PHASE DIAGRAM OF THE SYSTEM $K_2S_2O_8$-KOH-H_2O

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Phase diagram of the system $K_2S_2O_8$—KOH—H_2O has been investigated in a limited range of concentrations (up to c. 25 w% KOH) at 10, 20 30 and 40°C. Under the given conditions the solid potassium peroxydisulphate whose solubility was distinctly diminished by the presence of potassium hydroxide in the solution was found to coexist with the saturated solutions.

The results of most of the preceding papers dealing with the solubilities in multicomponent systems containing alkali metal and/or ammonium peroxydisulphates[1-5] indicate that the solubility of the respective peroxydisulphate is decreased by the presence of other substances (sulphates, peroxydisulphates, sulphuric acid or the respective hydroxide). The only exception was found with the system $K_2S_2O_8$-H_2SO_4-H_2O where with increasing content of sulphuric acid the solubility of potassium peroxydisulphate first slightly increases, then passes through a flat maximum and only then decreases monotonously[2]. In order to extend the available scope of data on the solubilities in the mentioned multicomponent systems, we have studied in the present paper the phase diagram of the system $K_2S_2O_8$-KOH-H_2O.

EXPERIMENTAL

Chemicals used: Potassium peroxydisulphate was recrystallized several times from a product of the reagent grade purity and from redistilled water and afterwards dried at 40°C. Saturated solution of KOH was prepared from a product of Lachema, Brno, of the reagent grade purity, to decrease the content of carbonate which might have been present in the original solid product. This clear saturated solution was then added in appropriate amounts to the solution under study.

Working procedure: The same apparatus and procedure were used for the preparation of saturated solution of potassium peroxydisulphate containing various amounts of KOH, as it was described in previous communications[1-5]. To attain the equilibrium it was only necessary to stir intensely an excess of solid peroxydisulphate with the coexisting solution for 1—3 h (according to the temperature used). No appreciable decomposition of peroxydisulphate to sulphate and oxygen occurred during this procedure.

Analyses: The content of potassium peroxydisulphate both in samples of saturated solution and in the coexisting solid phase was determined permanganatometrically according to Leblanc and Eckardt[6]. Potassium hydroxide was determined acidimetrically. To recalculate the solubility data expressed in weight units into volume units, also the densities of saturated solutions were determined, using pycnometric method.

TABLE I

Solubility Data in the System $K_2S_2O_8$–KOH–H_2O at 10, 20, 30 and 40°C and Densities of the Saturated Solutions

The solid phase is in all cases $K_2S_2O_8$.

$K_2S_2O_8$		KOH		Density
w%	mol/kg H_2O	w%	mol/kg H_2O	
		10°C		
2·861	$10·919 . 10^{-2}$	0·0	0·0	1·0177
2·074	$7·880 . 10^{-2}$	0·565	0·1034	1·0169
1·420	$5·406 . 10^{-2}$	1·411	0·2588	1·0195
0·939	$3·587 . 10^{-2}$	2·229	0·4103	1·0246
0·656	$2·520 . 10^{-2}$	3·044	0·5635	1·0307
0·395	$1·551 . 10^{-2}$	5·421	1·0260	1·0508
0·279	$1·109 . 10^{-2}$	6·630	1·2695	1·0671
0·205	$8·534 . 10^{-3}$	10·944	2·1956	1·1014
0·161	$6·932 . 10^{-3}$	13·938	2·8923	1·1281
0·114	$5·220 . 10^{-3}$	19·174	4·2310	1·1809
0·082	$4·060 . 10^{-3}$	25·148	5·9932	1·2393
		20°C		
4·604	$1·7853 . 10^{-1}$	0·0	0·0	1·0292
3·298	$1·274 . 10^{-1}$	0·912	0·1697	1·0266
2·637	$1·018 . 10^{-1}$	1·534	0·2853	1·0281
1·666	$6·470 . 10^{-2}$	3·079	0·5762	1·0355
1·317	$5·167 . 10^{-2}$	4·389	0·8270	1·0439
0·870	$3·458 . 10^{-2}$	6·037	1·1560	1·0574
0·707	$2·852 . 10^{-2}$	7·589	1·4751	1·0698
0·482	$2·011 . 10^{-2}$	10·842	2·1794	1·0987
0·315	$1·361 . 10^{-2}$	14·088	2·9338	1·1280
0·192	$8·926 . 10^{-3}$	20·251	4·5374	1·1859
0·173	$8·675 . 10^{-3}$	26·053	6·2949	1·2416
		30°C		
7·075	$2·817 . 10^{-1}$	0·0	0·0	1·0450
5·725	$2·266 . 10^{-1}$	0·812	0·1549	1·0395
4·986	$1·970 . 10^{-1}$	1·405	0·2675	1·0396
4·663	$1·841 . 10^{-1}$	1·657	0·3153	1·0396
4·061	$1·603 . 10^{-1}$	2·204	0·4191	1·0405
3·337	$1·319 . 10^{-1}$	3·048	0·5804	1·0437
2·782	$1·102 . 10^{-1}$	3·850	0·7350	1·0476
2·332	$9·286 . 10^{-2}$	4·765	0·9143	1·0522
1·779	$7·160 . 10^{-2}$	6·308	1·2232	1·0642
1·495	$6·068 . 10^{-2}$	7·370	1·4415	1·0703

