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Thermodynamic study of $CdCl_2$ in 2-propanol (5 mass %) + water mixture using potentiometry

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Summary

The potential difference (pd) measurements (E) are reported for galvanic cell without liquid junction: Cd(Hg) (l, satd.)$|$$CdCl_2$($b$) in Z$|$AgCl(s)$|$Ag(s) at different temperatures and various $CdCl_2$ molalities (b) in aqueous mixture of 2-propanol (containing 5 mass % 2-propanol), Z. From these values and using literature data for stability constants of the chlorocadmium complexes, the values of the standard pd of the cell were obtained at each temperature. These values served to calculate the standard thermodynamic quantities for the cell reaction, and also mean molal activity coefficients of $CdCl_2$. The corresponding thermodynamic results are discussed and compared with literature data.

Keywords: thermodynamic properties, cadmium chloride, 2-propanol + water mixed solvent, potentiometry.

Introduction

Potentiometric method using a galvanic cell without liquid junction was found to be an attracting experimental technique for studying the thermodynamic properties of electrolyte solutions in aqua-organic mixed solvents. This paper is an extension of our systematic investigation on thermodynamic properties of $CdCl_2$ in various aqua-organic solvents using potentiometry. Specifically, in previous works by our group, the bahaviour of the $CdCl_2$ has been studied in water mixtures with alcohol co-solvent: containing 10, 30, and 50 mass % 2-propanol (Višić & Mekjavić, 1993) or 2-methylpropan-2-ol (*tert.* butanol) (Tomaš et al., 2000), and also with 5, 10, and 15 mass % 2-butanol (Tomaš et al., 2005).

We have recently published data on the thermodynamic properties of $CdCl_2$ in 2-methylpropan-2-ol (5 mass %) + water mixture (Z) using a flow potentiometric method (Tomaš et al., 2011). Namely, the potential difference (pd) measurements have been carried out on the following galvanic cell:

$$\text{Cd(Hg) (l, satd.)} \,|\, CdCl_2(b) \text{ in Z} \,|\, \text{AgCl(s)} \,|\, \text{Ag(s)} \qquad (1)$$

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in the temperature range (293.15 K to 313.15 K) at 5 K intervals, for different $CdCl_2$ molalities (b).

In this work, analogous investigations were performed in 2-propanol + water mixture of the same content (*ie*., Z = 5 mass % 2-propanol), in order to determine the thermodynamic quantities of the cell reaction, and the stoichiometric mean molal activity coefficients of $CdCl_2$. The results from this study are compared with similar systems.

Within the potentiometric data analysis, the concentrations of all ionic species was calculated (Višić & Mekjavić, 1989) using data for the thermodynamic stability constants of chlorocadmium complexes in water medium, and for 10 mass % 2-propanol (Višić et al., 1993).

Materials and methods

$CdCl_2 \times H_2O$ and 2-propanol were *p.a.* purity (Merck). Before use, 2-propanol and water were distilled. Solvent mixture (Z) and concentrated electrolyte solution in Z (stock solution) were prepared by weight using $CdCl_2 \times H_2O$, water and 2-propanol. The molality ($b_{\mathrm{max.}}$) of the stock solution of $CdCl_2$ in Z was 0.0503 mol kg^{-1}, with salt mass fraction, w = 0.01002. Density of Z was measured using oscillating U-tube densimeter (Anton Paar, model DMA 4500 M) with precision of 1×10^{-5} g cm^{-3} (Bald et al., 2013).

In order to continuously obtain the pd (E_{i}) of the cell (1) at different molalities (b_{i}) of $CdCl_2$, we change electrolyte concentrations by adding a stock solution in Z (mass, m_{i}) to a cell containing an appropriate mass of solvent mixture (m_{Z}). The molality of $CdCl_2$ in the cell (1) after i$^{\mathrm{th}}$ addition (b_{i}) is given by the expression (Zhang et al., 1993):

$$b_{\mathrm{i}} = \frac{\sum_i m_i \times w / M}{m_{\mathrm{Z}} + m_i \times (1 - w)} \tag{2}$$

where M is the molar mass of cadmium chloride.

The preparation of electrodes, description of the cell, and of the equipment for pd measurements, and the measuring procedure itself were explained earlier (Tomaš et al., 2011).

