

Solubility Product Study of CdF₂ in a Mixed Solvent Medium and Related Ion-Pair Formation at 25 °C

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ABSTRACT

The solubility of CdF₂ in the mixed solvent (water₍₁₎+ethanol₍₂₎) with mass fraction, $w_1 = 0.9$, was determined by using solvent evaporating method in the presence of various concentrations (0.100, 0.200, 0.300, 0.400, 0.500, 0.600, 0.800 and 1.500 mol.L⁻¹) of NaCl at 25°C. The values of solubility and solubility product constant of CdF₂ in the mixed solvent were evaluated at zero ionic strength upon the extrapolation method. Then, the ion - pairing extension was calculated in the considered solution.

Keywords: Solubility product constant; Ion association; Mixed solvent

INTRODUCTION

Most physicochemical properties of ionic solutions are influenced by ionic strength and the solvent's dielectric constant. Indeed, in the context of ionic solution chemistry, solvent polarity, dielectric constant and ionic strength are of great importance. As it is clear, the solubility of an ionic compound in a given solvent or in a mixed solvent and the extend of ion association in an ionic solution depend on the polarity and dielectric constant of the solvent as well as on the ionic strength of the medium [1-3].

In turn, most of the theories that have been used to predict the extend of solubility of an ionic compound in a given solvent or in a mixed solvent and related ion association are based on changes in the electrostatic properties of the solvent, solute

and ion solvation as well as on the ionic strength of the medium [4-10].

EXPERIMENTAL

CdF₂ and other chemicals were purchased from Merck Company with high degree of purity and used without further purification. The mixed solvent (water₍₁₎ + ethanol₍₂₎) with mass fraction, $w_1=0.9$ was prepared from deionized water and fairly pure ethanol. Then, the solubilities, s (mol.L⁻¹), of CdF₂ in the prepared mixed solvent at the presence of various molarities of NaCl (0.100, 0.200, 0.300, 0.400, 0.500, 0.600, 0.800, 1.500) were determined by the solvent evaporating method at 25°C (Tab. 1 and Fig. 1).

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Table 1. Solubilities of CdF₂ with mass fraction, $w_1=0.9$ in mixed solvent (water (1)+ ethanol (2)) at various ionic strength, at 25°C

M(NaCl) mol.L ⁻¹	I mol.L ⁻¹	s(CdF ₂) mol.L ⁻¹
0	0.5349	0.1783
0.1	0.7168	0.2056
0.2	0.9566	0.2522
0.3	1.1335	0.2778
0.4	1.3789	0.3263
0.5	1.646	0.3820
0.6	1.8996	0.4332
0.8	2.2475	0.4825
1.5	4.6641	1.0547

*Each value of s is an average of five independent measurements.

Discussion

As we can see from figure 1, the solubility dependence of CdF₂ with ionic strength, I, is fairly linear on a wide range of ionic strength. The interception of the line with the y- axis for $I \rightarrow 0$ gives

$$s_0 = 0.031 \text{ mol.L}^{-1} (\pm 0.002) \quad (1)$$

where s_0 represents the solubility of CdF₂ in the mixed solvent (water (1) + ethanol (2)) with $w_1= 90$ at 25°C when I approaches zero.

Obviously the behavior of ions at $I \rightarrow 0$ can be assumed to be ideal and then $K_{sp(th)} = 4s_0^3$ for an ionic compound with the formula B₂A or BA₂. So, $K_{sp(th), CdF_2/mol^3L^{-3}} = 4s_0^3 = 1.1916 \times 10^{-4}$

On the other hand, it can be considered that the concentration solubility product constant ($K_{sp(c)}$) of CdF₂ in the saturated solution is: $K_{sp(c)} = 4s^3$ (2)

Thus, the values of $K_{sp(c)}$, at various ionic strengths for CdF₂ were obtained from the solubility values of table 1 at different ionic strengths. The results are shown in table 2.

