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Thermodynamics of the aqueous sodium and potassium sulfate system at the temperature 20^0C and 40^0C

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ABSTRACT

The diagram of the ternary system Na^+, K^{+}/SO_4^{2-} - H_2O was established at 20°C and at 40°C by means of analytical measurements. In the equilibrium phase diagram of Na^+, K^+/SO_4^{2-}-H_2O at 20°C there are two invariant points, three univariant curves and three regions of crystallization: K_2SO_4, $Na_2SO_4.10H_2O$ and $NaK_3(SO_4)_2$. The compositions (% w/w) of the invariant points are respectively 5.41% of Na_2SO_4/10.20% of K_2SO_4 and 22.38% of Na_2SO_4/5.72% of K_2SO_4. At 40°C the system presents two invariant points, three univariant curves and three regions of crystallization containing K_2SO_4, Na_2SO_4 or $NaK_3(SO_4)_2$.The composition (% w/w) of the invariant points are respectively 6.03% of Na_2SO_4/12.82% of K_2SO_4 and 30.65% of Na_2SO_4/5.98% of K_2SO_4.

KEYWORDS

Brine system;
Phase equilibrium;
Solubility diagram;
Double salts;
Mirabilite.

INTRODUCTION

The sea water and brines are very complex solutions. All systems representing these solutions have to be evaluated. The major ions to be considered are Na^+, K^+, Mg^{2+}, Cl^- and SO_4^{2-} in H_2O; they form a reciprocal quinary system[1,2].

The bibliographic data concerning this system are in large number and studies in a large range of temperature. However, these studies are incomplete and hardly exploited because of the dispersion of the numerical data. Indeed, concerning this system, four compounds are cited (Na_2SO_4, K_2SO_4, $NaK_3(SO_4)_2$ and $Na_2SO_4.10H_2O$) and more than 200 solubility data are given in literature and many isotherms were established from -3 to 150^0C[3-19] but, the experimental points are often incoherent. In order to increase the number of solubility data and modeling the quinary system, we proceeded in the establishment of the isotherms at 20 and at 40^0C of the ternary system Na^+, K^{+}/SO_4^{2-} -H_2O.

EXPERIMENTAL

Experimental method

For the establishment of isotherms at 20 and 40^0C of the ternary system Na^+, K^{+}/SO_4^{2-} -H_2O, "ensemble" and "wet residue" methods were used[20,21]. The mixtures, of a determined composition from a synthetic brine and keeped at the temperature study in a bath thermostat (Lauda K20 KS) (± 0.05^0C), were stirred during

TABLE 1: Solubility data of the ternary system Na^+, K^+/SO_4^{2-} - H_2O at 20^0C

Composition of the saturated solution (% w/w)			Solid phases
Na_2SO_4	K_2SO_4	H_2O	
0.00	10.06	89.94	KS
2.50	9.88	87.62	"
5.41	10.20	84.39	KS+N3KS
8.01	8.82	83.17	N3KS
10.65	7.97	81.39	"
13.22	7.54	79.24	"
14.54	7.29	78.17	"
15.81	6.86	77.33	"
17.37	6.42	76.20	"
19.40	6.35	74.25	"
20.00	6.07	73.93	"
22.33	6.01	71.65	"
21.81	5.70	72.49	"
22.38	5.72	71.90	N3KS+NS10
21.35	3.50	75.15	NS10
20.68	0.95	78.37	"
21.12	0.00	78.88	"

TABLE 2: Solubility data of the ternary system Na^+, K^+/SO_4^{2-} - H_2O at 40^0C

Composition of the saturated solution (% w/w)			Solid phases
Na_2SO_4	K_2SO_4	H_2O	
0,00	12.90	87.09	KS
2.21	12.65	85.13	"
3.39	12,65	83.95	"
6.03	12.82	81.14	KS+N3KS
9.72	11.68	78.59	N3KS
13.20	10.50	76.30	"
16.71	8.99	74.28	"
18,00	8.62	73.37	"
20.20	8,27	71.52	"
23.26	7.35	69.38	"
24.80	6.88	68.31	"
27.97	6.25	65.77	"
30.65	5.98	63.36	N3KS+NS
29.51	2.68	67.77	NS
29.27	0.00	70.72	"

