Thermodynamics of the Cell: Cd(Hg)(l,satd.) | CdCl$_2$ (m) | AgCl | Ag in (10, 30 and 50 Mass per Cent) Acetone-Water Mixtures

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The e.m.f of the cell: Cd(Hg)(l,satd.) | CdCl$_2$ (m), x mass per cent acetone-water mixture | AgCl(s) | Ag(s) with x = 10, 30 and 50 was measured in the temperature range from 293.15 to 313.15 K at 5 K intervals and in the molality range for CdCl$_2$ from 0.002 to 0.02 mol kg^{-1}. From the obtained values and using literature data for stability constants of cadmium chloride complexes, the standard e.m.f of the cell (E_m°) was determined for each temperature value. The values for E_m° were used to calculate: a) the standard thermodynamic quantities (ΔG°, ΔH° and ΔS°) for the cell reaction, b) the mean activity coefficients of CdCl$_2$, and c) the standard thermodynamic quantities ($\Delta_t G^\circ$, $\Delta_t H^\circ$ and $\Delta_t S^\circ$) for transfer of CdCl$_2$ from water to the investigated acetone-water mixtures. The values obtained were compared with analogous literature data for 2-propanol-water mixtures; the values obtained for $\Delta_t H^\circ$ and $\Delta_t S^\circ$ were also compared with analogous literature data for transfer of HBr electrolyte to the acetone-water and 2-propanol-water mixtures. The structure of these mixtures is discussed in view of the obtained values.

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INTRODUCTION

Investigations with the cell: Cd(Hg)(l,satd.) | CdCl$_2$ (m) | AgCl(s) | Ag(s) were performed in mixtures of water-methanol (to 100 mass per cent methanol),[1] water-ethanol (to 100 mass per cent ethanol),[2] and water-methanol (to 40 mass per cent methanol)[3] with unsaturated Cd-amalgam. Since CdCl$_2$ produces complex ions in solutions, in all these works the standard e.m.f. ($E°$) of the cell was calculated from the measured e.m.f. values on the assumption that the only complex present was [CdCl]$^+$; the same was assumed in calculations concerning the water solution.[1-5] In our work, however, in 2-propanol-water (to 50 mass per cent 2-propanol) mixtures[6] with saturated Cd-amalgam, it was shown that in mixtures with a lower dielectric constant, where the degree of complexation is higher, to calculate $E°$ the procedure should be used that takes into consideration the presence of all the complex ions.[7,8]

In this work the results of investigations with the mentioned cell in acetone-water mixtures are given, and in the processing of the measured e.m.f. literature data are used for the stability constants of cadmium chloride complexes in these solvents.[9] The aim of this work is to establish, by comparison with 2-propanol-water mixtures, the influence of the organic component in the solvent on the standard thermodynamic quantities of the cell reaction, on the values of the mean activity coefficients of cadmium chloride as well as on the standard thermodynamic quantities of cadmium chloride transfer from water to the mixed solvents.

The e.m.f. of the cell was measured in 10, 30 and 50 mass per cent acetone-water mixtures for ten CdCl$_2$ concentrations in the range from 0.002 to 0.02 mol kg^{-1} at 293.15 to 313.15 K at 5 K intervals.

EXPERIMENTAL

The CdCl$_2$ solutions of different molalities were prepared by weighing an aqueous stock solution containing 0.025 mol kg^{-1}, redistilled water, and acetone, distilled before use. The CdCl$_2$ and acetone were of *p.a.* purity (»Kemika«). The molality of each solution was accurate within ± 0.02 per cent.

The preparation of the saturated Cd(Hg) and AgCl | Ag electrode, a description of the cell and of the e.m.f. measuring equipment, as well as the measuring procedure were previously described.[7]

The average deviation of a single measurement from its mean value (obtained as earlier[7]) for 10 mass per cent acetone amounts to ± 0.05 mV, for 30 mass per cent it amounts to ± 0.07 mV, while for 50 mass per cent acetone it is ± 0.06 mV.

