

Study of the Transition Temperature of Mohr's Salt Analogue of Mn(II) by Distribution Measurement*

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Study of the distribution coefficient of the guest at tracer level with morphologically analogous host having a greater range of stability shows a prominent break at the transition temperature of the guest component. Mohr's salt, stable in the range of our observation (from 4° to 50°), has been used as host and Mn(II) as guest in the system with ^{54}Mn as radioactive tracer. The prominent change in the pattern of uptake between 12.5° and 13° has been assumed to be due to morphological transition of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot 6\text{H}_2\text{O}$.

TRANSITION temperatures of many compounds in the series $\text{M}'\text{M}''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (where $\text{M}' =$ monovalent cation and $\text{M}'' =$ divalent cation) have not been determined. Double salt of Mn(II) of the formula $(\text{NH}_4)_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot 6\text{H}_2\text{O}$ has been described in the literature¹, though data pertaining to its transition temperature are lacking. It has been established in our laboratory that in an isomorphous mixed crystal system the distribution factor between the host and the guest undergoes a prominent change at the point of transition of the guest component². It was concluded that the transition temperature of a guest component can be determined by the study of the distribution coefficient at different temperatures with a morphologically analogous host having a greater range of stability.

Our point of interest was to extend the same process for the determination of the transition temperature of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot 6\text{H}_2\text{O}$. It was also anticipated that this would give a clue as to the selection of temperature for the preparation of the salt in its different morphological states.

Materials and Methods

Mohr's salt of BDH Analar quality was used as host. Radioactive manganese (^{54}Mn) used as tracer in the experiment, was procured from BARC, Bombay. A few drops of carrier-free ^{54}Mn solution was added to a solution of inactive manganese sulphate (inactive manganese 2-3 mg). Manganese was precipitated as manganous sulphide by adding ammoniacal sulphide solution. The precipitate obtained was washed several times with hot water and then dissolved in dilute sulphuric acid. The operation was repeated and thus a stock solution of Mn(II) activity in 0.5N H_2SO_4 was prepared.

The first step in the study of the homogeneous distribution factor of the system was to prepare

a saturated solution of the host compound containing guest component. As a medium of study 0.5N H_2SO_4 was chosen. Sufficient amount of Mohr's salt was taken in a L-shaped tube, which contained 0.5N H_2SO_4 and to it was added ^{54}Mn activity. The tube was placed in a thermostat and shaken overnight to allow sufficient time for attaining saturation. Care was taken so that a little salt remained undissolved at the end.

The time required for attainment of equilibrium between the tracer in the solution and tracer inside the solid host component was then determined. A series of bulbs with a constriction at the mouth were taken and into each of them was inserted 25 ml of saturated solution of Mohr's salt containing ^{54}Mn activity. About the same amounts of Mohr's salt, ground to 120 mesh, was weighed and put into each of them. Bulbs were then fused at the constriction, immersed in the thermostatic-bath and shaken at a rate of 50-60 vibrations per minute. The temperature of the bath was the same as that of the saturated solution. At an interval of 12 hr a tube was opened and an aliquot of the solution was removed by a pipette with a filter paper cap fitted at the mouth to prevent any solid particle entering the solution. Activity left in the solution was measured with a GM counter and the activity remaining in the solid was computed therefrom. D was calculated according to the equation of Henderson and Kracek³.

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

A plot of D versus time showed that equilibrium was established within two days. To determine the distribution coefficient at different temperatures the solid phase was equilibrated in contact with the saturated solution for three days, giving an additional day in each case to allow for the safe margin. In order to examine the constancy of D , the solid surface was changed by introducing different amounts of solid into the ampoules.

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Studies were made from 4° to 50° . Temperature fluctuation of the cold-bath was within $\pm 0.5^\circ$ and sensitivity of the hot-bath was $\pm 0.1^\circ$.

Iron(II) in the saturated solutions at different temperatures was determined volumetrically by standard dichromate solution⁴.

Results and Discussion

The study of uptake of Mn(II) by Mohr's salt was made from 4° to 50° to find out whether there was any prominent change in the pattern of uptake in between these temperatures. In order to determine constancy in the distribution factor, the percentage of solid carrier was varied in all the experiments. In the case of mixed crystal formation D values should remain within experimental errors for different percentages of solid carrier. A scrutiny of the results presented in Table 1 shows that the constancy of the distribution factor with such variations are observed within reasonable limits above 13° . It can, therefore, be assumed that from 13° upwards the uptake follows the law of mixed crystal formation.

