Reports of the Academy of Sciences of the USSR

CHEMISTRY

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964. Volume 157, No. 4

CHEMISTRY

Academician of the Academy of Sciences of the Kirgiz SSR I. G. Druzhinin, M. Kydynov, S. A. Lomteva

A TERNARY COMPOUND OF LITHIUM, SODIUM, AND AMMONIUM SULFATES

Sulfates of the alkali metals in aqueous media show a pronounced tendency toward interaction reactions, forming double anhydrous and hydrated compounds or phases of variable composition ([1-4]). For certain sulfates the presence of two and three double compounds has been established. Thus, lithium sulfate with potassium and sodium sulfates forms compounds with molecular ratios Li : K and Li : Na = 1 : 1, 1 : 3, 2 : 1, etc. Double compounds, glaserite with the initial components, can give limited isomorphous mixtures ([1,2]). I. N. Lepeshkov, N. V. Bodaleva, and L. T. Kotova ([5]) studied the interaction of lithium, sodium, and potassium sulfates in an aqueous medium at 15-100° and established that a ternary salt of the composition $2Li_2SO_4 \cdot Na_2SO_4 \cdot K_2SO_4$ can crystallize from saturated solutions. The complex compounds and solid solutions obtained may be used as mineral fertilizers. The lithium contained in these compounds is a useful microelement that increases the frost resistance of plants.

In order to follow the interaction reactions between alkali-metal sulfates and ammonium sulfates, we decided to study the system: lithium sulfate–sodium sulfate–ammonium sulfate–water at 25°.

In terms of the composition of equilibrium solutions, this quaternary system includes three ternary systems. From sulfate solutions of lithium and sodium, in addition to the initial components, double compounds with the ratio Li : Na = 1 : 1 and a twelve-water salt 1 : 3 ([5]) are observed to separate. For both compounds, besides solubility data, refractive indices, transition temperatures, and crystal lattices were studied. From equilibrium solutions containing lithium and ammonium sulfates there crystallize, in addition to the initial components, a double compound 1 : 1 and solid solutions ([6]). Sodium and ammonium sulfates in aqueous medium react with formation of a double compound Na : NH_4 : H_2O = 1 : 1 : 4. The interaction of ammonium sulfate with lithium and sodium sulfates was studied at 25° by the isothermal solubility method.

For the investigation, chemically pure preparations of lithium, sodium, and ammonium sulfates were used and were twice recrystallized. Saturated solutions were kept in a thermostat for 12-16 hours until equilibrium was established. As

a rule, samples were taken on the second day. The establishment of stable equilibrium was controlled by chemical analysis for the content of SO_4 and Li ions. In determining the chemical composition of the equilibrium solution and the solid phase, the sulfate-ion content was found in the form of $BaSO_4$. Ammonium was determined by the Kjeldahl method, lithium by the volumetric periodate method, and sodium was calculated by difference. On the basis of the analytical data, the salt content in percentages was calculated for the liquid and solid phases, and a triangular diagram was constructed. The diagram was constructed according to the well-known Gibbs–Roseboom principle (see Table 1 and Fig. 1).

The quaternary system was studied by a nonvariant method. A solution of a nonvariant point corresponding to a ternary system and being in equilibrium with two solid phases was taken. To this solution the third salt was added in small portions. As a result, the figurative point of the section shifted inside the diagram up to the ternary point, from

Table 1

Data on the chemical composition of solutions and solid phases from lithium, sodium, and ammonium sulfates

Experiment no.	Solution composition, wt. %: Li_2SO_4	Solution composition, wt. %: Na_2SO_4	Solution composition, wt. %: $(NH_4)_2SO_4$	Solution composition, wt. %: sum of salts	Solution composition, % of total salts: H_2O	Solution composition, % of total salts: Li_2SO_4	Solution composition, % of total salts: Na_2SO_4	Solution composition, % of total salts: $(NH_4)_2SO_4$	Chemical formula of the solid phases
1	21.31	10.86	–	32.17	67.83	66.24	33.76	–	$Li_2SO_4 \cdot H_2O$ + $Li_2SO_4 \cdot 3Na_2SO_4 \cdot 12H_2O$

