

## SOLID SOLUTIONS IN THE SYSTEMS

 $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-K}_2\text{S}_2\text{O}_8$  AND  $(\text{NH}_4)_2\text{SO}_4\text{-K}_2\text{SO}_4$ 

## COEXISTING WITH SATURATED AQUEOUS SOLUTIONS

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Received August 14th, 1975

Distribution of cations between the coexisting liquid and solid solutions was determined using the earlier published data on the solubility in the system  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-K}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$  at 20, 30 and 40°C. This system was found to belong to type I of solid solutions according to Roozeboom's classification with considerable positive deviations from ideal behaviour. Temperature dependence of the cation distribution in both coexisting solutions is discussed as compared with the analogous dependence of the related system  $(\text{NH}_4)_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$  on the basis of data published by other authors.

In an earlier publication<sup>1</sup> on the solubility in the system  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-K}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$  it was stated that solid solutions of both peroxydisulphates of unlimited miscibility coexist with saturated aqueous solutions of the respective composition in the entire measured temperature range 20–40°C. At the same time it was found that mixed crystals containing up to *c.* 5 mass % of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  retain the crystallographic character of potassium peroxydisulphate crystallizing in triclinic system, whereas solid solution with a higher content of ammonium ion crystallize in monoclinic system, like pure ammonium peroxydisulphate. The precise boundary of transition of both structures was not investigated.

The presentation of data in the mentioned paper<sup>1</sup> was limited to mere report on the compositions of saturated aqueous solutions and of the coexisting solid phase, without any more detailed study of the relations of the distribution of both cations between the two coexisting phases which would have permitted to classify the system into one of the groups of solid solutions according to Roozeboom's classification<sup>2</sup>.

This problem forms the subject of the present communication where the earlier published experimental data are made use of<sup>1</sup>. The results of their analysis are then compared and discussed with analogous relations for the related system  $(\text{NH}_4)_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$ .

## RESULTS AND DISCUSSION

The dependence of the distribution of individual cations between both coexisting phases on their composition was quantitatively expressed on the one hand in the form of a diagram  $x_{\text{NH}_4,1}$  versus  $x_{\text{NH}_4,s}$  (where  $x_{\text{NH}_4,1}$  is the mole fraction of ammonium salt in saturated aqueous solution, related to the dry substance of total content of salts in the solution, and  $x_{\text{NH}_4,s}$  has the corresponding meaning for solid solution) (see Fig. 1) and on the other hand, by means of the correlation equation

$$\log \chi_{\text{NH}_4,1} = A \log \chi_{\text{NH}_4,s} + B, \quad (1)$$

where

$$\chi_{\text{NH}_4,i} = x_{\text{NH}_4,i} / (1 - x_{\text{NH}_4,i}). \quad (2)$$

Eq. (1), derived on the basis of certain thermodynamic concepts by Hill, Durham and Ricci<sup>3</sup>, was also employed to express quantitatively the distribution of cations between both coexisting solution phases in related systems of ammonium sulphate and further alkali metal sulphates<sup>4,5</sup>.

As can be seen from Fig. 1, the distribution curves of the system  $(\text{NH}_4)_2\text{S}_2\text{O}_8 - \text{K}_2\text{S}_2\text{O}_8 - \text{H}_2\text{O}$  show at all measured temperatures relatively considerable positive deviations from ideal behaviour which is represented in the diagram for an unlimited series of solid solutions by a diagonal. According to this finding, this system ranges into the Type I of solid solutions according to Roozeboom's classification<sup>2</sup>, similarly as the related system of sulphates of the same cations<sup>4</sup>. Comparison of the distribution curves of both systems reveals that the non-ideality in the system of peroxydisulphates is higher than with the analogous system of sulphates of both cations. It cannot be excluded that the relatively abrupt bend of the distribution curves in the region  $x_{\text{NH}_4,s} = 0.02 - 0.05$  in the system of peroxydisulphates is connected with the change of the crystalline structure of solid solutions from triclinic to monoclinic system which occurs just in this region. On the other hand both pure ammonium and potassium sulphates crystallize in the same crystallographic system and also the dimensions of their elementary lattice constants lie very close to each other and thus it is quite conceivable that also the course of the distribution curves in the system of sulphates is smoother (see Fig. 3).

Fig. 2 shows the graphically expressed dependence of cation distribution between both solution phases in the system of peroxydisulphates according to Eq. (1) for the measured temperatures. It is evident that at 20°C the experimental points can be fitted, for the practically whole measured range with sufficient approximation by a single straight line so that the actual form of Eq. (1) at the mentioned temperature is

$$\log \chi_{\text{NH}_4,1} = 0.676 \log \chi_{\text{NH}_4,s} + 1.215. \quad (3)$$

At 30° and 40°C the linear sections having practically the same slope  $A \approx 0.7$  become shorter, while the corresponding values of constant  $B$  decrease proportionally to the increasing temperature. Further course of this relation in the region of lower contents of ammonium ion in the coexisting solution phases can be roughly expressed also by straight lines with different slopes and sections on the coordinate-axis.

