is best removed by constructing the lines of the constant content of solvent (isosolvents). To represent the content of solvent in the solid phase it is suitable to use the rectangular projection of the spatial isotherm onto a plane normal to the base of the pyramid and parallel with one edge of the base. The best way of representation of the diagram are coordinates with scales marked in mol fractions n_i, n_{sal}, and n_{solv} defined as follows: n_i is the mol fraction of the i-th ion, given by the ratio of the number of mol of this ion to the number of mol of all ions of the uniform charge; n_{sal} is the mol fraction of the mixture of anhydrous salts, given by the ratio of the mol number of salt components of the system to the number of mol of all components of the system; n_{solv} is the mol fraction of the solvent, given by the ratio of the number of mol of the solvent to the number of mol of all components of the system. If components of a system contain cations A and B, anions C and D and a solvent, then it must hold for mol fractions: $n_A + n_B = 1$, $n_C + n_D = 1$, $n_{solv} + n_{sal} = 1$. The mol fractions, *e.g.* n_A, n_C, and n_{solv}, are determined by chemical analysis of the heterogeneous system (the saturated solution and the wet residue) and the point is to be represented in the diagram. The former two mol fractions determine the position of the central projection of the point onto the base of the pyramid. The latter mol fraction determines the coordinate of the solvent content in front elevation.

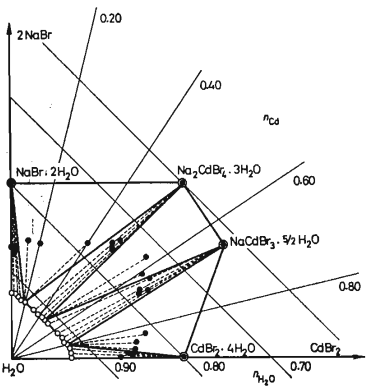

FIG. 2

The 25°C Isotherm for Ternary System 2 NaBr–$CdBr_2$–H_2O

○ Composition of saturated solution, ● composition of wet residue, ⊙ figurative point of compound.

EXPERIMENTAL

Preparation of Heterogeneous Mixtures

Heterogeneous mixtures were prepared by weighing all components of the system including water. The total weight of mixture was somewhere between 3 and 5 g. The mixtures were weighed into the 10 ml Erlenmayer flasks. The chemicals used for preparation of the heterogeneous mixtures, as well as the chemical substances necessary for analysis, were altogether of the analytical grade purity (Lachema, Brno). Redistilled water was used as a solvent.

Procedure

Heterogeneous samples sealed in the flasks were heated shortly (for 10 minutes) to the temperature about 35°C at first and afterwards tempered in a bath at the temperature $25 \pm 0{\cdot}05$°C and on a continuous oscillating motion for many days (at least a week).

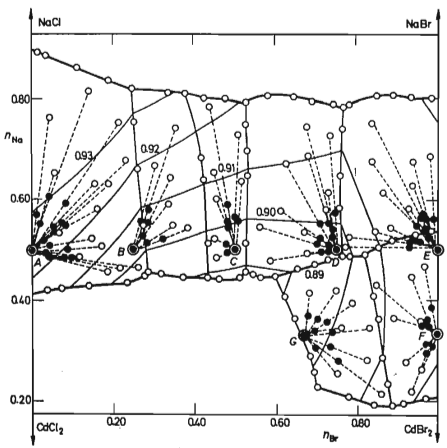

FIG. 3

Central Projection of the 25°C Isotherm for the Quaternary System 2 NaCl–2 NaBr–$CdCl_2$–$CdBr_2$–H_2O from the Apex of Representative Pyramid onto Its Base

○ Composition of saturated solution, ● composition of wet residue, ⊙ figurative point of compound (*A* $Na_2CdCl_4.3\,H_2O$, *B* $Na_2CdCl_3Br.3\,H_2O$, *C* $Na_2CdCl_2Br_2.3\,H_2O$, *D* $Na_2CdClBr_3.3\,H_2O$, *E* $Na_2CdBr_4.3\,H_2O$, *F* $NaCdBr_3.\frac{5}{2}\,H_2O$, *G* $NaCdClBr_2.\frac{5}{2}\,H_2O$).

Heterogeneous samples containing the solid phase and the saturated solution were separated by the following procedure: After a short keeping at a stillstand and at continuous tempering, a little amount of the saturated solution was dripped off into a weighing bottle for the crystals of the solid phase not to be entrained. The saturated solution with the solid phase was partly sucked off by a coarse-grained sintered glass at a slight underpressure during about 5 seconds and the wet residue was transferred into a weighing bottle. This method of the phase separation surpassed evidently all recommended complex procedures[12] by its reproducibility.

