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Study of Transition Temperature Through Mixed Crystal Formation. Part II.

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In continuation of our previous work, distribution measurements with cobalt sulphate as host and copper sulphate at tracer concentration as guest at different temperatures were undertaken in an aqueous medium. It has been observed that there is a continuous decrease in partition values with the rise of temperature upto 45.1° where there is a sharp change in partition value and above this temperature no uptake of copper by the host was recorded. Transition temperature of the host component, $CoSO_4.7H_2O$ has been found by this new method to be $45.1 \pm 0.05°$.

In view of the sharpness of the inflexion point it has been argued that in favourable circumstances, accurate transition temperature of the host component can be determined by the study of mixed crystal formation in the way proposed.

A glance at the literature[1-3] will show that different values in between 40°–50° have been reported as the transition temperature of $CoSO_4.7H_2O$ to $CoSO_4.6H_2O$. In our study of uptake of copper tracer by $CoSO_4.7H_2O$[4] we observed that distribution factors undergo diminishing trend upto the transition point of $CoSO_4.7H_2O$ to its lower hydrate. At the point of morphological change it was anticipated that a prominent change in the partition value may take place to help us to determine the transition point of $CoSO_4.7H_2O$ with a higher degree of precision.

It was further observed that the extent of uptake of copper by $CoSO_4.7H_2O$ at lower temperature is very high (e.g., $D = 1{\cdot}332$ at 5°)[4]. Maximum amount of copper that can be accommodated in $CoSO_4.7H_2O$ as $CuSO_4.7H_2O$ at a temperature below its transition point became, therefore, the subject matter of study.

EXPERIMENTAL

Cobalt sulphate, copper sulphate and all other reagents used were of B.D.H., AnalaR grade. The method of study of distribution coefficients was similar to that reported in our previous communication[4]. In these series of measurements the saturated solution of cobalt sulphate host impregnated with negligibly small amount of copper tracer was prepared in aqueous medium. It was found that the distribution factor comes out constant on equilibration of the system for 24 hrs. We however, equilibrated the system for 48 hr. to work at a safe margin. For better accuracy of result, each point in the curve represents an average value of the three distribution factors at each temperature. Verification for the constancy of D values was also examined in aqueous solution in both tracer and finite scale of the guest ion.

When distribution factors were studied to find out the maximum accommodation of copper in $CoSO_4.7H_2O$ as $CuSO_4.7H_2O$, a saturated solution of cobalt and copper was made in 0·5 N H_2SO_4 at a particular temperature. Powdered solid cobalt sulphate host was then added to the saturated solution containing finite amount of copper and was shaken for two days to attain complete equilibrium. Isolation of the mixed crystals containing finite quantities of copper was done at different temperatures in a specially designed apparatus which was reported in an earlier communication[5].

In order to obtain pure $CoSO_4.6H_2O$ free from copper about 200 gms. of cobalt sulphate were mixed with 2 gms. of copper sulphate and a fraction of about 25% was crystallised from the solution at a temperature in between 48° to 50°. The crystals were first washed with water, then with a mixture of water and alcohol (50 : 50) and finally water was removed with absolute alcohol at the same temperature and it was analysed. In all these cases copper, cobalt and sulphate were estimated in the usual ways[4] and water was determined by difference.

The method of determining the distribution coefficients at different temperatures was similar to that used by V. G. Khlopin[6] and finally the distribution coefficient, D, was calculated from the following expression due to Henderson and Kracek[7].

$$\left(\frac{\text{Tracer}}{\text{Carrier}}\right)_{\text{solid}} = D \quad \left(\frac{\text{Tracer}}{\text{Carrier}}\right)_{\text{solution}}$$

Experimental results are given in tables and figures.

