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Phase Equilibrium of Ternary System Cd^{2+}, $K^+//Cl^-$-H_2O at 298 K

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Solid-liquid equilibrium of ternary system Cd^{2+}, $K^+//Cl^-$-H_2O at 298 K were studied by an isothermal solution saturation method. Experimental results indicate that there are four univariant curves AE_1, E_1E_2, E_2E_3 and E_3B, three invariant points E_1, E_2, E_3 and four crystallization fields in the ternary system. The ternary system has two double salts $Cd_3KCl_7{\cdot}4H_2O$ and $KCdCl_3$. The crystallization zones of equilibrium solid phases are $CdCl_2{\cdot}H_2O$, KCl, $Cd_3KCl_7{\cdot}4H_2O$ and $KCdCl_3$, respectively. The composition of the invariant point E_1 is KCl and $KCdCl_3$. The composition of the invariant point E_2 is $Cd_3KCl_7{\cdot}4H_2O$ and $KCdCl_3$. The composition of the invariant point E_3 is $Cd_3KCl_7{\cdot}4H_2O$ and $CdCl_2{\cdot}5/2H_2O$. The physico-chemical properties of solution in the ternary system show regular changes along with the increased cadmium concentration. The results indicated that $CdCl_2{\cdot}5/2H_2O$ possessed the highest solubility among those three salts, which means a strong transfer of Cd ion and a high pollution risk of soil environment. The solubility of $KCdCl_3$ would be restrained as the salts existing together.

Key Words: Cadmium, Ternary system, Isothermal method, Solid-liquid equilibria.

INTRODUCTION

Cadmium exhibits strong chemical activity with transferring among the environmental sphere, composed of minerals, water, atmosphere, soil and organism. Soil is crucial in cadmium biological geochemical cycle because cadmium's biological cycling ability depends on its solubility in soil solution. There occurring complicated chemical reactions such as dissolution, precipitation, adsorption and desorption in soil solution. Among these reactions, ion exchange reaction plays an important role in controlling ion distribution for liquid-solid equilibrium[1-3]. Cadmium compounds make a salt-water system together with other compounds in soil.

The view of that the soluble trace heavy metals would be easily adsorbed are widely accepted[4]. Trace elements exist in soil solution as the forms of free ions or complexes, the adsorption by vegetable is related to the activities of the ions[5]. It's very useful for predicting the adsorption to carrying out the experiments of simulating the ions in soil solution[6,7]. The mobility of heavy metals mainly depends on their complexing with other ions[8]. Then the speciation, dissolution and desorption of cadmium compounds under natural conditions could be studied to predict their biological activities.

Few studies on solid-liquid equilibrium of salt-water system in soil under normal temperature have been conducted. Peng *et al.*[9] have reported a ternary system equilibrium containing vanadium salts in soil solution.

The following quaternary system containing cadmium salts at 298 K has been determined in earlier work: Cd^{2+}, Na^+//Cl^-, SO_4^{2-}-H_2O[10], $Cd^{2+}//Cl^-$, SO_4^{2-}-H_2O[11]. We're also focusing on the experiments of other related systems.

The ternary system Cd^{2+}, $K^+//Cl^-$-H_2O is a subsystem of multivariate systems for soil solution. So far, no report has been made on phase equilibria of this ternary system at 298 K. In this paper, the solid-liquid equilibria of the ternary system Cd^{2+}, $K^+//Cl^-$-H_2O are studied in detail at 298 K, which is the normal temperature in natural soil.

EXPERIMENTAL

Distilled water with conductivity less than 10-4 S m^{-1} and pH 6.6 was used to prepare the solid-liquid phase equilibrium experiments and for chemical analysis. The reagents used were of analytical purity grade and obtained from the following suppliers: $CdCl_2{\cdot}5/2H_2O$, 99.5 mss %; KCl, mass 99.5 % (Chengdu Hualikexi Chemical Reagent factory, China).

A SHZ-88 type thermostated vibrator with a precision ± 0.1 K was used for the solid-liquid equilibrium measurements. A YSI-pH100 digital acidometer with an uncertainty of 0.01 was used for determining pH values of equilibrium solution.

