Distribution of Isomorphous Salts between Aqueous and Solid Phases in Ternary Systems: Zinc-Ammonium Sulphate-Magnesium Ammonium Sulphate-H₂O systems

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Abu Elamayem Equation, the advanced equation of Dorner Hoskins and Kholpin's equations relate the distribution of ismorphous salts between solid and aqueous phases during non-equilibrium crystallization. The distribution of isomorphous salts zinc ammonium sulphate and magnesium ammonium sulphate between aqueous and solid phases in the ternary system has been studied at different concentrations of less soluble salt in the ternary systems. Experimental results have been explained by a proper choice of values of the parameters in Abu Elemeyam's equation. These parameters characterize a given system over a wide range of concentration and by the use of the parameters, the amount of less soluble salt crystallizing out of the ternary systems can be predicted.

INTRODUCTION

Rapid crystallization of a pair of isomorphous salts from an aqueous solution results in a solid solution which changes in composition continuously. Non-equilibrium state results when crystallization is carried out for short periods. Several equations have been proposed for studying the distribution of salts in ternary systems under equilibrium and non-equilibrium conditions.

The impurity distribution under true equilibrium condition is given by Kholpin's equation

$$\frac{x\rho_s}{m_s} = K_N\left(\frac{(1-x)\rho_1}{m_1}\right)$$

where x is the amount of the macro component,

ρ_s, ρ_1 are the densities of solid and liquid systems,

m_s, m_1 are the amounts of the solid and liquid phases,

K_N = micro impurity segregation constant.

The Berthelot-Nernst law (Cholpin[1]) may be written in the form

$$\frac{x}{c} = D\frac{(a-x)}{(b-c)} \tag{1}$$

where a and b are the total amounts of the salts, x and c are the amounts (in grams) in the solid phase, $(a - x)$ and $(b - c)$ are the amounts in the liquid and D is the distribution constant.

The logarithmic relation developed by Doerner and Hoskins[2] for the coprecipitation of radium and barium chlorides with sulphuric acid is of the form

$$\ln \frac{d}{e} = \lambda \ln \frac{n}{f} \qquad (2)$$

where e and f are the initial amounts and d and n are the final amounts of radium and barium chlorides in solution. λ is a constant.

Hill *et al.*[3] gives a semi-empirical relation

$$R_l / R_s^m = K \qquad (3)$$

where R_l and R_s are the mole ratios of salts A and B in the liquid and solid phases respectively, m is an empirical constant and K is the distribution constant.

Abu Elameyam[4] has worked out equations (4) and (5) for fractional crystallization of ismorphous salts in equilibrium and non-equilibrium systems respectively[4].

$$Y^2 w (K - 1) - y[(w + a)(K - 1) + 1] + Ka = 0 \qquad (4)$$

$$\frac{dy}{dw} = \frac{1}{w} \left(\frac{1}{1 + \dfrac{M_B}{M_A} \left\{ \dfrac{1}{K} \left(\dfrac{1 - w}{a - wy} - 1 \right) \dfrac{M_A}{M_B} \right\}^{1/m}} - y \right) \qquad (5)$$

where w = fraction by weight of original mixture separated as crystals,
   y = fraction by weight of less soluble salts in crystals and
   a = fraction by weight of less soluble salt in the original mixtures.
   M_A and M_B are the molecular weights of the two salts.
   K and m are constants employed in equation (3).
   As a special case, when m = 1, equation (5) reduces to

$$\frac{dy}{dw} = \frac{1}{w} \left(\frac{1}{1 + \dfrac{1}{K} \left(\dfrac{1 - w}{a - wy} - 1 \right)} - y \right) \qquad (6)$$

Equation (1) to (4) are proposed for systems in equilibrium while equation (5) is applicable to non-equilibrium systems.

The object of the present investigation is to study experimentally the distribution of a pair of ismorphous salts between aqueous and solid phases and examine the results from the standpoint of the above theoretical equations. The ismorphous zinc ammonium sulphate and magnesium ammonium sulphate salts have been selected for the study because the systems are of industrial importance as magnesium and zinc are the constituents of several common alloy systems.

EXPERIMENTAL

Triply distilled water was used in preparing aqueous solutions. All reagents employed were of AR grade.

The double salts $ZnSO_4$, $(NH_4)_2SO_4 \cdot 6H_2O$, $MgSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ were prepared by mixing hot component solutions of the respective salts in equimolar proportions and then rapidly cooling to $0°C$; crystals of the double salts obtained were filtered by suction and air dried. The composition was then checked by standard methods of analysis. A DCM micro system 1121 computer was used for the numerical integration work.