TABLE I
(*Continued*)

$K_2S_2O_8$		KOH		Density
w%	mol/kg H_2O	w%	mol/kg H_2O	
		30°C		
1·277	$5{\cdot}247 . 10^{-2}$	8·676	1·7175	1·0805
1·227	$5{\cdot}050 . 10^{-2}$	8·892	1·7635	1·0828
1·033	$4{\cdot}313 . 10^{-2}$	10·364	2·0851	1·0944
0·876	$3{\cdot}703 . 10^{-2}$	11·603	2·3632	1·1050
0·764	$3{\cdot}279 . 10^{-2}$	13·033	2·6950	1·1178
0·678	$2{\cdot}944 . 10^{-2}$	14·141	2·9592	1·1272
0·521	$2{\cdot}329 . 10^{-2}$	16·713	3·5995	1·1518
0·410	$1{\cdot}887 . 10^{-2}$	19·234	4·2666	1·1741
0·396	$1{\cdot}823 . 10^{-2}$	19·239	4·2673	1·1748
0·274	$1{\cdot}325 . 10^{-2}$	23·234	5·4143	1·2127
0·202	$1{\cdot}008 . 10^{-2}$	25·631	6·1602	1·2354
		40°C		
10·282	$4{\cdot}239 . 10^{-1}$	0·0	0·0	1·0638
9·323	$3{\cdot}835 . 10^{-1}$	0·753	0·1493	1·0592
8·050	$3{\cdot}291 . 10^{-1}$	1·466	0·2888	1·0563
6·975	$2{\cdot}841 . 10^{-1}$	2·212	0·4342	1·0575
6·091	$2{\cdot}478 . 10^{-1}$	2·983	0·5848	1·0581
5·255	$2{\cdot}137 . 10^{-1}$	3·785	0·7417	1·0599
4·712	$1{\cdot}918 . 10^{-1}$	4·402	0·8634	1·0624
4·161	$1{\cdot}698 . 10^{-1}$	5·185	1·0195	1·0662
3·665	$1{\cdot}501 . 10^{-1}$	6·040	1·1924	1·0702
3·366	$1{\cdot}383 . 10^{-1}$	6·625	1·3120	1·0732
3·277	$1{\cdot}348 . 10^{-1}$	6·784	1·3445	1·0734
2·877	$1{\cdot}189 . 10^{-1}$	7·581	1·5092	1·0795
2·642	$1{\cdot}097 . 10^{-1}$	8·227	1·6453	1·0832
2·421	$1{\cdot}011 . 10^{-1}$	8·951	1·8003	1·0882
2·141	$9{\cdot}014 . 10^{-2}$	9·991	2·0268	1·0960
1·735	$7{\cdot}397 . 10^{-2}$	11·504	2·3635	1·1087
1·496	$6{\cdot}339 . 10^{-2}$	12·812	2·6643	1·1181
1·291	$5{\cdot}657 . 10^{-2}$	14·281	3·0152	1·1306
1·051	$4{\cdot}692 . 10^{-2}$	16·083	3·4596	1·1464
0·769	$3{\cdot}555 . 10^{-2}$	19·206	4·2781	1·1751
0·512	$2{\cdot}470 . 10^{-2}$	22·816	5·3044	1·2092
0·393	$1{\cdot}955 . 10^{-2}$	25·238	6·0492	1·2298

RESULTS AND DISCUSSION

The found solubility data in the system $K_2S_2O_8$–KOH–H_2O measured for a limited range of potassium hydroxide concentrations (up to c. 25 w% KOH) at 10, 20, 30 and 40°C are presented in Table I in which the solubilities of potassium peroxydisulphate in pure water together with the respective densities are taken from paper[3]. It is evident from the Table that the presence of potassium hydroxide in the system diminished very distinctly the solubility of potassium peroxydisulphate at all temperatures of measurement. Although this decrease is generally conceivable if taken as the effect of identical ions, the real measured decrease of the solubility was much more pronounced in this case than *e.g.* in the case of $K_2S_2O_8$–K_2SO_4–H_2O (ref.[4]) or $Na_2S_2O_8$–NaOH–H_2O (ref.[5]). At all measured temperatures the densities of saturated solutions display a minimum, the position of which is shifted towards higher contents of KOH. The density of saturated solutions containing more than 10 w% KOH changes only negligibly with temperature, since it is actually affected by the density of the solution of KOH itself which at a constant concentration changes very little within the measured temperature interval. At contents of KOH less than 10 w% the density is influenced also by the presence of potassium peroxydisulphate and its course, with a minimum, is analogous to that observed earlier with the system[5] $Na_2S_2O_8$–NaOH–H_2O.

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REFERENCES

1. Balej J., Regner A.: This Journal *27*, 2208 (1962); *28*, 254, 1266, 3188 (1963); *30*, 1954 (1965); *31*, 361, 938, 4445 (1966); *32*, 2043, 4491 (1967); *33*, 2779 (1968); *34*, 1835 (1969).
2. Balej J., Regner A.: This Journal *34*, 2161 (1969).
3. Balej J., Regner A.: This Journal *25*, 1685 (1960).
4. Balej J., Regner A.: This Journal *25*, 1955 (1960).
5. Balej J., Regner A.: This Journal *35*, 1591 (1970).
6. Le Blanc M., Eckardt M.: Z. Elektrochem. *5*, 355 (1898).

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