TABLE 3: Composition of the isothermal invariant points at 20^0C

% Na_2SO_4 (w/w)	% K_2SO_4 (w/w)	% H_2O (w/w)	Solid phases
5.41	10.20	84.39	KS + N3KS
22.38	5.72	71.9	N3KS + NS10

three to four days in order to achieve an equilibrium between the phases. The saturated solutions taken with a pipette fitted with a filter tip glass powder and they are sucked by a vacuum pump, the saturated solution and salt precipitated are then separated. Each saturated solution is diluted by the addition of distilled water (10 ml in 100 ml) to avoid a rush in case of any change in temperature. The salt will precipitate obtained dilute (50 ml of distilled water) to the analyses. The liquid and solid were next separated and analyzed for Na^+, K^+ and SO_4^{2-}.

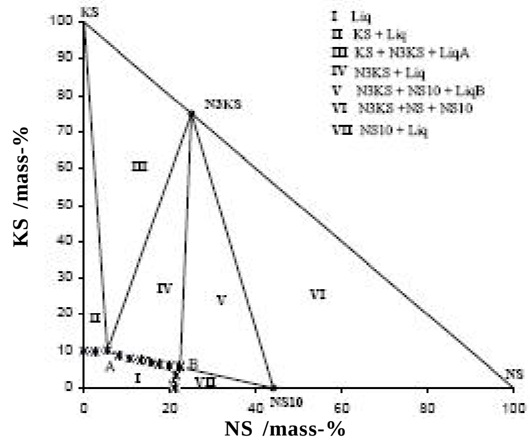

Figure 1: Solubility isotherm of the Na^+, K^+/SO_4^{2-} - H_2O system at 20°C

Chemical analysis

The composition of liquid and solid was determined by chemical analysis.

The Na^+ and K^+ content were determined by flame spectrophotometry[22] using a flame photometer 410 Sherwood instrument, which is measured by the radiated fraction of atom excite thermiquement by a wavelength λ correspond to a characteristic transition of the element to be dosed. The establishment of the curve requires the preparation of the solutions known concentration of between 0 and 8 ppm.

The concentration of SO_4^{2-} was measured by gravimetry by precipitation in the form of a salt not very soluble salt then calcined to a temperature below the temperature of fusion[23,24].

RESULTS AND DISCUSSION

The solubility data obtained at 20^0C and 40^0C are summarized respectively in TABLES 1 and 2. They are expressed in w/w percentages.

Three solid phases, K_2SO_4: (KS), $Na_2SO_4.10H_2O$: (NS10) and $NaK_3(SO_4)_2$: (N3KS), were observed at 20^0C (Figure 1). But at 40^0C (Figure 2) the three solid phases that were observed are KS, N3KS and

TABLE 4: Composition of the isothermal invariant points at 40^0C

% Na_2SO_4 (w/w)	% K_2SO_4 (w/w)	% H_2O (w/w)	Solid phases
6.03	12.82	81.15	KS + N3KS
30.65	5.98	63.37	N3KS + NS

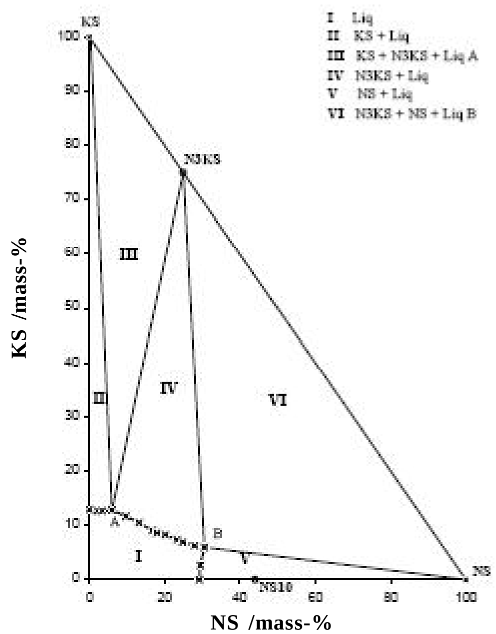

Figure 1: Solubility isotherm of the $Na^+, K^+/SO_4^{2-} - H_2O$ system at 20°C

Na_2SO_4: (NS). In fact at 40^0C the phase of NS10 disappears and the NS solid anhydride appears.

