CROATICA CHEMICA ACTA CCACAA **73** (2) 423–433 (2000)

ISSN-0011-1643
CCA-2656
Original Scientific Paper

Thermodynamics of Cadmium Chloride in *t*-Butanol – Water Mixtures ($w_{t\text{-BuOH}}$ = 10%, 30%, and 50%) from Electromotive Force Measurements

Renato Tomaš,[a] *Marija Višić,*[b] *and Ivica Mekjavić*[a,*]

[a] *Department of Physical Chemistry, Faculty of Chemical Technology, University of Split, Teslina 10, 21000 Split, Croatia*

[b] *Faculty of Natural Sciences and Arts, University of Split, Teslina 12, 21000 Split, Croatia*

Received February 11, 1999; revised October 18, 1999; accepted October 25, 1999

The e.m.f. of the cell: Cd(Hg)(l, satd.) | $CdCl_2$ (m) in a mixture of *t*-butanol – water | AgCl | Ag with 10, 30 and 50 mass per cent alcohol was measured in the temperature range 293.15–313.15 K at 5 K intervals and in the molality range $CdCl_2$ 0.002–0.02 mol kg^{-1}. From these values and using literature data for stability constants of the Cd chloride complexes, the values of the standard e.m.f. of the cell (E_m°) were obtained at each temperature. These values served to calculate the standard thermodynamic quantities ($\Delta_r G^\circ$, $\Delta_r H^\circ$ and $\Delta_r S^\circ$) for the cell reaction, the mean activity coefficients of $CdCl_2$, and also the standard thermodynamic quantities ($\Delta_t G^\circ$, $\Delta_t H^\circ$ and $\Delta_t S^\circ$) for $CdCl_2$ transfer from water to the investigated mixed solvents. All of the obtained values were compared with the values for 2-propanol – water and acetone – water mixtures; the values for $\Delta_t H^\circ$ and $\Delta_t S^\circ$ were also compared with those obtained for the transfer of electrolytes KCl, KBr and KI in the *t*-butanol – water mixtures. The values for enthalpy and entropy of the transfer provided an insight into the structure of the *t*-butanol – water mixtures.

Key words: potentiometry, cadmium chloride, *t*-butanol-water mixtures, thermodynamic quantities, activity coefficients

---

[*] Author to whom correspondence should be addressed.

INTRODUCTION

In earlier works, we investigated the e.m.f. of Cd(Hg)(l, satd.) | $CdCl_2$ (m) |AgCl | Ag cell in aqueous medium,[1] in 2-propanol – water mixtures (with 10, 30 and 50 mass per cent),[2] and also in acetone – water mixtures of the same contents.[3] This made it possible to determine the thermodynamic quantities of the cell reaction, the stoichiometric activity coefficients of cadmium chloride, and the thermodynamic quantities of $CdCl_2$ transfer from water into the mixed solvents. By comparing the obtained values, we established the influence of the organic component in the mixed solvent on these quantities, and based on thermodynamic quantities of the transfer, we gained an insight into the structure of the mixed solvents.

In this work, analogous investigations were performed in *t*-butanol – water mixtures of the same contents also for the purpose of establishing the effect of organic component on the cited thermodynamic quantities, and particularly in order to determine the expected similarity in thermodynamic quantities of transfer with 2-propanol – water mixtures.

E.m.f. measurements of the investigated cell were carried out in the temperature range from 293.15 to 313.15 K at 5 K intervals and at the molalities of $CdCl_2$ from 0.002 to 0.02 mol kg^{-1}.

To calculate the standard e.m.f. of the cell, we used the method that takes into consideration the presence of all the complex ions in the solution,[1] and for this purpose literature data were taken for the stability constants of Cd-chloride complexes in these mixtures.[4]

EXPERIMENTAL

The $CdCl_2$ solutions of different molalities were prepared as before.[2]

The preparation of electrodes, description of the cell and of the equipment for e.m.f. measurements, and the measuring procedure itself were explained earlier.[1]

The average deviation of each measurement from their mean value (obtained as earlier)[1] is ±0.07 mV.