RESULTS AND DISCUSSION

The mean values for the measured e.m.f. of the cell are presented in Table I.

TABLE I

Electromotive force (E/V) of the cell: Cd(Hg)(l,satd.) | CdCl$_2$ (m), in x mass per cent acetone-water | AgCl | Ag at different temperatures

m mol kg^{-1}	E/V				
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
			$x = 10$		
0.00200	0.79374	0.79542	0.79749	0.79935	0.80104
0.00300	0.78148	0.78302	0.78491	0.78654	0.78810
0.00400	0.77296	0.77453	0.77614	0.77783	0.77928
0.00500	0.76644	0.76803	0.76963	0.77104	0.77242
0.00600	0.76152	0.76302	0.76448	0.76580	0.76714
0.00700	0.75730	0.75878	0.76019	0.76143	0.76265
0.00800	0.75358	0.75499	0.75642	0.75754	0.75874
0.01000	0.74768	0.74903	0.75035	0.75153	0.75265
0.01500	0.73728	0.73844	0.73963	0.74061	0.74167
0.02000	0.73010	0.73116	0.73221	0.73323	0.73420
			$x = 30$		
0.00200	0.76791	0.76947	0.77091	0.77215	0.77350
0.00300	0.75674	0.75816	0.75945	0.76063	0.76185
0.00400	0.74915	0.75040	0.75169	0.75264	0.75377
0.00500	0.74317	0.74427	0.74557	0.74689	0.74810
0.00600	0.73851	0.73961	0.74087	0.74174	0.74274
0.00700	0.73475	0.73583	0.73695	0.73792	0.73900
0.00800	0.73154	0.73251	0.73363	0.73464	0.73568
0.01000	0.72599	0.72705	0.72807	0.72925	0.73006
0.01500	0.71662	0.71749	0.71851	0.71929	0.72013
0.02000	0.71014	0.71106	0.71189	0.71264	0.71342
			$x = 50$		
0.00200	0.73802	0.73909	0.74019	0.74110	0.74207
0.00300	0.72827	0.72915	0.73032	0.73104	0.73202
0.00400	0.72192	0.72257	0.72384	0.72446	0.72545
0.00500	0.71691	0.71772	0.71865	0.71911	0.72004
0.00600	0.71334	0.71402	0.71503	0.71568	0.71640
0.00700	0.70992	0.71064	0.71150	0.71215	0.71291
0.00800	0.70734	0.70804	0.70899	0.70954	0.71025
0.01000	0.70258	0.70329	0.70429	0.70487	0.70561
0.01500	0.69497	0.69558	0.69641	0.69709	0.69787
0.02000	0.69000	0.69101	0.69168	0.69200	0.69280

These values were used to calculate the E_m° of the cell according to the relation[7]

$$E' = E + (RT/2F) \ln [(m(Cd^{2+})/m^\circ) (m(Cl^-)/m^\circ)^2] -$$

$$- (3RT/F)AI^{1/2}/(1 + BaI^{1/2}) - (3RT/2F) \ln [1 + M\Sigma_x m(X)] = \qquad (1)$$

$$= E_m^\circ - (3RT/2F) C (I/m^\circ)$$

which was obtained by using the Nernst equation for the cell reaction

$$Cd(s) + 2AgCl(s) = 2 Ag(s) + (Cd^{2+} + 2 Cl^-) . \qquad (2)$$

In relation (1), E denotes the measured e.m.f. for a particular $CdCl_2$ molality, $m(X)$ denotes the molality of the ion X, m° is 1 mol kg^{-1}, A and B are Debye-Hückel constants calculated by using the values of the dielectric constants of the solvents from literature,[10] I denotes the ionic strength of the solution, a is the ion-size parameter (taken to be 0.45 nm), M is the molar mass of the solvent, $\Sigma_X m(X)$ is the total molality of all ionic species, and C is the empirical constant.

