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Equilibrium in Water Ternary Systems: MgH_2Y–CaH_2Y, CaH_2Y–BaH_2Y, CaH_2Y–SrH_2Y

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In a weakly acidic medium the reaction of magnesium salt with ethylenediaminetetraacetic acid forms sparingly soluble, perfectly filterable $MgH_2Y\cdot6H_2O$ (Y^{4-} – anion of ethylenediaminotetraacetic acid) [1–2]. Research carried out by the authors revealed that there is a possibility to produce pure inorganic salts like MgF_2 in the reaction of $MgH_2Y\cdot6H_20$ with magnesium fluoride [3–6]. In the reaction of soluble inorganic magnesium salts with fluorides a fine-crystalline hard to filter product is formed whose washing brings large losses. Investigations on the conditions of the production of pure inorganic magnesium salts *via* the complex with ethylenediaminetetraacetic acid, basing on technical raw materials, encourage us to establish the equilibria in three systems: MgH_2Y–CaH_2Y–H_2O, CaH_2Y–BaH_2Y–H_2O, CaH_2Y–SrH_2Y–H_2O.

Simultaneously investigations carried out by the authors on the solubility of magnesium, strontium, barium and calcium salts of ethylenediaminetetraacetic acid, in the dependence on pH, show the existence of a distinguished solubility minimum [7]. It suggested that pH could have an influence on the course of solubility isotherms in ternary systems containing aforementioned salts. Data concerning equilibrium in the system CaH_2Y–Na_2H_2Y–H_2O have been reported [8]. All used reagents were of analytical grade.

Preparation of $MgH_2Y\cdot6H_2O$, $CaH_2Y\cdot2H_2O$, $SrH_2Y\cdot3.5H_2O$ and $BaH_2Y\cdot6H_2O$ salts: $MgH_2Y\cdot6H_2O$ was obtained according to [6]. To the mixture of water suspension of EDTA acid at about 25°C ammonia solution was introduced in small portions in two times molar excess with respect to acid. After introducing the whole amount of ammonia, the reaction suspension was stirred to obtain clear solutions of $(NH_4)_2H_2Y$ and then MgO was added in the 1:1 molar ratio at about 80°C. After introducing the required amount of MgO, the mixture was stirred to attain the complete solubility of MgO and fading ammonium odour in vapours. After cooling to 15°C, $MgH_2Y\cdot6H_2O$ was crystallized. Obtained crystals were separated on the vacuum filter, rinsed with distilled water to the absence of NH_4^+ ions in the filtrate and were dried at about 60°C.

Calcium, barium and strontium salts of ethylenediaminetetraacetic acid were prepared according to the following procedure: To the water suspension of ethylenediaminetetraacetic acid, kept at about 70°C and intensively stirred, portions of carbonates of calcium, strontium or barium, in the molar ratio 1:1, were added. After completing the reaction, the system was filled up with distilled water to obtain clear solutions and then the mixture was cooled to 15°C. Formed crystals of $CaH_2Y \cdot 2H_2O$, $SrH_2Y \cdot 3.5H_2O$ and $BaH_2Y \cdot 4H_2O$ were filtered on the vacuum filter and, after washing successively with distilled water and acetone, were dried at about 60°C.

Setting-up equilibrium systems: The following hydrates were used for the preparation of analysed systems: $MgH_2Y \cdot 6H_2O$, $CaH_2Y \cdot 2H_2O$, BaH_2Y4H_2O and $SrH_2Y \cdot 3.5H_2O$ obtained according to the described procedure. Saturated solutions were prepared by dissolving suitable salts in water at about 50°C in amount and proportions allowing to get solid phase after cooling. To ensure equilibrium, the systems were kept in a thermostat at 20°C (with the accuracy of ±0.1°C) by at least 24 hours. The total amount of crystalline systems was about 200 g. After reaching equilibrium, the pH values of filtrates were measured. To analyse equilibrium composition portions of the solutions were taken with a pipette, weighed and the contents of Ca, Mg, Sr and Ba were determined. Solid phases being in the equilibrium with solutions were separated on a vacuum filter, washed with acetone, dried and the content of suitable cations was determined.

Analysis of equilibrium solutions: Weighed samples of solutions were evaporated to dryness, ignited and then dissolved in the acid. In the case of MgH_2Y and CaH_2Y systems, the content of Ca and Mg were determined by complexometric titration [9]. In the system $BaH_2Y–CaH_2Y–H_2O$ barium was analysed in the form of chromate and calcium left in the solution after precipitation of barium chromate, by complexometric titration.

