The investigation of ionic association in the CdF_2 solution with the mixed solvent (water +ethanol +propanol) at $25°C$

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## ABSTRACT

Using the mixed solvents, (water +ethanol + propanol), the solubility of CdF_2 was determined by evaporating method at $25°$ C. The results showed that the sollbility, s, of CdF_2 decreases by decreasing the dielectric constant of the mixed solvent .Once the solubility of CdF_2 was determined, the concentration solubility product, $K_{sp(c)}=4s^3$, was calculated .Furthermore ,by estimating the mean activity coefficient, $f_\pm$, of CdF_2 in the solution upon the extended Debye-Hückel theory, the model solubility Product constant of the salt, $K_{sp(m)}=4s^3 f_\pm^3$ was calculated .On the other hand we concluded the equilibrium constant of ion pair formation , K_{IP}, on the basis of Fuoss contact ion pair model and we obtained the value of ion pair concentration in the mixed solvents, (water 85% +ethanol l5% + propanol 10%). The value of thermodynamic solubility product constant, $K_{sp(th)}$, of CdF_2 in the mixed solvent was evaluated at zero ionic strength upon the extrapolation method and the value of ion pair concentration was calculated in the considered solution and compared by fuoss model.

Keywords: Dielectric constant; Fuoss model; Ion-Pair formation

INTRODUCTION

The solubility, s, of CdF_2 depends on the dielectric constant of the solvent, temperature and some other factors. By considering the mean activity coefficients of Cd^{2+} and F^- ions in the solution, $f_\pm$, the following solubility product constant can be considered:

$$CdF_{2(s)} \Leftrightarrow Cd^{2+}{}_{(aq)} + 2F^-{}_{(aq)} \qquad (1)$$
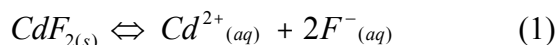
$$K_{sp(a)} = 4s^3 f_\pm^3 \qquad (2)$$

where $K_{sp(a)}$ is the solubility product constant of CdF_2 in terms of activities , $f_\pm$ is the mean activity coefficient, and s

represents the solubility of CdF_2 in terms of molarity.

In turn, the value of concentration solubility product constant, $K_{sp(c)}$ of the ionic salt, CdF_2, can be calculated experimentally by measuring the solubility, $s/molL^{-1}$ of CdF_2:

$$K_{sp(c)} = 4s^3 \qquad (3)$$

On the other hand, the model solubility product constant, $K_{sp(m)}$ can be estimated by estimating the mean activity coffiecint, $f_\pm$, of the salt by using the extended Debye-Hückel model [2].

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$$K_{sp(m)} = 4s^3 f_{\pm}^3 \tag{4}$$

Now we consider the following ion pair formation .

$$Cd_{(aq)}^{2+} + F_{(aq)}^- \Leftrightarrow [CdF]_{ion-pair}^+ \tag{5}$$

$$K_{IP} \approx \frac{[ion-pair]}{[Cd^{2+}][F^-]} \tag{6}$$

We can estimate, on the basis of the Fuoss model, the contact ion pair formation constant :

$$K_{IP} = 2.522 \times 10^{21} a^3 \; e^{1.674 \times 10^{-3} z^2 / a \varepsilon T} \tag{7}$$

where a is the ion size in centimeters, T in Kelvin, and K_{IP} in $L.mol^{-1}$ and ϵ is the dielectric constant of the solvent [1].

Once, the value of K_{IP} estimated upon the equation(7) ,the calculation of ion pair concernteration, [ion-pair] = x/molL^{-1} is quality straight forward:

$$K_{IP} = \frac{x}{(s-x)(2s-x)} \tag{8}$$

or

x=K$_{IP}$ (s-x)(2s-x) (9)

Now, the thermodynamic solubility product constant, K$_{sp(th)}$ is :

K$_{SP(th)}$=(s-x)(2s-x)^{2}f$_\pm$^{3} (10)

while, $f_\pm$, can be estimated upon a suitable model, for example, the extended Debye-Hückel theory.

In general the following trend may be observed

$$K_{sp(c)} > K_{sp(m)} > K_{sp(th)} \tag{11}$$

This trend is due to the nonideality of solution and ionic association phenomenon.

EXPERIMENTAL SECTION

CdF_2 and other chemicals were purchased from Merck company with a high degree of purity and used without further purification. The test solutions with respect concentrations were prepared by using deionized water and considered compounds.