Experiment no.	Solution composition, wt. %: Li_2SO_4	Solution composition, wt. %: Na_2SO_4	Solution composition, wt. %: $(NH_4)_2SO_4$	Solution composition, wt. %: sum of salts	Solution composition, % of total salts: H_2O	Solution composition, % of total salts: Li_2SO_4	Solution composition, % of total salts: Na_2SO_4	Solution composition, % of total salts: $(NH_4)_2SO_4$	Chemical formula of the solid phases
2	18.87	10.62	4.80	34.29	65.71	55.03	30.97	14.00	$Li_2SO_4 \cdot H_2O$ + $Li_2SO_4 \cdot 3Na_2SO_4 \cdot 12H_2O$ + $2Li_2SO_4 \cdot Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$
3	24.69	–	3.09	37.78	72.22	88.87	–	11.13	$Li_2SO_4 \cdot H_2O$ + solid solution
4	24.35	1.45	10.78	36.58	63.42	66.57	3.96	29.47	$Li_2SO_4 \cdot H_2O$ + $2Li_2SO_4 \cdot Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$ + solid solution

Experiment no.	Solution composition, wt. %: Li_2SO_4	Solution composition, wt. %: Na_2SO_4	Solution composition, wt. %: $(NH_4)_2SO_4$	Solution composition, wt. %: sum of salts	Solution composition, % of total salts: H_2O	Solution composition, % of total salts: Li_2SO_4	Solution composition, % of total salts: Na_2SO_4	Solution composition, % of total salts: $(NH_4)_2SO_4$	Chemical formula of the solid phases
5	23.94	1.33	11.09	36.36	63.64	65.84	3.66	30.50	$Li_2SO_4 \cdot (NH_4)_2SO_4$ + $2Li_2SO_4 \cdot Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$ + solid solution
6	21.13	–	13.58	34.71	65.29	60.87	–	39.13	$Li_2SO_4 \cdot (NH_4)_2SO_4$ + solid solution
7	6.23	–	40.46	46.69	53.31	13.39	–	86.64	$Li_2SO_4 \cdot (NH_4)_2SO_4$ + $(NH_4)_2SO_4$
8	9.13	4.70	32.26	46.09	53.91	19.81	10.20	69.99	$Li_2SO_4 \cdot (NH_4)_2SO_4$ + $(NH_4)_2SO_4$ + $2Li_2SO_4 \cdot Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$

Experiment no.	Solution composition, wt. %: Li_2SO_4	Solution composition, wt. %: Na_2SO_4	Solution composition, wt. %: $(NH_4)_2SO_4$	Solution composition, wt. %: sum of salts	Solution composition, % of total salts: H_2O	Solution composition, % of total salts: Li_2SO_4	Solution composition, % of total salts: Na_2SO_4	Solution composition, % of total salts: $(NH_4)_2SO_4$	Chemical formula of the solid phases
9	5.36	9.08	34.44	48.88	51.12	10.97	18.58	70.45	$Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$ + $(NH_4)_2SO_4$ + $2Li_2SO_4 \cdot Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$
10	–	9.69	36.70	46.39	53.61	–	20.89	79.11	$Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$ + $(NH_4)_2SO_4$
11	10.39	15.38	10.29	36.06	63.94	28.81	42.66	28.53	$Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$ + $Na_2SO_4 \cdot 10H_2O$ + $2Li_2SO_4 \cdot Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$
12	–	22.66	16.42	39.08	60.92	–	57.98	42.08	$Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$ + $Na_2SO_4 \cdot 10H_2O$