DISCUSSION

It will be evident from the Table 1 that the distribution factor comes out constant in aqueous solution over a wide range of temperatures. Cobalt sulphate, therefore, takes up copper through mixed crystal formation in aqueous solution. Values of distribution co-efficient in aqueous medium at different temperatures have been shown [Fig. 1, curve (A)]. For a comparative view distribution co-efficients determined in acid solution were also shown in [Fig. 1, curve (B)]. Though the two curves (A) & (B) are almost similar in nature, the distribution values at corresponding temperatures differ to a considerable extent. In the curve (A), the value at 45·1° is of particular interest. At this temperature the partition value is comparatively small and it does not fall in the same line drawn through the points found at lower temperatures. The uptake of copper by cobalt sulphate after 45·1° is either nil or negligibly small. The sudden change in partition value at 45·1° can only be explained if we assume that at 45·1° certain fraction of the heptahydrated host component has been transformed to its lower hydrated form and both the phases of the host components $CoSO_4.7H_2O$ and $CoSO_4.6H_2O$ exist side by side. The comparatively small uptake in question is only due to heptahydrated cobalt sulphate fraction. Our calculations of D values are based on the assumption that the solid phase consists of only heptahydrated cobalt sulphate and such a change in *D* value is expected. Further increase of temperature even by 0·1° brings us to a zone of no uptake. From these points in view the method in question is very sensitive. In consideration of the sensitivity of the thermostat (±0·05°), the transition temperature of $CoSO_4.7H_2O$ should therefore be 45·1°±0·05°.

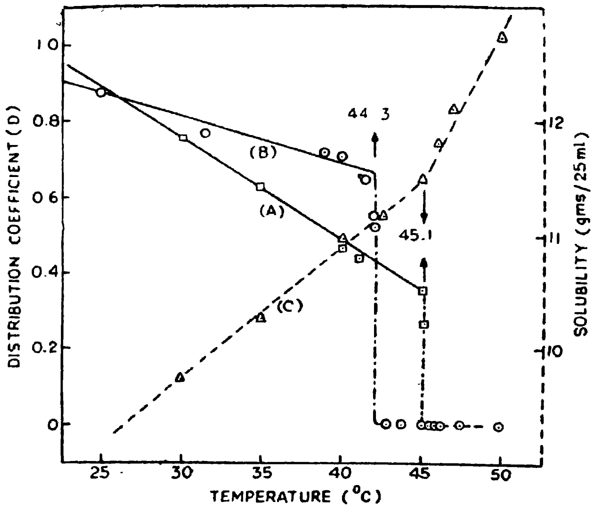

Fig. 1. On the study of transition temperature of $CoSO_4.7H_2O$—$6H_2O$ through mixed crystal formation between $CoSO_4.7H_2O$ as host and copper tracer as guest.

Curve (A) and (B) :

Study of transition point as determined from the variation of homogeneous distribution coefficient at different temperatures in aqueous and in 0·5*N* H_2SO_4 medium respectively.

——Left hand side scale.

Curve (C) :

Transition temperature of $CoSO_4.7H_2O$ as measured from the variation of solubility of cobalt sulphate in aqueous medium with respect to temperature.

——Right hand side scale.

It is evident from the Fig. 1, curve (B) that the characteristic change in phase transformation appears at a lower temperature in 0·5 *N* H_2SO_4 medium than what is found in aqueous medium. This phase transformation at lower temperature is due to the presence of H_2SO_4 and perhaps that of the tracer component in question. In order to avoid the effect due to the presence of H_2SO_4 the measurements have been carried out in aqueous medium and the results were shown in Table 1. The concentration of the guest ion in question was nearly $2{\cdot}5\times10^{-2}$ *M*. The chemical similarity of the host and the guest may annul the effect due to the presence of guest ion to a considerable extent. We also measured the distribution coefficients with the guest ion in question having nearly $1{\cdot}4\times10^{-2}$ *M* and $5{\cdot}0\times10^{-2}$ *M* concentration respectively at 45°, 45·1° and 45·2°. At each time the transition temperature comes out to be the same as was observed with guest ion concentration of nearly $2{\cdot}5\times10^{-2}$ *M*, though the partition values do not remain the same at all concentrations of copper. It can therefore be concluded that in such systems where the guest ion concentration is small, the effect of guest ion concentration is negligible and the transition

TABLE 1

The distribution of copper tracer in preformed $CoSO_4.7H_2O$ and its saturated solution in aqueous and in 0·5 N H_2SO_4 medium respectively.

Temperature (°C)	Fraction of cobalt in the solid phase (%)	Fraction of copper tracer in the solid phase (%)	D
Series-A.			
30	34.92	28.91	0.7577
	35.12	28.91	0.7513
	36.59	30.15	0.7482
			Av. 0.7517
45	35.93	17.10	0.3660
	34.11	15.82	0.3631
	35.01	15.82	0.3488
			Av. 0.3593
45.1	35.40	12.68	0.2650
	33.62	11.10	0.2464
	35.91	12.68	0.2691
			Av. 0.2502
45.2	34.83	—	—
	35.74	—	—
	34.89	—	—
Series-B.			
25	44.22	40.66	0.8644
	44.29	41.11	0.8780
	44.32	41.11	0.8768
			Av. 0.8730
44	38.41	25.86	0.5590
	37.35	24.16	0.5351
	38.63	25.86	0.5548
			Av. 0.5496
44.3	35.10	22.20	0.5277
	35.56	22.85	0.5367
	35.14	22.20	0.5269
			Av. 0.5304
44.4	35.22	—	—
	35.54	—	—
	33.80	—	—

N.B. (a) Initial copper concentration, $2.5 \times 10^{-2} M$ (approx.).