A WZS-1 Abbe refractometer was used for measuring refractive index with an uncertainty of 0.0001.

General procedure: An isothermal solution method was used in the solid-liquid equilibrium experiments for the quaternary system. The system points for quaternary system were obtained by adding the third component gradually on the basis of the ternary saturation points at 298 K. The respective mixtures were placed in 100 mL plastic bottles for the solubility experiments and then the bottles were placed in the thermostated vibrator (SHZ-88). The solubility bottles with solution-solid mixtures were stirred for one week to promote the establishing of the equilibrium, the temperature was controlled at T = (298.2 ± 0.1) K. Experiments results show that the equilibria are attained in nearly 10 days. The solutions were taken out periodically for chemical analysis. When the components of the solution did not change, the equilibrium was established.

After equilibration finished, wet crystals were separated from the liquid phase by vacuum filtration using a sintered glass crucible and dried for X-ray diffraction study. A Rigaku D/mas-3C X-ray diffraction analyzer (Japan) was used for solid phase X-ray diffraction analysis.

The densities of the solution were measured using a density bottle with a precision of ± 0.2 mg and the bottle was thermostatted at T = (298.2 ± 0.1) K. Corresponding properties of the solution were determined by the above listed instruments.

Detection method: Cadmium concentration was determined by EDTA complexation (uncertainty of less 0.5 %), chlorine concentration was determined by argentometric method (uncertainty of less 0.5 %), potassium concentration was determined by back titration method of sodium tetraphenylboron and quaternary ammonium salt (uncertainty of 0.5 %).

RESULTS AND DISCUSSION

Solid-liquid phase equilibrium: The phase equilibrium experimental results for solubilities for the ternary system Cd^{2+}, $K^+//Cl^-$-H_2O at T = 298 K are given in Table-1. The respective ion concentration values in the equilibrium solution were expressed in mass fractions w %. The compositions of dry salt were expressed in g/100 g. In order to plot the ternary system diagram, dry salt values are necessary. Using the respective dry salt values calculated, the ternary phase diagram was plotted.

There are two double salts $Cd_3KCl_7·4H_2O$ and $KCdCl_3$ existing in the ternary system. The crystallization zones of equilibrium solid phases are $CdCl_2·H_2O$ (E_3FB), KCl (AE_1G), $Cd_3KCl_7·4H_2O$ (E_2E_3N) and $KCdCl_3$ (E_1E_2M), respectively. Cadmium chloride ($CdCl_2·H_2O$) has the smallest crystallization field, while the double salt $KCdCl_3$ has a larger crystallization field than those of others.

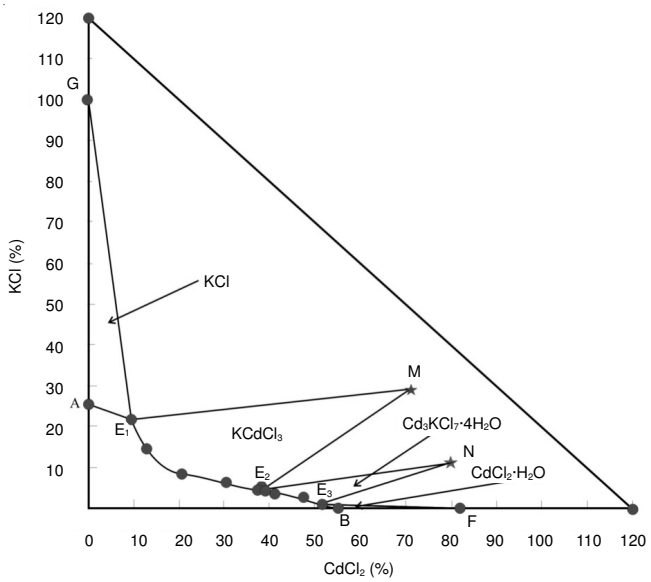


Fig. 1. Isothermal solubilities phase diagram of the ternary system Cd^{2+}, $K^+//Cl^-$-H_2O at 298 K