Experiment no.	Solution composition, wt. %: Li_2SO_4	Solution composition, wt. %: Na_2SO_4	Solution composition, wt. %: $(NH_4)_2SO_4$	Solution composition, wt. %: sum of salts	Solution composition, % of total salts: H_2O	Solution composition, % of total salts: Li_2SO_4	Solution composition, % of total salts: Na_2SO_4	Solution composition, % of total salts: $(NH_4)_2SO_4$	Chemical formula of the solid phases
13	14.09	16.08	6.95	37.12	62.88	37.96	43.32	18.72	$Li_2SO_4 \cdot 3Na_2SO_4 \cdot 12H_2O$ + $Na_2SO_4 \cdot 10H_2O$ + $2Li_2SO_4 \cdot Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$
14	9.49	20.98	–	30.41	69.59	31.01	68.99	–	$Li_2SO_4 \cdot 3Na_2SO_4 \cdot 12H_2O$ + $Na_2SO_4 \cdot 10H_2O$

corresponding to solutions in equilibrium with three solid phases: one initial component, a double compound, and the newly formed triple salt. There are six boundary lines corresponding to the simultaneous crystallization of two salts on the diagram. The area of the triangle is divided into seven fields. The upper field (*I*) corresponds to solutions in equilibrium with monohydrated lithium sulfate. Field *II* corresponds to solutions from which solid solutions and the double anhydrous compound of composition $Li_2SO_4 \cdot (NH_4)_2SO_4$ (1 : 1) crystallize. Field *III* is characterized by solutions from which anhydrous ammonium sulfate separates. Within field *IV* the double complex of sodium and ammonium sulfates crystallizes, and in field *V*—mirabilite. Field *VI* corresponds to the formation of the hydrated double compound from lithium and sodium sulfates with a ratio of (1 : 3 : 12).

Of greatest interest is field *VII*, corresponding to separation of the triple compound of composition: $2Li_2SO_4 \cdot Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$. It is elongated along the lithium sulfate–ammonium sulfate side, with a tendency to broaden within the crystallization range of the double complex of lithium and sodium sulfates.

Fig. 1. Solubility isotherm of the system Li_2SO_4—Na_2SO_4—$(NH_4)_2SO_4$—H_2O at 25°

Figure 1: Fig. 1. Solubility isotherm of the system Li_2SO_4—Na_2SO_4—$(NH_4)_2SO_4$—H_2O at 25°

In addition to establishing the triple compound by means of the chemical diagram, this triple complex was studied by other methods. The triple salt was isolated from solutions, thoroughly pressed between sheets of filter paper, and analyzed. Analysis established the content (in %): lithium sulfate 37.16, sodium sulfate 25.52, ammonium sulfate 24.24, water 12.78, at the molecular ratio $2Li_2SO_4 \cdot Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$ (2 : 1 : 1 : 4). The data found chemically and those determined from the diagram agree well with one another. For greater certainty, the triple salt was also examined under a microscope. The crystals of the triple salt belong to the monoclinic system. Refractive indices: $N_p = 1.514$, $N_m = 1.510$, $N_g = 1.505$. The specific gravity was found pycnometrically and proved to be 3.023. The triple salt is insoluble in organic solvents (ethyl alcohol, acetone, benzene, carbon tetrachloride, and others).

Fig. 1. Solubility isotherm of the system Li_2SO_4—Na_2SO_4—$(NH_4)_2SO_4$—H_2O at 25°.

To study the ternary systems, about 60 experiments were carried out, and for the quaternary system we performed 46 chemical analyses. In the present article only selected data for the quaternary system, based on 14 experiments, are given.

Institute of Inorganic and Physical Chemistry
Academy of Sciences of the Kirgiz SSR

Received
6 IV 1964

CITED LITERATURE

1. J. H. Van' t Hoff, *Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen insbesondere des Strassfurter Salzlagers*, Leipzig, 1912 (monograph).

2. I. G. Druzhinin, A. P. Yanko, *Izv. Kirg. fil. AN SSSR*, issue 1, 63 (1954).

3. I. N. Lepeshkov, N. V. Bodaleva, L. T. Kotova, *ZhNKh*, **3**, issue 12, 2781 (1958).

4. A. N. Campbell, E. M. Kartzmark, *Canad. J. Chem.*, **37**, 9, 1409 (1959).

5. I. N. Lepeshkov, N. V. Bodaleva, L. T. Kotova, *ZhNKh*, **7**, issue 7 (1962).

6. J. A. Skarulis, H. A. Horan et al., *J. Am. Chem.*, **5**, 11, 3096 (1954).

Note: Figure translations are in progress. See original paper for figures.