The estimation of the activity coefficient of ions in a given solution by using a suitable model and the calculation of the modeled solubility product, $K_{sp(m)}$, is a quite straight forward process

$$K_{sp(m)} = 4s^3 \gamma_{\pm}^3 \quad (3)$$

So we used the extended Debye - Huckel model to estimate the mean activity

$$\text{coefficient: } \log \gamma_{\pm} = \frac{Az_+z_- \sqrt{I}}{1 + aB\sqrt{I}} \quad (4)$$

where $A=0.5059$ at 25°C for water as solvent, a is a measure of the hydrated ion size, and $B=0.328$ at 25°C for water as solvent.

Table 2. The values of $K_{sp(c)}$, CdF₂ in the mixed solvent, (water(1)+ethanol (2)) with mass fraction, $w_1=0.9$ at various ionic strengths at 25°C

S(CdF ₂)/mol.L ⁻¹	$K_{sp(c)}/mol^3L^{-3}$	$\ln K_{sp(c)}/mol^3L^{-3}$	I total mol.L ⁻¹
0.1783	0.02267	3.7867	0.5349
0.2056	0.03476	3.3592	0.7168
0.2522	0.06416	2.7463	0.9566
0.2778	0.08575	2.4563	1.1335
0.3283	0.1389	1.9740	1.3789
0.3820	0.2229	1.5010	1.646
0.4332	0.3251	1.1236	1.8996
0.4825	0.4493	0.8000	2.2475
1.0547	4.6929	1.5460	4.6641

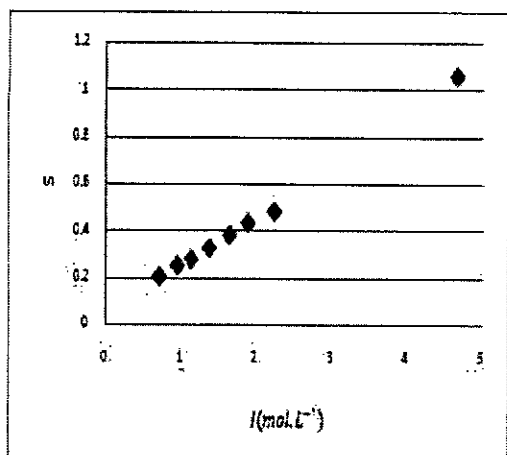


Fig 1. Plot of s versus I for the solubilities of CdF_2 in (water(1)+ethanol(2)) with mass fraction, $w_1=0.9$ in the presence of various molarities of NaCl at 25°C .

To apply the equation (4) for evaluating the mean activity coefficient, γ_{\pm} , of the ions in the mixed solvent at the same temperature, we estimate the value of A and B relative to the mixed solvent as follows:

$$A' = \frac{A(d_{\text{mixed}}/d_{\text{water}})^{\frac{1}{2}}}{(D_{\text{mixed}}/D_{\text{water}})^{\frac{3}{2}}} \quad (5)$$

$$B' = \frac{B}{(D_{\text{mixed}}/D_{\text{water}})^{\frac{1}{2}}} \quad (6)$$

where d and D represent density (g cm^{-3}) and dielectric constant respectively. So,

$$A' = \frac{0.5059(0.9713/1)^{\frac{1}{2}}}{(76.28/78.54)^{\frac{3}{2}}} = 0.5241 \text{ "at } 25^\circ\text{C"}$$

$$B' = \frac{0.328}{(76.28/78.54)^{\frac{1}{2}}} = 0.3328 \text{ "at } 25^\circ\text{C"}$$

The ion size a in the eq.(4) can be evaluated as follow:

$$a_{\pm} = \frac{1}{2}(a_+ + a_-) = \frac{1}{2}(5\text{\AA} + 3.5\text{\AA}) = 4.25\text{\AA} \quad (7)$$

By substituting the above values in eq .(4) it is obtained

$$\gamma_{\pm}(\text{in the mixed solvent}) = 0.41995 \quad (8)$$

and then

$$\begin{aligned} K_{sp(m)} &= K_{sp(c)}\gamma_{\pm}^3 \\ &= (2.2673 \times 10^{-2})(0.41995)^3 \\ &= 2.2673 \times 10^{-2} \times (0.41995)^3 \\ &= 1.679 \times 10^{-3} \end{aligned} \quad (9)$$