To calculate the $m(Cd^{2+})$ and $m(Cl^-)$ for a particular $CdCl_2$ molality, the values from literature[9] were taken of the thermodynamic stability constants (K_n°) for the reactions

$$Cd^{2+} + n \, Cl^- = [CdCl_n]^{(2-n)+}, \qquad (n = 1, 2, 3 \text{ and } 4). \qquad (3)$$
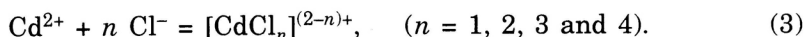
This constant can be given by the following relation

$$K_n^\circ = K_n' \, K_y \qquad (4)$$

where K_n' is the concentration stability constant, *i.e.*

$$K_n' = (c([CdCl_n]^{(2-n)+})/c^\circ / [(c(Cd^{2+})/c^\circ) (c(Cl^-)/c^\circ)^n] , \qquad (5)$$

and

$$K_y = [y([CdCl_n]^{(2-n)+})] / \{[y(Cd^{2+})] [y(Cl^-)]^n\} . \qquad (6)$$

In these expressions $c(X)$ is the concentration of ion X, c° denotes 1 mol dm^{-3}, $y(X)$ is the activity coefficient of ion X. By applying the Debye-Hückel

equation for the activity coefficient of the individual ion, the following K_n' dependence on the solution ionic strength is obtained

$$\ln K_n' = \ln K_n^\circ + \Delta z^2 A I^{1/2}/(1 + B a I^{1/2}) + (\ln 10)\Delta C_n I/c^\circ . \qquad (7)$$

In Eq. 7, $\Delta z^2 = z^2([CdCl_n]^{(2-n)+}) - z^2(Cd^{2+}) - nz^2(Cl^-)$, $-\Delta C_n = C([CdCl_n]^{(2-n)+}) - C(Cd^{2+}) - nC(Cl^-)$. In these expressions, z and C are the charge and the empirical constant for the particular ion, while the other symbols have already been mentioned. The values for ΔC_n are also from Ref. 9.

The values for K_n° and ΔC_n at 298.15 and 313.15 K for 10 mass per cent acetone, and at 298.15 and 308.15 K for 30 and 50 mass per cent acetone were taken directly from Ref. 9, while at other temperatures the K_n° values were determined from the plot $\ln K_n^\circ$ against T^{-1}, and for ΔC_n by interpolation.

The calculation procedure was as follows: starting from the ionic strength obtained from the analytical concentration of Cd^{2+} and Cl^- ions, the K_n' values were calculated first, then the concentration of ion species in the solution, then the new ionic strength and the new K_n' values. This procedure was continued untill the ionic strength was reached at which the K_n' values became constant. A detailed description of this procedure is found in works.[6,7,] The data for the solvent density required in calculating the initial ionic strength were taken from literature.[11] The number of iterations needed to reach constant K_n' values depended on the dielectric constant of the solvent (D) and on the $CdCl_2$ molality, and it was between 4 to 5 iterations with lower molalities and a higher D, to 8–9 iterations needed with higher molalities and a lower D.

From the final ionic strength, the equilibrium concentrations for all the ionic species are expressed as molalities, and by using equation (1) the E_m° of the cell and its standard deviation are calculated by the least-squares method. These values are given in Table II.