From 12.5° downward a significant divergence in D values with variation in the percentage of solid carrier is observed. At these points D value diminishes with increase in the percentage of solid carrier. In the presence of preponderant amount of host solid the change is not so prominent at about 12.5° , but as the temperature is lowered this divergence increases. Fig. 1 shows that at 12.5° and 10° the uptake follows Freundlich's law of adsorption isotherm.

Mohr's salt is a well known compound in the hexahydrated double sulphate series and is known to be stable in the range of our study. This is further corroborated by the solubility curve of the compound in the range of our study where solubility of the host plotted against temperature describe a smooth straight line course. It can, therefore, be concluded that $(\text{NH}_4)_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot 6\text{H}_2\text{O}$ undergoes a morphological change between 12.5° and 13°C . It can further be concluded that other morphological state of the salt exists below the 13°

TABLE 1 — DISTRIBUTION OF ^{54}Mn BETWEEN PREFORMED $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ CRYSTALS AND ITS SATURATED SOLUTION IN $0.5N$ H_2SO_4 ACID

[Initial manganese(II) concentration = $2.469 \times 10^{-4} M$ the solubility of Mohr's salt at 10° and 40° are respectively $0.700M$ and $1.071M$]

Temperature °C	Fraction (%) of Fe^{2+} in the solid phase	Fraction (%) of tracer ^{54}Mn with solid phase	D
4	34.53	20.03	0.493
	54.53	23.36	0.254
	67.44	22.53	0.139
10	31.10	11.68	0.291
	41.40	14.42	0.238
	50.51	15.76	0.168
	60.81	17.95	0.141
12.5	40.67	17.04	0.300
	51.68	22.47	0.278
	58.64	26.06	0.248
13	30.81	11.54	0.293
	40.67	16.81	0.294
	50.67	19.79	0.240
	59.84	26.68	0.244
		Av.	0.268
15	40.65	11.64	0.192
	40.77	11.91	0.196
	40.44	11.22	0.186
		Av.	0.191
30	27.44	10.54	0.312
	39.53	12.81	0.225
	48.33	17.81	0.232
	57.80	23.52	0.225
		Av.	0.248
40	22.29	6.33	0.235
	32.07	11.26	0.269
	44.13	14.45	0.213
		Av.	0.239
50	22.34	6.95	0.260
	30.53	14.05	0.372
	40.92	16.71	0.290
		Av.	0.307

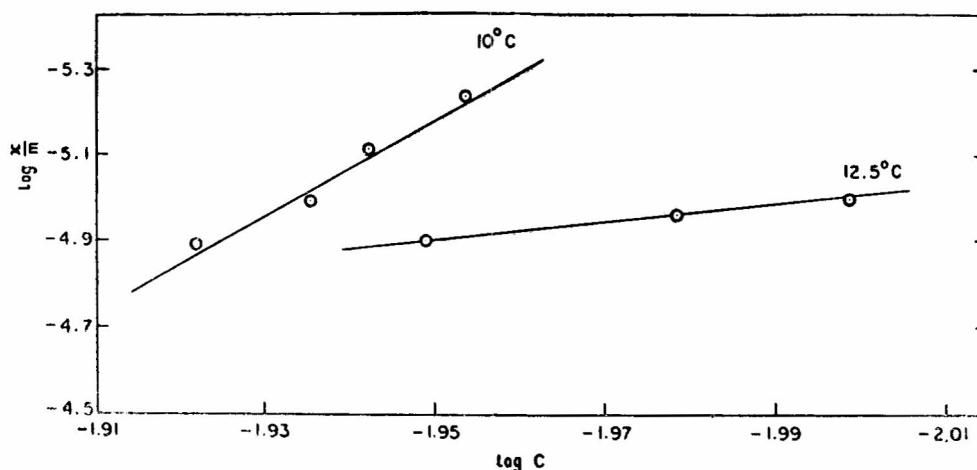


Fig. 1 — Freundlich adsorption isotherm of carrying x/E of manganese tracer by preformed $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ [x , amount of manganese carried (g/litre); c , concentration of manganese remaining in solution (g/litre); m , amount of host solid (g/litre)]

and any attempt to isolate $(\text{NH}_4)_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot 6\text{H}_2\text{O}$ should be done above 13° . In fact the salt prepared at 20° was analysed and found to contain 6 molecules of water of crystallization. However, salt prepared at 10° on analysis showed no difference in the number of molecules of water of crystallization. Probably the ether morphological state is metastable with respect to the stable hexahydrated variety, and its existence can be shown only through mixed crystal formation. The range of our study was, however, limited and so further change at higher temperature may be missed.

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