The mixed solvent, (water + ethanol + propanol), at various percents of ethanol and propanol were prepared from deionized water and ethanol and propanol.

Then the solubility of CdF_2 in each mixture was determined by the solvent evaporating method at $25.0°C$ (table 1) [3-15].

Table1. Solubility, s, molL^{-1}, of CdF_2 in the mixed solvent, (water + ethanol + propanol) at $25.0°C$

Mass Percent of ethanol	Mass Percent of Propanol	s/mol L^{-1}
5	10	0.1529
10	10	0.1130
5	20	0.0665

DISCUSSION

The dielectric constant of the mixed solvent ε_{m-s} can be esmitated by the following approximation:

$$\varepsilon_{m-s} = X_w \varepsilon_w + X_e \varepsilon_e + X_p \varepsilon_p \tag{12}$$

where subscrıpts m-s, w ,e and p refer to mıxed solvent, water and ethanol and propanol respectıvely, and X is mole fraction, ε_w and ε_{m-s} represent the dielectric constant of water and mixed solvent at $25.0°C$ respectively.

The respective dielectric constants, which were estimated by Eq. (12), along with respective solubilities, are summarized inTable 2.

Table 2. Solubilities of CdF_2 in various " water + ethanol + propanol" mixtures at $25.0°C$ as a function of dielectric constant of the mixture

Mass Percent of ethanol	Mass Percent of Propanol	Mole fraction of water X	ε_{mix}	$s/mol.l^{-1}$
0	0	1.0000	78.54	0.3258
5	10	0.05172	75.4164	0.1546
10	10	0.03381	74.0959	0.1130
5	20	0.015996	73.0310	0.0665

Based on eq (7), one can estimate the value of K_{IP} for the equilibrium (5) and then calculate the concentration of the ion-pair in each saturated solution by using eq. (13).

Setting $[CdF]^+ = x$ and $[Cd^{2+}]_{free} = s - x$ and $[F^-]_{free} = 2s - x,$ we will obtain the following equation:

$$K_{IP} = \frac{xf_{ip}}{(s-x)(2s-x)f_{\pm}^2} \quad (13)$$

$$f_{\pm}^2 K_{ip}x^2 - (3sf_{\pm}^2 K_{ip} + f_{ip})x + 2s^2 f_{\pm}^2 K_{ip} = 0 \quad (14)$$

The values of $f_{\pm}$ and f_{ip} can be estimated using the extended Debye-Hückle law

$$\text{Log}_{10}f_{\pm} = -\frac{A|Z_+ Z_-|\sqrt{I}}{1+aB\sqrt{I}} \quad (15)$$

The value of A and B for water as solvent at $25°C$ is 0.504 and 0.328 respectively and a=4.25Å for CdF_2 in the solution. A' and B' for the mixed solvent can be calculated at the same temperature, as follow:

$$A' = \frac{A(d_{mixed}/d_{water})^{\frac{1}{2}}}{(\varepsilon_{mixed}/\varepsilon_{water})^{\frac{3}{2}}} \quad (16)$$

$$B' = \frac{B}{(\varepsilon_{mixed}/\varepsilon_{water})^{\frac{1}{2}}} \quad (17)$$

d represents the density of the solvent in terms of(g cm^{-3}) (table3).

In order to estimate $f_{\pm}$ and f_{IP} we may at the first approximation, set I=3s and conclude an approximate value for $f_{\pm}$ and f_{i-p} upon eq. (15). Inserting these values in Eq. (14) we conclude an approximate value of x. Iterating the procedure and taking I= 3s- 2x, we will obtain more accurate values of $f_{\pm}$, f_{ip} and x. The final results of the iterating calculation of ion-pair concentration in the mixed solvent (water 85%+ethanol 5% +propanol 10%) at $25°C$ are summarized in table 4.