The general experimental procedure[5, 6] consists of dissolving a pair of salts in the proper ratio by weight in a suitable amount of water. The resulting solution was kept in a thermostat at $35°C$ for 6 h at the end of which crystals formed were separated from the mother liquor, and the analysis of the crystals and mother liquor were carried out. For the analysis of the crystals and mother liquor obtained for system the following procedures were adopted.

The moist crystals were dissolved in water and the solution made up to known volume. An aliquot of the solution was diluted and 5 mL buffer solution with pH = 10 (ammonium chloride-NH_3 buffer) was added and titrated with 0.05 M EDTA with Erio-T as indicator to get the amounts of both zinc and magnesium present in the aliquot. The amount of zinc alone was determined from a second aliquot (acidified with 2 mL with hexamine to maintain pH with xylenol orange indicator. By adopting the same procedure[7-9] the mother liquor was also analysed to check the results of analysis of the solid phase.

The analyses so made yield the amount of the two salts in the solid phase which also contain a small amount of adhering mother liquor. A correction was applied in all analyses for the amounts of salts present in the adhering mother liquor. The method employed is identical with Schreinmaker's method (Glasstone, 1953)[10].

The correction factor ranged between 0.0005 to 0.01 for zinc-magnesium ammonium sulphate.

RESULTS AND DISCUSSION

The results are presented in Table-1 and Fig. 1 to verify equations (1), (2) and (5) for different 'a' values. The distribution constants λ and D calculated from experimental data for different 'a' are given in columns 11 and 12 respectively in these tables. The last column gives Y theory calculated from Euler's method of successive approximations. The results show that the equations (1) and (2) are not strictly applicable to this system. For alums and picromeites Hill et. al.[3] have shown that the values of m are around 1 and 0.8 while that of K varies from 1.2 to 15.5. To fix the value of K for each system, a trial value of K was obtained from the relation $K = [S_1/S_2]_1^{5/2}$ given by Hill et. al.[3] where S_1 and S_2 are the solubilities of the two isomorphous salts in each system. But the value thus calculated holds good when the system is in equilibrium. The following procedure was therefore employed for fixing the value of K by inspection. Using computer fits, a series of values of Y for various W values were calculated using several values of K (cf. Appendix II) around the equilibrium value. That value of K which gave rise to the set of W, Y values which were in good agreement with experimental values was accepted and this value of K (K_{expt}) was taken as a

TABLE-1

EXPERIMENTAL AND THEORETICAL VALUES: FRACTIONAL CRYSTALLIZATION
STUDIES OF ZINC/MAGNESIUM AMMONIUM SULPHATE-WATER SYSTEM

Temperature = 35 ± 0.01°C   K = 1.65, M = 1.00

Ex. No	Wt. of water g	Corrected weight of the salts in moist crystals of		Corrected wt. of moist crystals W14+W15	D	W	Y_{expt}	Y_{theory}
		ZAS salt W14	Mg Am sulphate salt W15					
a = 0.9: Initial wt of Zn salt = 9 g, Initial wt of Mg salt = 1 g.								
1.	12.07	6.548	0.528	7.076	1.70	2.19	0.721	0.925	0.922
2.	14.09	6.172	0.495	6.667	1.69	2.23	0.667	0.926	0.925
3.	17.08	5.393	0.418	5.811	1.69	2.08	0.581	0.928	0.927
4.	20.02	4.571	0.329	4.900	1.78	2.10	0.490	0.933	0.931
5.	22.00	4.712	0.361	5.073	1.65	1.94	0.507	0.929	0.928
	17.05	5.479	0.426	5.905	1.70	2.11	0.593	0.925	0.927
a = 0.666: Initial wt of Zn salt = 10 g, Initial wt of Mg salt = 5 g.								
1.	12.05	8.245	3.358	11.603	1.50	2.29	0.774	0.711	0.715
2.	14.20	8.102	3.185	11.287	1.64	2.43	0.752	0.718	0.713
3.	17.09	7.490	2.939	10.429	1.56	2.09	0.695	0.718	0.728
4.	20.08	7.016	2.675	9.691	1.57	2.03	0.646	0.724	0.727
5.	22.05	6.975	2.517	9.492	1.71	2.27	0.633	0.735	0.726
	17.06	7.566	2.935	10.500	1.61	2.22	0.700	0.721	0.722
a = 0.5: Initial wt of in Zn salt = 5 g, Initial wt of Mg salt = 5 g.								
1.	12.02	3.669	2.940	6.709	1.58	2.15	0.670	0.562	0.567
2.	14.08	3.423	2.530	5.952	1.64	2.12	0.595	0.575	0.581
3.	17.03	2.966	2.068	5.034	1.69	2.07	0.503	0.589	0.582
4.	20.08	2.556	1.695	4.252	1.73	2.04	0.425	0.601	0.595
5.	22.00	2.378	1.549	3.928	1.74	2.02	0.393	0.605	0.599
	17.04	2.998	2.156	5.175	1.68	2.08	0.517	0.586	0.585
a = 0.333: Initial wt of Zn salt = 5 m, Initial wt of Mg salt = 10 g.								
1.	12.05	4.290	6.909	11.199	1.66	2.70	0.747	0.383	0.374
2.	14.02	4.152	6.467	10.619	1.70	2.67	0.708	0.391	0.383
3.	17.07	3.740	5.835	9.575	1.57	2.12	0.638	0.393	0.399
4.	20.04	3.519	5.189	8.708	1.66	2.20	0.581	0.404	0.404
5.	22.03	3.428	5.044	8.472	1.65	2.14	0.565	0.405	0.402
	17.04	3.826	5.889	9.715	1.65	2.37	0.648	0.395	0.392
a = 0.1: Initial wt of Zn salt = 1 g, Initial wt of Mg salt = 9 g.								
1.	14.04	0.664	4.533	5.197	1.56	1.95	0.519	0.128	0.131
2.	17.02	0.574	3.669	4.243	1.63	1.96	0.424	0.135	0.136
3.	20.00	0.329	1.889	2.218	1.69	1.85	0.222	0.148	0.145
4.	22.01	0.387	2.284	2.671	1.67	1.86	0.267	0.145	0.143
5.	24.05	0.292	1.664	1.956	1.69	1.82	0.196	0.149	0.149
	19.42	0.449	2.808	3.257	1.65	1.89	0.326	0.141	0.141