From these results it follows that for the studied system  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-K}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$ , the dependence of the cation distribution between both coexisting solution phases on their composition cannot be described quantitatively in a single form. This seems rather surprising, with respect to the not too great extent of measured temperatures. However, it cannot be excluded that this result is caused by the fact that the equilibrium composition of solid phases is not sufficiently attained in their entire volume. This problem has already been suggested when estimating the results of analogous relations in the system  $(\text{NH}_4)_2\text{SO}_4\text{-Cs}_2\text{SO}_4\text{-H}_2\text{O}$  at 0°C (see<sup>5</sup>). The system in question, *i.e.*, aqueous solutions of peroxydisulphates, is unstable and undergoes spontaneous decomposition under the formation of corresponding hydrogen sulphates and oxygen as final products. This decomposition can be detected already after a few hours and of course it proceeds the faster, the higher is the temperature. Therefore, in order to avoid possible negative effects of decomposition products on the measured solubility data the samples of coexisting phases were

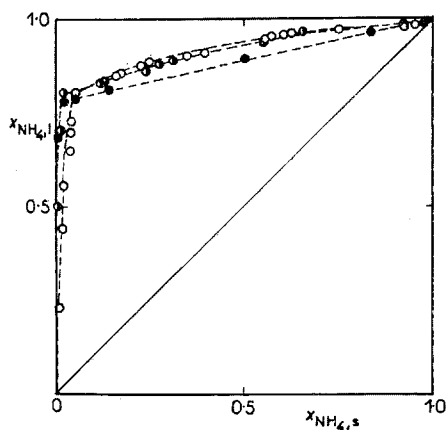


FIG. 1

Distribution Curve of Ammonium Ion between Both Coexisting Solution Phases in the System  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-K}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$  at  $\circ$  20,  $\bullet$  30,  $\bullet$  40°C

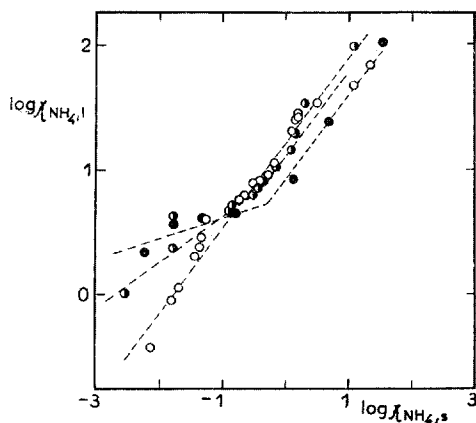


FIG. 2

Dependence of the Ammonium Ion Distribution on the Composition of Both Coexisting Phases in the System  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-K}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$  according to Eq. (1) at  $\circ$  20,  $\bullet$  30,  $\bullet$  40°C

taken after the shortest possible time, necessary for attaining the steady composition of saturated aqueous solution, while neglecting the requirement of equilibrium composition in the bulk of coexisting solid solutions. It is therefore probable that within the time spans used for equilibration (6–8 h at 20°C and 2–3 h at 40°C) the separation of crystals or eventual recrystallization of solid solutions took place only in surface layers which was satisfactory for decisive composition of the corresponding saturated solutions, but not in the bulk phase of solid solution.

To verify these assumptions the results of the studied system were compared with analogous results obtained with the related system  $(\text{NH}_4)_2\text{SO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$  which had been investigated by a number of authors<sup>4,6-11</sup> in the temperature interval 0–100°C. In respect of the perfect stability of this system in aqueous solutions it is possible to wait for the establishing of the equilibrium conditions in both solution phases for an unlimited time and accordingly, in all recent studied the samples for analysis of both phases were taken only after some days or even weeks. In spite of this the agreement of experimental data of different authors on cation distribution between both phases for the same or nearly the same temperatures is not quite satisfactory in all cases (see Fig. 3).

The temperature dependence of cation distribution can be estimated on the basis of the data of Bovalini and Fabris<sup>8</sup> who measured this system in the interval 0 to 96.5°C. Temperature intervals of other authors are rather narrow so that certain differences in the positions of distribution curves can rather be due to experimental inaccuracies. The data of Weston<sup>7</sup> for 30°C are, moreover, evidently charged with the erroneous assignment of the corresponding coexisting phases which was unfortunately taken over even in monograph<sup>12,13</sup>. Nevertheless, the course of cation distribution curves for various temperatures indicates (see Fig. 3) that the deviation from ideal behaviour decreases with increasing temperature. The scatter of experimental data of different authors however, is too great to allow to express this temperature dependence of distribution with sufficient reliability. Evaluation of the dependence of distribution on the composition of coexisting solution phases according to Eq. (1), as illustrated in Fig. 4, proves on the one hand that even with this system the mentioned dependence cannot be expressed over the whole composition range (for the same temperature) by a single straight line, on the other hand it shows that the character of this dependence remains quite analogous over the whole temperature range of 0–100°C.