Results and discussion

The potentiometric results (E_{i}) for the cell (1) in 5 mass % 2-propanol (Z) at the different $CdCl_2$ molalities (b_{i}) and at all operating temperatures (T) are compiled in Table 1.

Table 1. Experimental data for cadmium chloride in Z at different temperatures

$10^3\,b$ / mol kg^{-1}	E / V	$10^3\,b$ / mol kg^{-1}	E / V
T = 293.15 K		T = 298.15 K	
4.123	0.77699	4.224	0.77757
7.686	0.75940	7.800	0.76027
10.732	0.75037	10.720	0.75144
13.358	0.74445	13.390	0.74539
15.672	0.74023	15.724	0.74126
17.720	0.73704	17.784	0.73804
19.525	0.73450	19.610	0.73570
21.150	0.73250	21.151	0.73368
22.528	0.73082	22.641	0.73206
23.862	0.72940	23.894	0.73066
25.098	0.72823	25.122	0.72948
26.129	0.72721	26.232	0.72841
27.160	0.72631	27.177	0.72751
28.030	0.72552	28.117	0.72669
28.920	0.72490	28.998	0.72594
T = 303.15 K		T = 308.15 K	
4.161	0.78030	4.193	0.78143
7.699	0.76154	7.730	0.76344
10.755	0.75667	10.732	0.75417
13.382	0.74650	13.399	0.74810
15.684	0.74244	15.664	0.74382
17.730	0.73930	17.674	0.74057
19.530	0.73671	19.545	0.73803
21.107	0.73480	21.170	0.73597
22.559	0.73305	22.633	0.73428
23.878	0.73173	23.943	0.73288
25.049	0.73053	25.146	0.73169
26.175	0.72941	26.245	0.73066
27.194	0.72851	27.241	0.72977
28.100	0.72771	28.162	0.72896
28.953	0.72691	29.010	0.72822

Table 1. (Continued)

$10^3 b$ / mol kg^{-1}	E / V
T = 313.15 K	
4.151	0.77440
7.682	0.76502
10.710	0.75575
13.346	0.74958
15.626	0.74545
17.667	0.74226
19.477	0.73965
21.106	0.73758
22.565	0.73593
23.866	0.73453
25.066	0.73328
26.179	0.73218
27.183	0.73127
28.108	0.73042
28.971	0.72964

The values of E from Table 1 were used to calculate the standard molal pd (E_b°) for the cell reaction:

$$\mathrm{Cd(s)} + 2\ \mathrm{AgCl(s)} \rightleftharpoons 2\ \mathrm{Ag(s)} + \mathrm{Cd^{2+}(Z)} + 2\mathrm{Cl^{-}(Z)} \tag{3}$$

according to the relation,

$$E' = E + \frac{RT}{2F}\ln[(b(\mathrm{Cd}^{2+})/b^{\circ})(b(\mathrm{Cl}^{-})/b^{\circ})^2] - \frac{3RT}{F}\ln(10)\, A_b\,(I/b^{\circ})^{1/2}/(1 + a_0 B_b\,(I/b^{\circ})^{1/2}) - \\ - \frac{3RT}{2F}\ln[1 + M_Z\ \Sigma_x b(\mathrm{X})] = E_b^{\circ} - \frac{3RT}{2F}\ln(10)\, C\, I\, /b^{\circ} \tag{4}$$

This relation was obtained using a combination of the Nernst equation and the Debye-Hückel equation for the mean activity coefficient. Here I denotes ionic strength, and b° = 1 mol kg^{-1}. The following data are needed to solve Eq. (4):

a) a value for the ion-size parameter (a_0); a_0 = 0.45 nm (Višić et al., 1993),
b) the molar mass and mass fraction of water and of 2-propanol; these data are used to determine the mean molar mass (M) of investigated mixed solvent Z,
c) Debye-Hückel constants (A_b, B_b); these constants were calculated using literature data for the relative permittivity, ε_r (Åkerlöf, 1932) and the density, d (from the present study) of the solvent Z: the properties (ε_r, d) at different temperatures are given in Table 2.
d) the equilibrium molalities of all ionic species, given by the term $\Sigma_x b(X)$, as well as the cell pd (E) for each cadmium chloride molality.