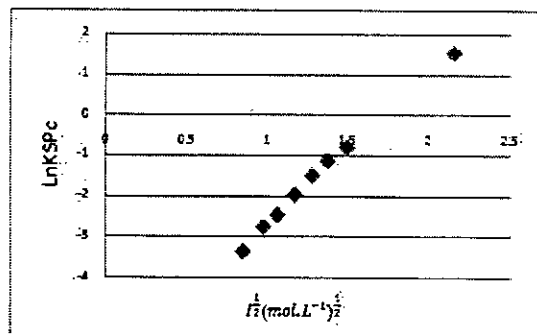


Fig. 2. Plot of $\ln K_{sp(c)}$ versus $I^{1/2}$ in the mixed solven, (water (1)+ethanol (2)) with mass fraction $w_1=0.9$ at various ionic strength at 25°C .

Summarizing, the values of $K_{sp(th)}$, $K_{sp(m)}$ and $K_{sp(c)}$ are 1.1916×10^{-4} , 1.6792×10^{-3} and 2.2673×10^{-2} respectively.

Now, we assume that the Debye - Huckel model is adequate for estimating the mean activity coefficients, γ_{\pm} , and that the difference between $K_{sp(th)}$ and $K_{sp(m)}$ comes from the ion association phenomenon in the studied solution. For simplicity, we only consider the ion pair formation, and neglect the other kinds of ion association. So, if we denote the concentration of CdF^+ ion pair in the saturated solution of CdF_2 in the mixed solvent, (water (1)+ethanol (2)) with $w_1 = 0.9$, at 25°C by x (in mol.L^{-1}), then the following equation would be available :

$$\begin{aligned} \frac{K_{sp(th)}}{\gamma_{\pm}^3} &= (s-x)(2s-x)^2 \\ \Rightarrow x^3 - 5sx^2 + 8s^2x - 4s^3 + \frac{K_{sp(th)}}{\gamma_{\pm}^3} &= 0 \end{aligned} \quad (10)$$

Solving the eq (10) obtained a reasonable value of x :

$$x = 0.1580 \text{ molL}^{-1} \text{ (see table 3)}$$

It is worthwhile to consider the fact that the non-ideality of electrolyte solutions is

due partly to the activity coefficients of ions in the solution and partly to the ion – association phenomenon [7-14]. Indeed, when two ions of opposite charges approach enough one another, an ion – pair species may be formed [14-20]. For instance, CdF⁺ ion – pair may be formed in the saturated solution of CdF₂ in the mixed solvent, water + Ethanol, as follow:

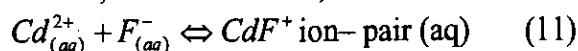


Table 3. The results of iterating calculations for obtaining a reasonable value of α , α =[ion-pair], in the mixed solvent (water (1) + ethanol(2)) with mass fraction $w_1=0.9$ at 25°C.

Iteration	γ_{\pm}	$\alpha / \text{mol.L}^{-1}$
1	0.41995	0.1430
2	0.51344	0.1564
3	0.52810	0.1578
4	0.52976	0.1580
5	0.530004	0.1580

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CONCLUSION

The solubility of CdF₂ in the mixed solvent (water (1) + ethanol (2)) with mass fraction, $w_1=0.9$ increase linearly with increasing the ionic strength in a wide range of NaCl concentration from (0.1 to 1.5)/ molL⁻¹ as a background salt. The value of thermodynamic solubility product constant of CdF₂ in the mentioned mixed solvent could be estimated on the value of the solubility of the considered ionic compound at zero ionic strength upon extrapolating method. The saturated solution of CdF₂ in the mixed solvent with the presence of NaCl is highly non – ideal. The non - ideality is partly due to the mean activity coefficients and partly due to the ion association phenomenon.