Analysis

The water content in samples was determined as the weight difference of initially weighed and at 300°C dried up samples. At this temperature no component is present in a form of a hydrate[13]. The hydrolytic release of hydrogen halides from samples on drying does not set in. The content of cadmium was determined by a complexometric titration with the solution of Chelaton 3 in a diluted HNO_3 medium adding hexamethylenetetramine and using Xylenol Orange as an indicator[14]. The contents of chlorides and bromides were determined by a slow potentiometric titration with a solution of silver nitrate in a weakly acid medium. We used an automatic potentiometric titrator designed by us[15].

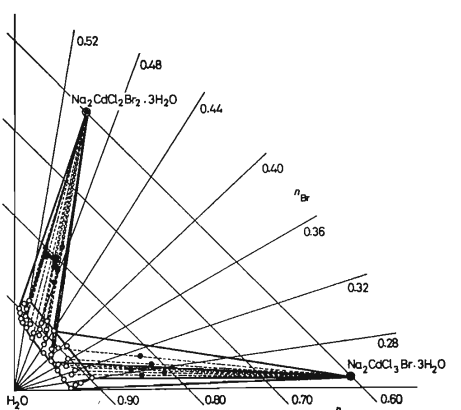

FIG. 4

Rectangular Front Elevation of a Part of the 25°C Isotherm for the Quaternary System 2 NaCl–2 NaBr–$CdCl_2$–$CdBr_2$–H_2O onto the Plane Perpendicular to the Base of Representative Pyramid

○ Composition of saturated solution, ● composition of wet residue, ⊙ figurative point of compound.

RESULTS AND DISCUSSION

The results of the measurements are summarized in Figs 1–4. In Fig. 1 the course of the 25°C isotherm is represented in the ternary diagram of the system 2 NaCl–$CdCl_2$–H_2O. The figurative points of the compounds $CdCl_2.\frac{5}{2}H_2O$, $Na_3Cd_4Cl_{11}.14\,H_2O$, $Na_2CdCl_4.3\,H_2O$, and NaCl are visible in the diagram. All found compounds show the congruent solubilities. The course of the diagram is in a good agreement with the results obtained by other authors[16] who studied the same system.

Fig. 2 illustrates the results obtained when investigating the system 2 NaBr–$CdBr_2$–H_2O. In the diagram the compounds are visible the stoichiometric composition of which is given by the formulas: $CdBr_2.4\,H_2O$, $NaCdBr_3.\frac{5}{2}H_2O$, $Na_2CdBr_4.5\,H_2O$, and $NaBr.2\,H_2O$. The compound $Na_2CdBr_4.3\,H_2O$ shows the incongruent solubility. Existence of these compounds is mentioned in some older papers quoted in tables[16]. The course of the the isotherm, however, is given nowhere.

Fig. 3 represents the central projection of the isotherm of quaternary diagram for the system 2 NaCl–2 NaBr–$CdCl_2$–$CdBr_2$–H_2O. The isotherm shows the figurative points the stoichiometric composition of which is $Na_2CdCl_4.3\,H_2O$, $Na_2CdCl_3Br.3\,H_2O$, $Na_2CdCl_2Br_2.3\,H_2O$, $Na_2CdClBr_3.3\,H_2O$, $Na_2CdBr_4.3\,H_2O$, $NaCdBr_3.\frac{5}{2}H_2O$, $NaCdClBr_2.\frac{5}{2}H_2O$. The water content follows, of course, from rectangular front elevations of particular regions of the isotherm. The compounds $Na_2CdCl_3Br.3\,H_2O$ and $Na_2CdBr_4.3\,H_2O$ show the incongruent solubility. Plotted lines of constant water content enable to visualize the course of the area of saturated solutions in space. From the figure it is also evident that two parts of the diagram remain unsolved. They seem to be the regions of mixed crystals. The arrangement of the regions is obviously so complicated that the inaccuracy of the analytic determination interferes and the solution of this part of the diagram is beyond the scope of Schreinemakers' procedure.

In Fig. 4 there is a rectangular front elevation of two regions of the isotherm of the quaternary diagram. They are the regions in which the compounds $Na_2CdCl_3Br.3\,H_2O$ and $Na_2CdCl_2Br_2.3\,H_2O$ crystallize. The figure is an example of graphical procedure when determining the number of hydration molecules of water in compounds. Further parts of isotherm were projected analogously.

The constructed quaternary diagram proves that in the system NaCl–NaBr–$CdCl_2$–$CdBr_2$–H_2O the formation of solid phases occurs during crystallization the stoichiometric composition of which corresponds to chlorobromocadmates. Nothing but the existence of these compounds, of course, cannot be considered to be an evidence of heterogeneity of the coordination sphere of the central ion Cd^{2+} in these crystalline compounds. The problem of their structure will be only solved.

As the used method is concerned it may be comprehensively said that Schreinemakers' analytical method proves to be good even for the construction of quaternary diagrams in spite of its time-consuming character and laboriousness. Limits of its

applicability are given by the accuracy of the determination of the content of system components in both phases.

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