In the system $CaH_2Y–SrH_2Y–H_2O$, calcium was determined by extraction with acetone from solutions containing calcium and strontium nitrates(V) [10]. Calcium present in the extract and strontium present in the precipitate were then determined by complexometric titration. Investigations carried out on the ternary component systems were based on the analysis of composition of equilibrium solutions and respective solid phases. Obtained experimental data are presented graphically in Figs. 1–3, in the form of isotherms of solubility, prepared at 20°C and pH values of saturated solutions. In all cases two curves of solutions saturated respectively against salt's hydrates are present and the euthonic point, where the saturated solution is in equilibrium with both hydrates in the solid phase is observed. In the system $MgH_2Y–CaH_2Y–H_2O$ (Fig. 1) increase in the concentration of CaH_2Y causes initially considerable decrease in MgH_2Y solubility. Further increase in the concentration of CaH_2Y (above $2 \cdot 10^{-3}$ mole/dm^3) does not influence the magnesium salt solubility. In this system it could be found that the shape of solubility isotherm depends on the change of pH. Isotherms of solubility for the system $CaH_2Y–BaH_2Y–H_2O$ are given in Fig. 2. The shape of curves indicate that the increase in barium salt concentration causes an insignificant decrease of CaH_2Y solubility, while solubility of BaH_2Y is practically constant during introducing calcium salt to the solution.

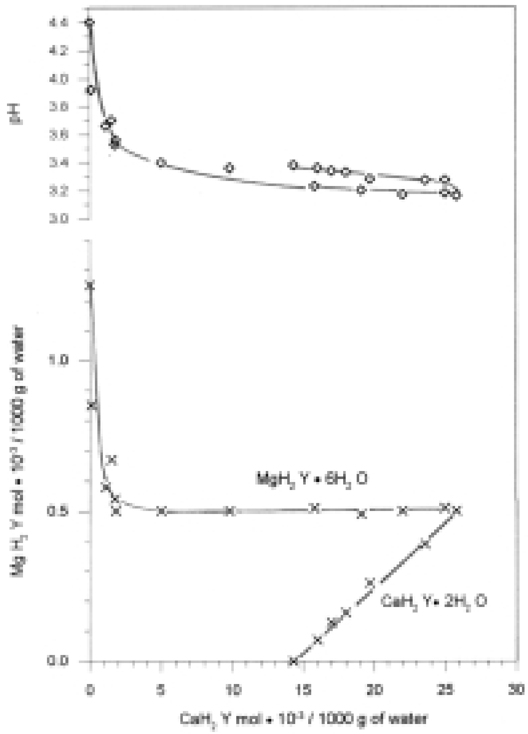

Figure 1. Equilibrium in the MgH_2Y–CaH_2Y–H_2O system.

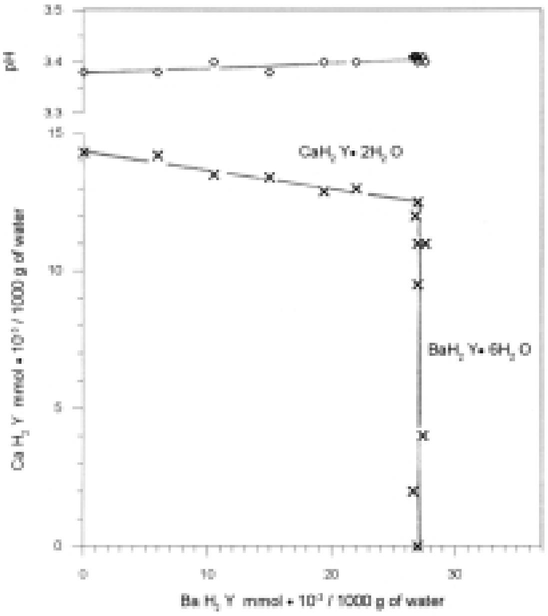

Figure 2. Equilibrium in the CaH_2Y–BaH_2Y–H_2O system.

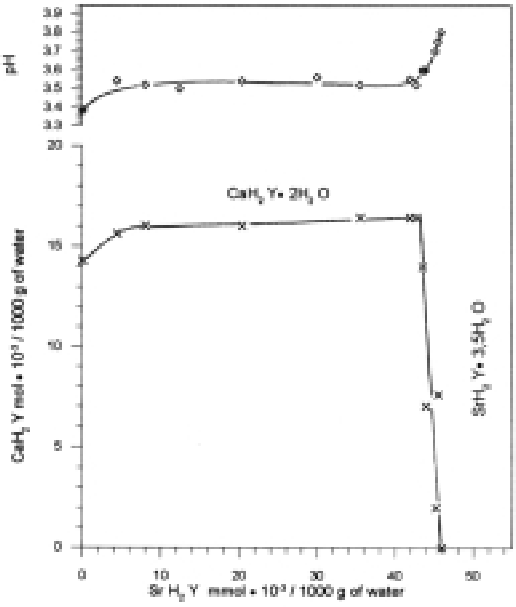

Figure 3. Equilibrium in the CaH_2Y–SrH_2Y–H_2O system.

Fig. 3 presents the solubility isotherm and values of pH of the system CaH_2Y–SrH_2Y–H_2O. In this case the influence of solubility of calcium salt on the solubility of strontium salt and *vice versa* is insignificant.

Changes in chemical reaction of saturated solutions, together with changes in their composition, cause a significant disturbance in common phenomenon of mutual saturation of salts. In the literature the similar dependence was reported for the MgH_2Y–Na_2H_2Y–H_2O system [8].

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