(b) Experimental data in series A and B were determined in aqueous and in 0·5*N* H_2SO_4 *medium* respectively.

TABLE 2

A study on the extent of uptake of finite amount of copper by $CoSO_4.7H_2O$ *and the composition of the mixed crystal at* 4°

Copper and cobalt ratio in the solution phase	Extent of cobalt crystallised (%)	Extent of copper co-separated (%)	D
9.15 : 90.85	30.92	30.62	0.9863
	40.53	40.69	1.0070
	46.44	46.48	1.0010
			Av. 0.9903
35.92 : 64.08	38.90	32.87	0.7691
	44.20	37.58	0.7597
	52.44	45.60	0.7760
			Av. 0.7630
44.96 : 55.04	37.16	28.86	0.6858
	44.78	35.59	0.6609
	53.86	44.28	0.6797
			Av. 0.6755
52.04 : 47.96	35.36	34.96	0.9826
	38.67	44.89	1.2570
	44.90	53.47	1.4100
68.90 : 31.10	33.94	34.70	1.0340
	40.96	47.22	1.2880
	44.49	55.99	1.5870

point lies within the temperature fluctuation of the thermostat range (±0·05°). It may be mentioned here that the transition temperature of $CoSO_4.7H_2O$ derived by the vapour pressure method[3] is 45·1° which is same as that obtained by our method.

It is to be noted that in an earlier investigation[8] the transition temperature of $CoSO_4.7H_2O$ was determined through mixed crystal formation with ^{60}Co as guest and $FeSO_4.7H_2O$ as host, where a higher value of the transition temperature (47±0·5°) was reported. The authors, however, detected two forms of monoclinic $CoSO_4.7H_2O$. Transition temperature of thus far unknown metastable variety of $CoSO_4.7H_2O$ was found to be 30°. It was assumed by the authors that because of the sudden rise of the partition values after the transition point (30°) the unknown variety could not exercise any appreciable influence on the distribution co-efficient at higher temperature. But from critical analysis of the data[9] it was evident that the curve above 30° would have been steeper which would bring it in close agreement with our data. It is therefore, essential for the correct determination of transition temperature that the characteristic nature of the curve at lower temperature should undergo thorough investigation.

In view of the fact that there is almost no uptake of copper by cobalt sulphate above 45·1°, it can be inferred that probably hexahydrated copper sulphate morphologically analogous to hexahydrated cobalt sulphate which is stable in this particular range does not exist.

We have also verified the transition temperature of the host component by measuring the solubility of $CoSO_4.7H_2O$ at different temperatures in presence of trace amount of copper along with each distribution measurement and the transition point found by solubility method is in close agreement with that derived by the new mode of approach [Fig. I, curve (C)].

In order to have an idea about the maximum accommodation of copper by $CoSO_4.7H_2O$ as $CuSO_4.7H_2O$ we performed the distribution measurements with different amounts of copper at 5° and it has been found (table 2), that upto about 45% of copper was taken up by cobalt through mixed crystal formation. Solid phase in one of such cases has also been isolated in the way described in an earlier communication[5] and was analysed. The composition of the solid phase was found to be a mixture of $CoSO_4.7H_2O$ and $CuSO_4.7H_2O$.

It is, further, to be noted that we could not detect any copper in 50 gms of hexahydrated cobalt sulphate crystallised from an aqueous solution containing about 200 gms of cobalt sulphate at a temperature (48°–50°). Cobalt sulphate was analysed for copper by electrolysing its aqueous solution by using platinum electrodes and testing the deposit on the cathode after dissolving in HNO_3 with KI and starch in the usual way. The limit for detection of copper is 0·1 mg. As we could not detect any copper in the crystallised sample, the presence of copper will be less than 0·1 mg. and thus the purity of cobalt sulphate was of higher order than that of the AnalaR variety. It can, therefore, be claimed to be a very simple and useful procedure for the preparation of pure cobalt sulphate free from copper.

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