Accordingly, the observed course of the relation between composition of both solution phases in the system  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{--K}_2\text{S}_2\text{O}_8\text{--H}_2\text{O}$ , expressed according to Eq. (1), which has different shapes at different temperatures of measurement, seems to be, with respect to the relatively narrow temperature interval, rather surprising. Up to now, it can be hardly decided to what extent this phenomenon is caused by the real nature of the system and to what extent by the non-satisfactory equilibrium composition of the coexisting solid solutions when short equilibration

time was used. Even the hitherto published data on the related system  $(\text{NH}_4)_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$ , which is temperature stable, cannot be taken as sufficiently reliable for obtaining decisive quantitative conclusions concerning the effect of composition and temperature on the distribution of individual components of the system between both coexisting solution phases. Evidently, a suitable technique will to be chosen for the given purpose enabling, at least for temperature stable systems, that the equilibrium between the coexisting phase might be really attained, as it has already been pointed out in previous communication<sup>5</sup>. Of course it is questionable, whether an equilibrium composition can be at all attained in the bulk of the solid solution within a reasonable time of experiment, at small gradients of chemical potentials of their components in the direction from the surface of the solid solution which is in contact with the coexisting liquid solution at normal or even lower temperatures, when the transport rate in the solid phase is extremely low, or whether the possible cause of the frequent disagreement of experimental data of different authors and of different experimental techniques are the up to now not sufficiently elucidated effects of energy contents of the real solid phases<sup>14</sup>.

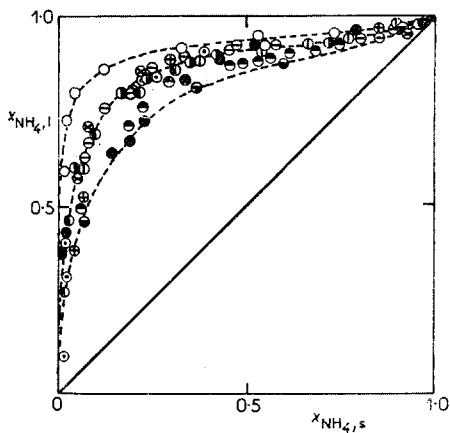


FIG. 3

Distribution Curves of Ammonium Ion between Both Coexisting Solution Phases in the System  $(\text{NH}_4)_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$  according to Experimental Data of Various Authors

Bovalini, Fabris<sup>8</sup> for: 0 (○), 35 (●), 50 (⊙), 70 (⊕), and 96.5°C (⊖). Calvo, Simons<sup>4</sup> (⊖), Fock<sup>6</sup> (⊕), Weston<sup>7</sup> (⊙), Beloposkii and coworkers<sup>9</sup> (⊕), Hill and Loucks<sup>10</sup> (⊙), Flatt and coworkers<sup>11</sup> (⊖), all for 25°C.

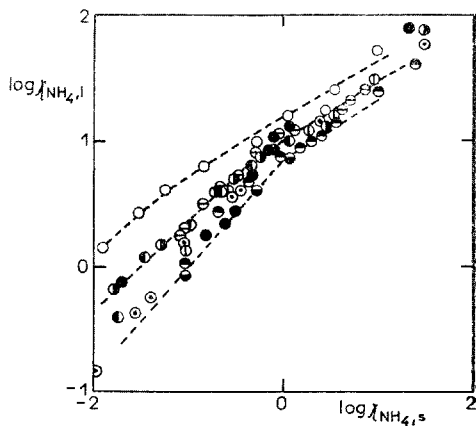


FIG. 4

Dependence of the Ammonium Ion Distribution on the Composition of Both Coexisting Phases in the System  $(\text{NH}_4)_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$  according to Experimental Data of Different Authors

Meaning of experimental points the same as in Fig. 3.

## REFERENCES

1. Balej J., Regner A.: *This Journal* 27, 2208 (1962).
2. Roozeboom H. W. B.: *Z. Phys. Chem.* 8, 504 (1891).
3. Hill A. E., Durham G. S., Ricci J. E.: *J. Amer. Chem. Soc.* 62, 2723 (1940).
4. Calvo C., Simons E. L.: *J. Amer. Chem. Soc.* 74, 1202 (1952).
5. Balej J., Shevchuk V. G.: *This Journal* 39, 3423 (1974); 40, 3290 (1975).
6. Fock A.: *Z. Kryst. Mineral.* 28, 375 (1897).
7. Weston A.: *J. Chem. Soc.* 121, 1229 (1922).
8. Bovalini E., Fabris E.: *Gazz. Chim. Ital.* 65, 619 (1935).
9. Belopolskii A. P., Shpunt S. Ya., Alexandrov N. P.: *Kalij* 3, 25 (1936).
10. Hill A. E., Loucks Ch.: *J. Amer. Chem. Soc.* 59, 2095 (1937).
11. Flatt R., Brunisholz G., Merbach A.: *Helv. Chim. Acta* 51, 2017 (1968).
12. *Gmelins Handbuch der Anorganischen Chemie*, 8. Ausg., *System Nr. 23, Ammonium*, p. 510. Verlag Chemie, Berlin 1936.
13. *Spravochnik po Rastvorimosti Solevykh Sistem*, Vol. I, p. 341. Goskhimizdat, Moscow 1953.
14. Eysseletová J.: Private communication.

Translated by V. Čermáková.