There are four univariant curves AE_1, E_1E_2, E_2E_3 and E_3B, three invariant points E_1, E_2, E_3 and four crystallization fields in the ternary system. The composition of the invariant point E_1 is KCl and $KCdCl_3$ of which content was 52.70 and 4.11 %, respectively. The composition of the invariant point E_2 is $Cd_3KCl_7·4H_2O$ and $KCdCl_3$ of which content was 52.70 and 4.11 %, respectively. The composition of the invariant point E_3 is $Cd_3KCl_7·4H_2O$ and $CdCl_2·5/2H_2O$ of which content was 52.70 and 4.11 %, respectively. The experiment results indicated that $CdCl_2·H2O$ possessed the highest solubility among

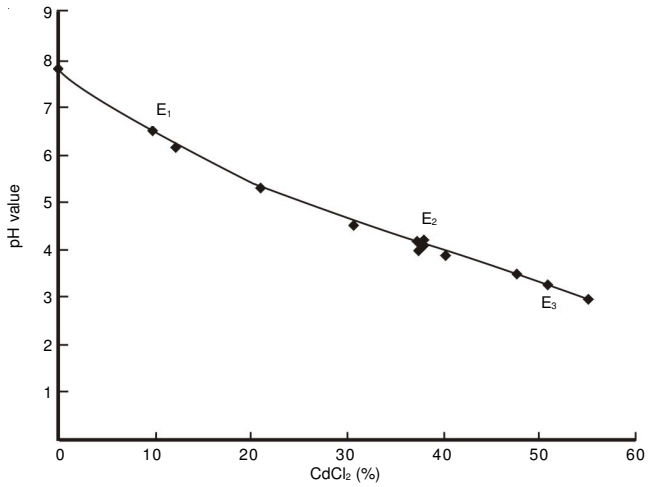
TABLE-1
ISOTHERMAL SOLUTION PHASE EQUILIBRIUM OF SOLUBILITIES OF THE TERNARY SYSTEM Cd^{2+}, $K^+//Cl^-$-H_2O AT 298 K

No.	Composition of solution (w %)		Physico-chemical properties		Equilibrium solid
	w($CdCl_2$)	w(KCl)	Density (g/cm^3)	pH	
1	0.00	25.56	1.1844	7.78	KCl
2,E_1	9.38	21.51	1.2496	6.57	KCl + $KCdCl_3$
3	12.03	14.39	1.2162	6.07	$KCdCl_3$
4	20.56	8.45	1.2739	5.33	$KCdCl_3$
5	30.56	5.89	1.3805	4.58	$KCdCl_3$
6	38.14	4.08	1.4881	4.25	$KCdCl_3$
7,E_2	37.63	4.50	1.4818	4.07	$KCdCl_3$ + $Cd_3KCl_7·4H_2O$
8	54.95	0.00	1.7482	2.97	$CdCl_2·5/2H_2O$
9,E_3	50.88	1.25	1.7222	3.22	$Cd_3KCl_7·4H_2O$ + $CdCl_2·5/2H_2O$
10	47.63	2.72	1.6084	3.5	$Cd_3KCl_7·4H_2O$
11	39.99	3.69	1.5144	3.87	$Cd_3KCl_7·4H_2O$
12	37.74	4.55	1.4840	4.1	$Cd_3KCl_7·4H_2O$ + $KCdCl_3$
13	37.42	4.45	1.4851	4.14	$Cd_3KCl_7·4H_2O$ + $KCdCl_3$

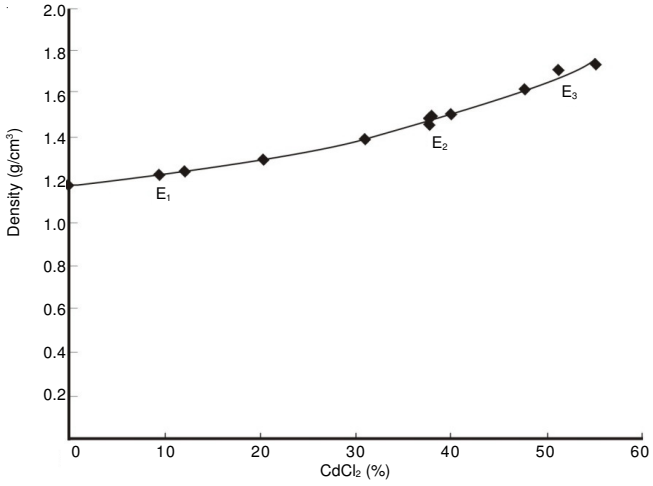
w %: Mass fraction.

those four salts, the order of the four salts solubility is $KCdCl_3$ < KCl < $Cd_3KCl_7{\cdot}4H_2O$ < $CdCl_2{\cdot}5/2H_2O$, which means a strong transfer of cadmium ion and a high pollution risk to soil environment. And the solubility of NaCl would be restrained as the salts existing together.