The E_m° values from Table II can be expressed in the following equations for the temperature range from 293.15 to 313.15 K:

$$E_m^\circ \ (x = 10)/V = 0.77840 - 98.06 \times 10^{-5} \ T/K + 82.86 \times 10^{-8} \ T^2/K^2 , \qquad (8)$$

$$E_m^\circ \ (x = 30)/V = 0.35732 + 175.44 \times 10^{-5} \ T/K - 400.00 \times 10^{-8} \ T^2/K^2 , \qquad (9)$$

$$E_m^\circ \ (x = 50)/V = 0.89598 - 161.30 \times 10^{-5} \ T/K + 68.57 \times 10^{-8} \ T^2/K^2 . \qquad (10)$$

Standard thermodynamic quantities for the cell reaction (2) were determined from the E_m° and its temperature coefficient (dE_m°/dT) derived from Eqs. (8) to (10). The values for 298.15 K are found in Table III together with the values for water solution from Ref. 6. The values of deviations were calculated from the standard E_m° deviation.

TABLE II

Standard e.m.f. of the cell: Cd(Hg)(l,satd.) | CdCl$_2$(m) in x mass per cent acetone-water | AgCl | Ag at different temperatures

T/K	E_m°/V	$s(E_m^\circ)$/mV	E_m°/V	$s(E_m^\circ)$/mV	E_m°/V	$s(E_m^\circ)$/mV
	x = 10		x = 30		x = 50	
293.15	0.56221	0.08	0.52800	0.10	0.48213	0.10
298.15	0.55954	0.04	0.52462	0.15	0.47585	0.12
303.15	0.55739	0.06	0.52143	0.12	0.47024	0.10
308.15	0.55493	0.10	0.51850	0.10	0.46397	0.13
313.15	0.55256	0.09	0.51429	0.13	0.45814	0.09

The values for ΔG° indicate that the extent of reaction (2) decreases with increasing the acetone content in the solvent, i.e. with decreasing the dielectric constant. The same was found when dealing with 2-propanol-water mixtures.[6] From the data obtained for ΔH° it is seen that there is a continuous increase in the reaction exothermic character as the acetone content in the solvent is increased, while for ΔS° there is a continuous decrease. In 2-propanol-water mixtures,[6] however, there is a certain discontinuity for ΔH°, namely, the reaction exothermity decreases up to 30 mass per cent 2-propanol, after which it is increased, while ΔS° only from 10 mass per cent 2-propanol begins to decrease with an increasse in the 2-propanol content. It is obvious that this difference is conditioned by the character of the organic component in the solvent.

The stoichiometric activity coefficients ($\gamma_\pm$) of cadmium chloride for individual molalities are calculated according to the Nernst equation

$$E = E_m^\circ - (RT/2F) \ln \{4[(m/m^\circ)\gamma_\pm]^3\} , \tag{11}$$

TABLE III

Standard thermodynamic quantities for the cell reaction (2) in x mass per cent acetone-water mixtures at 298.15 K

x	ΔG°/kJ mol^{-1}	ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}
0[a]	−110.66 ± 0.02	−133.95 ± 0.07	−78.1 ± 0.2
10	−107.98 ± 0.01	−135.97 ± 0.05	−93.9 ± 0.1
30	−101.24 ± 0.03	−137.53 ± 0.09	−121.7 ± 0.2
50	−91.83 ± 0.03	−161.11 ± 0.13	−232.4 ± 0.4

[a] Values from Ref. 6.

for the cell reaction (2), provided that cadmium complexes do not occur in the solution. The values of E for different molalities were taken from Table I, while E_m° was taken from Table II. The values for 298.15 K are found in Table IV.

TABLE IV

Mean activity coefficients $\gamma_\pm$ of $CdCl_2$ at different molalities in x mass per cent acetone-water mixtures at 298.15 K

$x/\%$	$m/\text{mol kg}^{-1}$					
	0.002	0.005	0.007	0.01	0.015	0.02
10	0.715	0.554	0.505	0.457	0.409	0.377
30	0.567	0.414	0.369	0.327	0.284	0.258
50	0.354	0.233	0.200	0.170	0.141	0.123

The obtained values are in agreement with the Debye-Hückel theory; namely, the $\gamma_\pm$ for each solvent decreases with an increase in the $CdCl_2$ molality, and for each molality with an increased acetone content in the solvent, *i.e.* with a decrease of its dielectric constant.

