POTENTIOMETRIC STUDY OF THE STABILITY CONSTANTS OF CADMIUM CHLORIDE COMPLEXES FROM 1 TO 1000 BAR AT 25°C

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Potentiometric measurements have been performed using an isothermal cell with liquid junction. A solid contact Cd-selective electrode ("Niko-analit") and a specially designed reference electrode [1] were used. Measurements were performed in solutions of constant $Cd(NO_3)_2$ concentration (0.01*m*) and variable concentration of KCl (0, 0.025, 0.53 and 1.4*m*) at 25°C and pressure from 1 to 1000 bars.

The electrodes were calibrated using Cd $(NO_3)_2$ solutions at pressures of 1-1000 bars and 25°C. At all pressures, the calibration data (*E*, vs. pCd) define a straight line close to theoretical Nernstian slope (30±0.5mV/pCd). E^o decreases by 10±0.5mV with a pressure increase from 1 to 1000 bar (Fig.1).

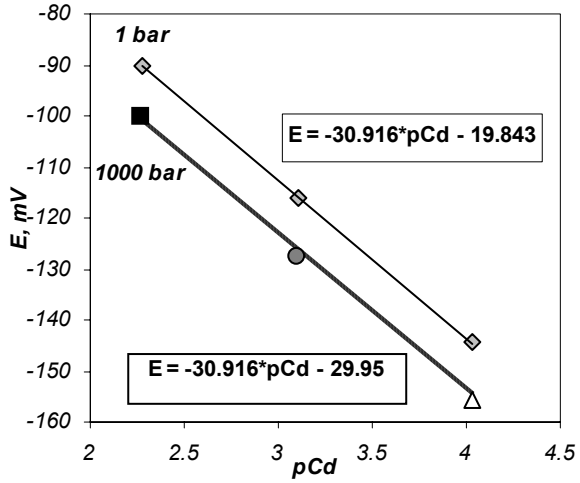

Fig.1. Calibration curves for the Cd-selective electrode for 1 and 1000 bar pressures at 25°C.

In order to verify the electrode system, a 0.01m $Cd(NO_3)_2$ solution was first titrated with a KCl solution and cadmium chloride stability constants (β_1, β_2, β_3, β_4) were determined. The obtained values of stability constants are in a good agreement with previous estimates (Tab. 1.).

Table1. Calculated stepwise constants of cadmium chloride complexes at 25°C and 1 bar: comparison with the Critical Database and the SLOP'98 ($CdCl_n^{2-n} + Cl^- = CdCl_{n+1}^{1-n}$)

	lgK_n			
	$CdCl^+$	$CdCl_2^0$	$CdCl_3^-$	$CdCl4_2^-$
Critical Database	1,98±0,03	0,62±0,1	0,2±0,15	–
SLOP'98 and Sverjnsky, 1997 [4]	1.97	0.61	-0.18	-0.93
This study Bazarkina, Zotov	1,95±0,05	0,47±0,1	-0,013±0,3	-0,83±0,5

Experimental data obtained at 25°C and 1-1000 bar pressures are given in Table 2. Experimental results are also given for the corrected e.m.f. values, $\Delta E_{corrected} = \Delta E_{measured} - \Delta E_{calibration}$.

Table2. Experimental data at 25^{0}C and 1 – 1000 bar

P, bar	mCd(NO$_3$)$_2$=0.01 mol						
	$\Delta E_{measured}$, mV ($\Delta E_{measured}=E_p-E_{p=1\ bar}$)			$\Delta E_{calibration}$, mV	$\Delta E_{corrected}$, mV $\Delta E_{corrected}=\Delta E_{measured}-\Delta E_{calibration}$		
	*m*KCl				*m*KCl		
	0.025 *mol*	0.53 *mol*	1.4 *mol*		0.025 *mol*	0.53 *mol*	1.4 *mol*
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
200	-3.2	-2.1	-1.5	-2.2	-1.0	0.1	0.7
500	-5.2	-4.7	-3.6	-5.4	0.2	0.7	1.8
700	-7.1	-6.2	-5.0	-7.6	0.5	1.4	2.6
900	-9.7	-7.6	-6.3	-9.7	0.0	2.1	3.4
1000	-10.8	-8.4	-7.0	-10.8	0.0	2.5	3.9

Subsequent interpretation of the experimental results was based on the correlation of nonsolvation contribution to $CdCl_n$ partial molar volumes with the number of ligands, Cl^-, in the comlex [2].

The corresponding equilibrium calculating was carried out using the GIBBS computer code [3] and Slop'98 database.

As a result, estimated values of partial molar volumes of cadmium chloride complexes and their HKF parameters (a_1 - a_4) were determined: V^o ($CdCl^+$) = 8.11, V^o ($CdCl_{2\ aq}$) = 31.88, V^o ($CdCl_3^-$) = 50.52, V^o ($CdCl_4^{2-}$) =68.58 cm^3 mol^{-1}. All the stability constants of cadmium chloride complexes, lgβ_n, show very weak pressure dependencies. Thus, lg β_n decreases by 0.06-0.13 as pressure rises from 1 to 1000 bar (Fig. 2).

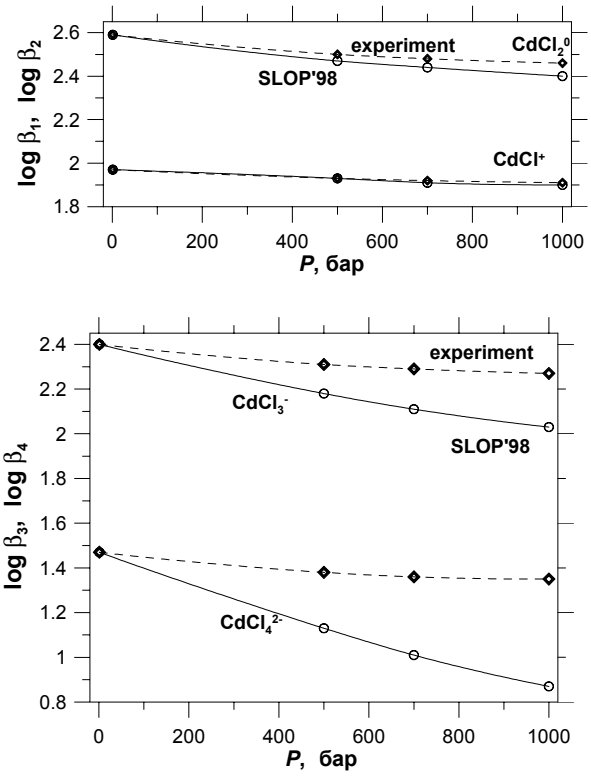

Fig.2. Logarithms of stability constants for cadmium chloride complexes as a function of pressure (1 – 1000) bar at 25^{0}C logβ_n= Cd^{2+} + nCl^- = $CdCl_n^{2-n}$

This research was supported by the Program of Leading Scientific Schools (6722.2006.5).

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Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(24)'2006
ISSN 1819 – 6586
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2006
URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2006/informbul-1_2006/hydroterm-2e.pdf

Published on July, 1, 2006