characteristic constant of the system. It is significant to note that the experimental values of Y (Y_{expt}) agree with a given set of theoretical values (Y_{theory})calculated using a particular value of K. When the value of K is changed even by 1% the coincidence between the experimental and theoretical values of Y is lost. It may thus be emphasised that so long as the correct value of K is chosen, there is complete agreement between the theoretical and experimental values of Y and the coincidence is not therefore fictitious. The values of K and M were chosen as K = 1.65 and m = 1 and the values of Y and w were calculated by Euler's approximation technique.

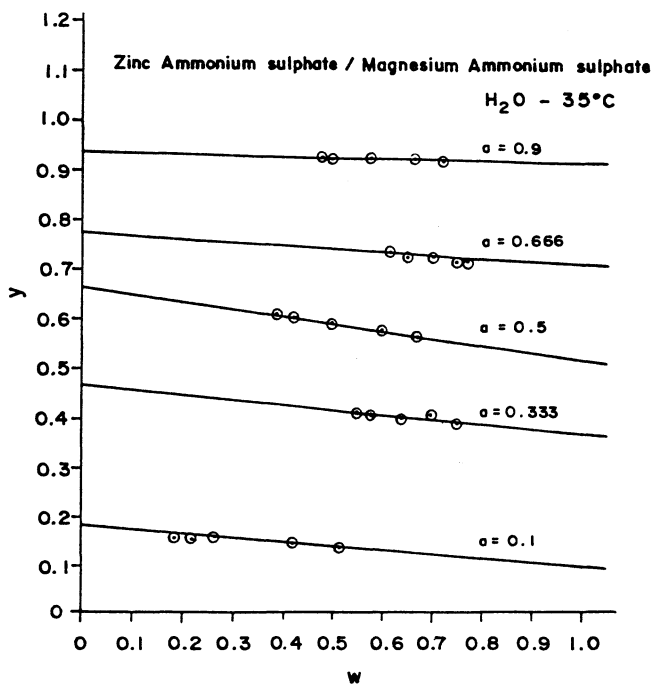Fig.   Zinc ammonium sulphate/magnesium ammonium sulphate H_2O-35°C

From the results we understand the inapplicability of the equations (1) and (2).

The nonconstancy of λ and D shows that the equilibrium model employed does not hold good. By applying the Abu Elemayem equation, which is applicable to non-equilibrium model, it is seen that both λ and D are fairly constant. In modern industry crystallization and the phenomenon of crystal growth play an important role in semiconductor and nonlinear optic studies. By applying this equation the actual salts incorporated in the system during non-equilibrium crystallization can be predicted, by the present investigations. λ can be related to total precipitation rate and number of active sites available for precipitation. The importance of this equation is that it is possible to calculate theoretically the amount of less soluble magnesium and zinc salts that will be present in a given weight of crystals (expressed as weight fraction W) that separate during crystallization.

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