Physical and chemical properties of the solutions: The isothermal solution phase equilibrium experimental results of properties of the ternary system Cd^{2+}, $K^+//Cl^-$-H_2O at 298 K are tabulated in Table-1. According to the data, relationships between the density properties of the solutions and the weight percentage values of $CdCl_2$ are shown in Fig. 2.



(a) pH-composition



(b) Denisity-composition

Fig. 2. Physico-chemical properties-composition diagrams of the ternary system Cd^{2+}, $Na^+//Cl^-$-H_2O at 298 K

According to Table-1 and Fig. 2, the density properties of equilibrium solution of the ternary system Cd^{2+}, $K^+//Cl^-$-H_2O at 298 K changed regularly with the changing of the liquid phase concentration. pH values tended to decrease with the increasing of $CdCl_2$ concentration, while the densities values tended to increase with the increasing of $CdCl_2$ concentration.

Conclusion

The solid-liquid equilibria of the ternary system Cd^{2+}, $K^+//Cl^-$-H_2O at 298 K were studied by the isothermal solution saturation method. There is a double salt ($Na_2CdCl_4{\cdot}3H_2O$) existing in the ternary system (Cd^{2+}, $K^+//Cl^-$-H_2O) at 298 K. Using the experimental results, phase diagram of the system was plotted, which consists of three univariant curves, three crystallization fields and two invariant points.

The results indicated that $CdCl_2{\cdot}H_2O$ possessed the highest solubility among those three salts, the order of the four salts solubility is $CdCl_2{\cdot}H_2O$ > $NaCdCl_4{\cdot}3H_2O$ > NaCl, which means a strong transfer of cadmium ion and a high pollution risk to soil environment.

Physico-chemical properties-composition diagrams for the ternary system Cd^{2+}, $K^+//Cl^-$-H_2O at 298 K were plotted by using the analytical data. The pH and density properties of equilibrium quaternary system changed regularly with the concentration change of the liquid phase.

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REFERENCES

1. W.L. Lindsay, Chemical Equilibria in Soils, New York: JohnWiley & Sons, pp. 57-77 (1979).
2. Z.L. He, Q.X. Zhou and Z.M. Xie, Soil Chemical Equilibria of Pollutant and Essential Elements, Beijing: China Environmental Press, pp. 129-160 (1998).
3. G.F. Yu, X. Jiang, W.X. He and Z.G. He, *J. Environ. Sci.*, **2**, 508 (2007).
4. S.A. Barber, Soil Nutrient Bioavailability: A Mechanistic Approach, New York, John Wiley, p. 93 (1984).
5. B.P. Knight, A.M. Chaudri, S.P. McGrath and K.E. Giller, *Environ. Pollut*., **99**, 293 (1998).
6. M.A. Pavan, F.T. Bingham and P.F. Pratt, *Soil Sci. Soc. Am. J*., **46**, 1201 (1982).
7. P.F. Bell, R.L. Chaney and J.S. Angle, *Plant Soil*, **130**, 51 (1991).
8. J. Brugger, D.C. Mcphail, J. Black and L. Spiccia, *Geochim. Cosmochim. Acta*, **65**, 2691 (2001).
9. Y. Peng, Y. Zeng, L. Zhou and Y.B. Li, *J. Mineral. Petrol*., **25**, 118 (2005).
10. Y. Huang, S.J. Ni, S.H. Sang and P.D. Wang, *Acta Physico-Chim. Sin*., **24**, 333 (2008).
11. F. Zou, Huangyi, Y. Peng and Y. Zeng, *Chem. Eng*., **39**, 70 (2011).