Figure 1 shows the dependence of $\gamma_\pm$ on the dielectric constant for the solutions 0.002 and 0.02 mol kg^{-1} $CdCl_2$ in the mixtures of acetone-water, 2-propanol-water,[6] and for the water solution.[6]

It can be seen from the plots that the stoichiometric activity coefficients at the same dielectric constant are lower in the acetone-water mixtures than in the 2-propanol-water ones; this points to the specific influence of the organic component in the solvent and is caused by a different degree of complexation in these two mixed solvents.[9]

The E_m° values from Table II make it possible to calculate the standard Gibbs free energy for the transfer process

$$CdCl_2 \text{ (in } H_2O) = CdCl_2 \text{ (in } x \text{ mass per cent acetone)} \qquad (12)$$
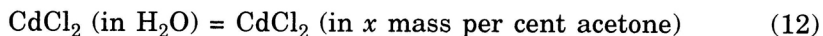
according to the expression

$$\Delta_t G^\circ = 2F[(E_x^\circ)_w - (E_x^\circ)_s] \qquad (13)$$

where $(E_x^\circ)_w$ and $(E_x^\circ)_s$ denote the standard e.m.f. of the cell in aqueous solution and in a mixed solvent on a mole-fraction scale calculated from E_m°
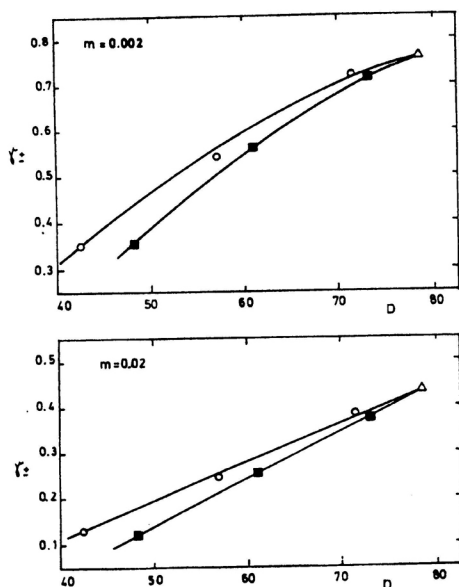
Figure 1. Dependence of $\gamma_\pm$ on the dielectric constant of solvents: acetone-water (■), 2-propanol-water (o)(Ref. 6) and aqueous solution (Δ)(Ref. 6) for m = 0.002 and 0.02 mol kg^{-1} CdCl$_2$.

by using the known relation.[12] For the temparature range from 293.15 to 313.15 K, the following equations were obtained:

$$\Delta_t G^\circ \ (x = 10)/\mathrm{J\ mol^{-1}} = -27502 + 184.87 \ T/\mathrm{K} - 28.67 \times 10^{-2} \ T^2/\mathrm{K^2} \ , \quad (14)$$

$$\Delta_t G^\circ \ (x = 30)/\mathrm{J\ mol^{-1}} = 53217 - 343.47 \ T/\mathrm{K} + 63.96 \times 10^{-2} \ T^2/\mathrm{K^2} \ , \quad (15)$$

$$\Delta_t G^\circ \ (x = 50)/\mathrm{J\ mol^{-1}} = -49712 + 294.87 \ T/\mathrm{K} - 25.36 \times 10^{-2} \ T^2/\mathrm{K^2} \ . \quad (16)$$

These expressions served to derive the temperature dependence of transfer entropy ($\Delta_t S^\circ$), and then of the transfer enthalpy ($\Delta_t H^\circ$) by using the known relations. The values for 298.15 K are given in Table V. The deviations were calculated from standard deviations for E_m° in a mixed solvent and in an aqueous solution.