Table 3. The values of K$_{IP}$, $f_{\pm}$ f_{IP}, in the mixed solvent at $25°C$

ethanol % by mass	propanol % by mass	$f_{\pm}$	f_{ip}	K_{IP}
0	0	0.3114	0.6143	5.6060
5	10	0.4272	0.6536	6.446
10	10	0.4511	0.6717	6.8602
5	20	0.5012	0.7079	7.2263

Table4. The values of I, $f_{\pm}$, x, for CdF_2 in the mixed solvent (water 85%+ethanol 5% +propanol 10%) at $25°C$

I	$f_{\pm}$	x
0.4638	0.4272	0.04927
0.3653	0.4498	0.05159
0.3606	0.4510	0.05171
0.3604	0.4511	0.05172
0.3604	0.4511	0.05172

In addition the plot of lnK$_{sp(c)}$ versus $I^{1/2}$ in the mixed solvent (water 85%+ethanol 5% +propanol 10%) at $25°C$ is shown in (Fig.1.).

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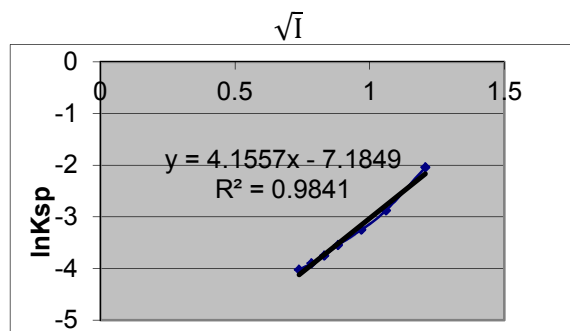
Fig.1. Plot of lnK$_{sp(c)}$ versus $I^{1/2}$ in the mixed solvent (water 85%+ethanol 5% +propanol 10%) at $25°C$.

The intercept of this plot, represents the value of ln K$_{th}$, while K$_{sp(th)}$ is related to the following equilibrium in the considered mixed solvent(water 85%+ethanol 5% +propanol 10%).

$$CdF_{2(s)} \Leftrightarrow Cd^{2+}{}_{(aq)free} + 2F^-{}_{(aq)free}$$
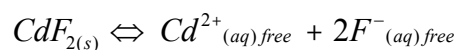
$$K_{sp(th)} = a_{Cd^{2+}_{free}} a^2_{F^-_{free}}$$

In order to calculate the value of x=[ion-pair], we need the value of $f_\pm$. This value can be calculated upon equation (15). To do this we need the value of ionic strength, I. In the first approximation, we set I=3s and calculate the first $f_\pm$ upon equation (15) and insert its value in eq (19) to obtain the first value of x, denoting by x$_1$.

$$CdF_{2(s)} \Leftrightarrow Cd^{2+}{}_{(aq)} + 2F^-{}_{(aq)}$$
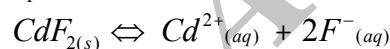
$$K_{sp(th)} = (2s-x)^2(s-x)f_\pm^3 \qquad (18)$$

or

$$[x^3 - 5sx^2 + 8s^2x] + \left[\left(\frac{K_{sp(th)}}{f_\pm^3}\right) - 4s^3\right] = ○ \quad (19)$$

s=solubility of CdF_2 in the satuated solutıon in $(mol.L^{-1})$.

(2s-x)= molarity of free F^- ions
(s-x)= molarity of free Cd^{2+} ions
x= the molarity of ion- pair in the saturated solution at 298K.

In the second step we set I=3s-2x$_1$ and repeat the above calculaition and conclude a new value for x denoting by x$_2$. We repeat this procedure until the difference between two concecutive values of x becomes less than 1% of x.We consider the ultimate value of x as the concentration of ion –pair in the saturated solution of CdF_2 in the mixed solvent (water 85%+ethanol 5% +propanol 10%) at 25°C. The results of the itterating calculations are gathered in table (5).

Table 5. The values of $f_\pm, I, x$ of CdF_2 in the mixed solvent (water 85%+ethanol 5% +propanol 10%) at $25°C$

I	$f_\pm$	x
0/4638	0/4272	0/0877
0/2884	0/4730	0/1001
0/2636	0/4822	0/1017
0/2604	0/5103	0/1017

CONCLUSION

The experimental results (table1) show that the solubility of CdF_2 in the mixed solvent, (water+ ethanol + propanol), decreases with increasing the mass percent of ethanol and propanol. This trend is along with decreasing dielectric constant of the mixed solvent.

In addition the value of K$_{IP}$ increases during decreasing dielectric constant of the mixed solvent. The values of ion-pair concentration, x, in the mixed solvent (water 85%+ethanol 5% + propanol 10%) at $25°C$ were obtained by using Fouss model and the thermodynamic solubility product constant that was obtained by extrapolation method. Comparison of these values showed insignificant difference.

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