Determination of the E_b^o can be performed either by extrapolation of E' from Eq. (4) to zero ionic strength or by the least-squares method. To calculate $b(Cd^{2+})$, $b(Cl^-)$, and b (of the remaining ionic species) for each molality of $CdCl_2$, it is necessary to consider the complexation reaction in investigated mixed solvent Z (Višić & Mekjavić, 1989):

$$Cd^{2+} + nCl^- \rightleftharpoons CdCl_n^{(2-n)+} \qquad (n = 1, 2 \text{ i } 3) \tag{5}$$

Inasmuch as the iterative procedure has been described in detail in our previous papers (Tomaš et al., 2004 and 2011), only a short ouline will be provided here. Namely, for a given cadmium chloride molality, the stoichiometric ionic strength of the solution is first calculated as $I = 3\ b\ d$, and the concentration stability constants, K'_n, for the complex forming reactions (5) are estimated at this ionic strength using next relation:

$$\ln K'_n - \Delta z_n{}^2 A_c (I/c^o)^{1/2}/(1 + B_c a_0 (I/c^o)^{1/2}) = \ln K_n^o + (\ln 10)\Delta C_n I/c^o \tag{6}$$

These stability constants are then served to calculate the concentration of each ionic species. Initial concentrations thus obtained are used to calculate the new ionic strength and stability constant values. The treatment is repeated until a satisfactory constancy of K'_n values is obtained. In Eq. (6) ΔC_n is an empirical constant, c^o = 1 mol dm^{-3}, and $\Delta z_n^2 = (2 - n)^2 - n - 4$, where z is the charge of each ionic species. The parameters ΔC_n and K_n^o (thermodynamic stability constant) were determined experimentally for water medium, and for 10 mass % 2-propanol (Višić et al., 1993). For the present study, ΔC_n and K_n^o, are interpolated from literature data; values at different temperatures for mixed solvent Z are reported in Table 2.

The obtained equlibrium concentrations of all ionic species were then expressed as molalities, and using Eq. (4) the standard molal pd, E_b^{o}, and its standard deviation were determined using the least-squares method. These values are listed in Table 3.
Regression analysis showed that dependence of E_b^{o} on T can be adequately fitted by the second-order polynomial.

$$E_b^{\mathrm{o}}(T) = a + bT + cT^2 \tag{7}$$

Table 2. Parameters of Eq. (6) in Z at different temperatures

T / K	293.15	298.15	303.15	308.15	313.15
K_1^{o}	121	123	128	132	136
K_2^{o}	517	575	610	644	678
K_3^{o}	409	448	448	507	537
ΔC_1	0.192	0.191	0.189	0.187	0.185
ΔC_2	0.375	0.380	0.379	0.379	0.379
ΔC_3	0.477	0.475	0.467	0.459	0.452
ε_{r}	76.74	74.96	73.21	71.50	69.78
d / g cm^{-3}	0.98962	0.98840	0.98692	0.98522	0.98330

Table 3. Standard potential difference (E_b^{o}) of cell (1) in Z at different temperatures

T / K	$E_b^{\mathrm{o}} \pm \sigma(E_b^{\mathrm{o}})$ / V
293.15	0.56840 ± 0.00009
298.15	0.56579 ± 0.00008
303.15	0.56405 ± 0.00016
308.15	0.56149 ± 0.00012
313.15	0.55893 ± 0.00008

The polynomial coefficients a, b and c, obtained by fitting Eq. (7) to the experimental results are presented in Table 4, together with their standard deviations.

Table 4. Adjustable coefficients a, b and c of Eq. (7) in system $CdCl_2$–Z

a / V	0.5157 ± 0.282
$10^4\, b$ / V K^{-1}	7.824 ± 4.32
$10^6\, c$ / V K^{-2}	–2.057 ± 1.75

From the first derivate of Eq. (7), according to relation

$$\Delta_r S^o = \mathrm{d}\, E_b^o / \mathrm{d}T = \; z\, F\, (b + 2\, cT), \quad (z = 2) \tag{8}$$

the standard entropy ($\Delta_r S^o$) of the cell reaction (3) in Z is obtained. The standard Gibbs energy ($\Delta_r G^o$) is calculated according to the expression,

$$\Delta_r G^o = -zFE_b^o \tag{9}$$

while the standard enthalpy ($\Delta_r H^o$) can be calculated from the relationship,

$$\Delta_r H^o = \Delta_r G^o + T\, \Delta_r S^o \tag{10}$$

The standard thermodynamic quantities for the cell reaction (3) in Z at 298.15 K are given in Table 5. The data for water medium are, for comparision, listed in the same table. The deviations were calculated from the standard deviation for E_b^o.