The values for $\Delta_t G^\circ$ of the transfer of CdCl$_2$ from water to a mixed solvent are positive, the more so the higher is the content of acetone in it, which was also established for the transfer to 2-propanol-water mixtures.[6]

The values for $\Delta_t H°$ and $\Delta_t S°$ are negative and decrease continually with an increase in the acetone content of the solvent. With 2-propanol-water mixtures,[6] however, it was found that the transfer to the solvent with a lower 2-propanol content is accompanied by an increase in enthalpy and entropy, while the transfer to the solvents with a higher 2-propanol content is followed by their decrease.

TABLE V

Standard thermodynamic quantities for the transfer of $CdCl_2$ from water to acetone-water mixtures containing x mass per cent of acetone at 298.15 K

x	$\Delta_t G°/kJ\ mol^{-1}$	$\Delta_t H°/kJ\ mol^{-1}$	$\Delta_t S°/J\ K^{-1}\ mol^{-1}$
10	2.13 ± 0.03	-2.02 ± 0.08	-13.9 ± 0.2
30	7.67 ± 0.04	-3.63 ± 0.10	-37.9 ± 0.2
50	15.66 ± 0.04	-27.17 ± 0.12	-143.7 ± 0.3

It should be noted that an analogous observation was made for $\Delta_t H°$ and $\Delta_t S°$ with the transfer of HBr electrolyte from water to 2-propanol-water mixtures,[13,14] and acetone-water mixtures[15,16] respectively, and which was attributed to the structure of these solvents. According to Kundu et al.,[17] the processes that create structure are exothermic and are accompanied by decreased entropy whereas the processes which destroy structure are endothermic and are accompanied by increased entropy. As for the transfer to the mixtures with smaller proportions of 2-propanol the $\Delta_t H°$ and $\Delta_t S°$ values are positive, it follows that ions break more structure in the mixed solvents than in water, i.e. lower amounts of added 2-propanol promote the three-dimensional structure of water. However, with the transfer to the mixtures with a higher 2-propanol content, as well as to all investigated acetone-water mixtures, where $\Delta_t H°$ and $\Delta_t S°$ values are negative, the ions break more structure in water than in these mixtures. It may be concluded, accordingly, that the same insight into the structural changes accompanying the transfer from water to 2-propanol-water or acetone-water mixtures can be obtained by using the electrolyte of type 1–1 or 2–1.

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SAŽETAK

Termodinamika članka: Cd(Hg)(l, zas.) | CdCl$_2$ (m) | AgCl | Ag u 10, 30 i 50%-tnoj smjesi aceton-voda

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Mjerena je EMS članka: Cd(Hg)(l, zas.) | CdCl$_2$ (m), smjesa aceton-voda | AgCl(s) | Ag(s) (w = 10%, 30%, 50%) u temperaturnom području (293,15...313,15) K u intervalima od 5 K, u području molalnosti CdCl$_2$ (0,002...0,02) mol kg^{-1}. Iz tih vrijednosti, uz uporabu literaturnih podataka za konstante stabilnosti kloro-kompleksa Cd određene su za pojedine temperature standardne EMS članka (E_m°). Te su vrijednosti uporabljene za izračunavanje: a) standardnih reakcijskih prirasta ($\Delta_r G^\circ$, $\Delta_r H^\circ$ i $\Delta_r S^\circ$) za reakciju članka, b) prosječnih koeficijenata aktiviteta CdCl$_2$ i c) standardnih termodinamičkih veličina ($\Delta_p G^\circ$, $\Delta_p H^\circ$ i $\Delta_p S^\circ$) za prijenos CdCl$_2$ iz vode u proučavana miješana otapala. Dobivene vrijednosti uspoređene su s vrijednostima za smjese 2-propanol-voda, a vrijednosti za $\Delta_p H^\circ$ i $\Delta_p S^\circ$ također su uspoređene s onima za prijenos elektrolita HBr u smjese aceton-voda i 2-propanol-voda. Te su vrijednosti omogućile raspravu o strukturi tih smjesa.