The solubility field of N3KS is important at 40^0C, whereas the liquidus curves at 20^0C is small. and at 40^0C are given respectively in TABLE 3 and in TABLE 4.

The compositions of the isothermal invariant points at 20^0C

Superscripts

NS - Na_2SO_4 ; NS10 - $Na_2SO_4.10H_2O$; KS - K_2SO_4; N3KS - Na_2SO_4 $3K_2SO_4$

REFERENCES

[1] L.Zayani, R.Rokbani, M.Trabelsi-Ayadi; J.Therm. Anal.Cal., **57**, 575 **(1999)**.

[2] N.Kbir Ariguib, D.Ben Hassen Chehimi, L.Zayani; J.Pure.Appl.Chem., **73**, 761 **(2001)**.

[3] W.F.Linke; 'Solubilities: Inorganic and Metal-Organic Compounds; 4th Ed., American Chemical, **1**, **2**.

[4] S.Babor; J.Bol.Soc.Chim.Quim., **17**, 5 **(1917)**.

[5] N.S.Kurnakov, S.F.Zemcuzny; J.Russ.Physik-Chem.Ges., **51**, 1 **(1920)**.

[6] O.K.Yanateva, V.T.Orlova; Zhur Prikled Khim., **4**, 193 **(1948)**.

[7] B.Y.Juan Damilano, S.J.Babor; Bol.Soc.Chim. Quim., **21**, 26 **(1961)**.

[8] A.Seidell; J.Amer.Chem.Soc., **27**, 53 **(1951)**.

[9] M.Articova, O.D.Kashkarov; Izv Akad Nauk Turkm SSSR Ser Fiz-Tekh Khim Nauk, **5**, 79 **(1983)**.

[10] O.K.Yanateva, V.T.Orlova; Zhur.Neorg.Khim., **4**, 193 **(1959)**.

[11] E.F.Soloveva; Tr.Vses Nauch IssI Inst.Galurgii., **31**, 180 **(1956)**.

[12] M.Motoyama, M.Kadota; Oka S.Junkastsu., **25**, 134 **(1971)**.

[13] I.Lunky Yanova, G.N.Podzorei; **12**, 2786 **(1962)**.

[14] E.I.Pylkova, E.I.Akhumov; J.Neorg.Khim.Russian., **7**, 193 **(1962)**.

[15] O.K.Yanateva, V.T.Orlova; Zhur.Priklad.Khim., **32**, 2397 **(1959)**.

[16] E.F.Soloveva; Trudy.VNIIG., **52**, 70 **(1967)**.

[17] M.Motoyama.M.Kadota, S.Oka Nippon, Kaisui Gakkai-Shi; **24**, 189 **(1971)**.

[18] M.P.Choulgina; Khartchouk Yanaeva Izvest Neorg Khim Akad Nauk SSSR, 22, 198 **(1955)**.

[19] E.V.Pylcova; Rus.J.Inorg.Chem., **10**, 935 **(1965)**.

[20] A.Chretien; Ann.Chim., **12**, 22 **(1929)**.

[21] F.A.H.Schreinemaker; A.A.Haz' Phys.Chem., **11**, 76 **(1893)**.

[22] P.W.West, P.Folse, D.Montgomery; Anal.Chem., **22**, 667 **(1950)**.

[23] Official Methods of Analysis, Association of Official Analytical Chemists, **331**, 1 **(1990)**.

[24] G.Charlot; Methodes of Chemical Analysis, 914 **(1966)**.