Table 5. Standard thermodynamic quantities for the cell reaction (3) in water medium and solvent Z at 298.15 K

mass %	$\Delta_r G^o$ / kJ mol^{-1}	$\Delta_r H^o$ / kJ mol^{-1}	$\Delta_r S^o$ / J K^{-1} mol^{-1}
0 (Višić & Mekjavić, 1993)	–110.66 ± 0.02	–134 ± 5	–78 ± 10
5 (present study, Z)	–109.18 ± 0.01	–129 ± 13	–65 ± 25

As seen from Table 5 the standard Gibbs energy for both solvents has the negative sign, which proves that the cell reaction (3) is spontaneous. The values for the standard enthalpy and entropy change are also negative. It can be seen that the cell reaction (3) is exothermic and lead to decrease in entropy. It can also be seen that the spontaneity ($\Delta_r G^o$) of reaction (3) decreaces with adding 2-propanol in water. The same was reported for the aqueous mixtures with 5 mass % 2-butanon, 2-butanol, or *t*-butanol (Tomaš et al., 2004, 2005, and 2011).

In this work, the stoichiometric mean molal activity coefficient ($\gamma_\pm$) of cadmium chloride in Z was calculated using the data for E and E_b^o of the cell (see Tables 1 and 3), according to the Nernst equation for the cell reaction (3):

$$E = E_b^o - (RT/2F)\ln\left\{4[(b/b^o)\gamma_\pm]^3\right\} \tag{11}$$

provided that chlorocadmium complexes were not formed in the solution. Table 6 shows the obtained $\gamma_{\pm}$ values of $CdCl_2$ in 5 mass % 2-propanol (Z) at each molality and at different temperatures. Values of $\gamma_{\pm}$ for cadmium chloride in 5 mass% 2-propanol (Z) were not found in literature.

Table 6. Stoichiometric mean molal activity coefficients ($\gamma_{\pm}$) of $CdCl_2$ in Z at different temperatures

	b(CdCl2) / mol kg^{-1}						
T / K	0.003	0.005	0.007	0.009	0.010	0.015	0.020
293.15	0.697	0.599	0.542	0.503	0.487	0.432	0.397
298.15	0.691	0.594	0.535	0.495	0.479	0.423	0.387
303.15	0.678	0.583	0.527	0.489	0.474	0.419	0.381
308.15	0.672	0.577	0.525	0.485	0.469	0.413	0.377
313.15	0.665	0.570	0.520	0.479	0.462	0.410	0.368

According to the values given in Table 6, activity coefficients decrease with increasing $CdCl_2$ molality, as well as decrease with increasing tempertaure. This result is expected from Debye-Hückel theory. A corresponding behaviour has been found in our earlier studies of the same electrolyte in aqueous ketone (Tomaš et al., 2004) and aqueous alcohols (Tomaš et al., 2005 and 2011) at the same mass fractions. When comparing the $\gamma_{\pm}$ values from present study with those for water medium (Višić & Mekjavić, 1993), it can be seen that these values are higher in water. Obviously, this is related to the degree of complexation. Analogy was established with aqueous mixtures with 5 mass % 2-butanone, 2-butanol, and *t*-butanol (Tomaš et al., 2004, 2005, and 2011). Furthermore, values of $\gamma_{\pm}$ for cadmium chloride at the same mass fraction (Z = 5 mass %) are similar; certain differences are due to influence of relative permittivity and nature of organic component in the mixed solvent.

Conclusions

The present investigation of thermodynamic properties of cadmium chloride in aqueous mixture with 5 mass % 2-propanol (Z) can be summarised as following: For the present system $CdCl_2$ in Z, was determined standard molal potential difference for the cell reaction at different temperatures: this value decreases with an increase in the temperature. At constant temperature, the mean molal activity coefficient of cadmium chloride decreases with an increase in the molality of solution. At fixed molality, the mean molal activity coefficient of cadmium chloride decreases with an increase the temperature. The cell reaction is spontaneous, exothermic and leads to reduced in entropy.

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