RESULTS AND DISCUSSION

Table I presents the mean values of e.m.f. for the investigated cell.

These values serve to determine the standard e.m.f. (E_m°) of the cell at different temperatures, which in turn makes it possible to obtain the cited thermodynamic quantities.

TABLE I

Electromotive force (E/V) of the cell: Cd(Hg) (l, satd.) | $CdCl_2$ (m) in t-butanol – water mixtures ($w_{t\text{-BuOH}}$ = 10%, 30%, 50%) | 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
			w = 10%		
0.0020	0.79053	0.79304	0.79535	0.79724	0.79923
0.0030	0.77822	0.78063	0.78261	0.78433	0.78609
0.0040	0.77008	0.77236	0.77422	0.77579	0.77747
0.0050	0.76400	0.76600	0.76776	0.76942	0.77103
0.0060	0.75878	0.76060	0.76255	0.76401	0.76554
0.0070	0.75449	0.75614	0.75784	0.75925	0.76078
0.0080	0.75040	0.75224	0.75420	0.75557	0.75711
0.0100	0.74487	0.74652	0.74803	0.74937	0.75082
0.0150	0.73465	0.73605	0.73744	0.73863	0.73986
0.0200	0.72764	0.72906	0.73035	0.73148	0.73251
			w = 30%		
0.0020	0.76427	0.76697	0.76959	0.77195	0.77403
0.0030	0.75351	0.75630	0.75853	0.76057	0.76239
0.0040	0.74596	0.74802	0.75057	0.75252	0.75428
0.0050	0.74021	0.74278	0.74495	0.74625	0.74812
0.0060	0.73551	0.73795	0.74004	0.74176	0.74353
0.0070	0.73169	0.73409	0.73614	0.73792	0.73962
0.0080	0.72834	0.73062	0.73262	0.73454	0.73615
0.0100	0.72303	0.72526	0.72703	0.72909	0.73081
0.0150	0.71390	0.71599	0.71777	0.71922	0.72081
0.0200	0.70744	0.70936	0.71113	0.71250	0.71387
			w = 50%		
0.0020	0.73910	0.74127	0.74348	0.74530	0.74741
0.0030	0.72935	0.73126	0.73308	0.73471	0.73621
0.0040	0.72321	0.72514	0.72690	0.72835	0.72979
0.0050	0.71822	0.72000	0.72164	0.72303	0.72437
0.0060	0.71419	0.71610	0.71772	0.71905	0.72048
0.0070	0.71108	0.71281	0.71427	0.71554	0.71693
0.0080	0.70818	0.70980	0.71143	0.71266	0.71406
0.0100	0.70343	0.70508	0.70663	0.70781	0.70914
0.0150	0.69526	0.69684	0.69829	0.69943	0.70075
0.0200	0.68965	0.69119	0.69257	0.69369	0.69476

The procedure itself is carried out using the Nernst equation applied to the cell reaction

$$Cd(s) + 2\,AgCl(s) = 2\,Ag(s) + Cd^{2+}(aq + t\text{-BuOH}) + 2\,Cl^{-}(aq + t\text{-BuOH}), \quad (1)$$

which in the final form is given by[1]

$$E' = E + (RT/2F)\ \ln\ [(m(\mathrm{Cd}^{2+})/m^{\mathrm{o}})(m(\mathrm{Cl}^{-})/m^{\mathrm{o}})^2] - \\ -(3RT/F)AI^{1/2}/(1 + BaI^{1/2}) - (3RT/2F)\ \ln\ [1 + M\Sigma_{\mathrm{x}}m(\mathrm{X})] = \\ = E_m^{\mathrm{o}} - (3RT/2F)\ C\ (I/m^{\mathrm{o}}). \tag{2}$$

In relation (2) E denotes the e.m.f. of the cell for each molality of $\mathrm{CdCl_2}$, $m(\mathrm{Cd}^{2+})$ and $m(\mathrm{Cl}^-)$ are the molalities of ion Cd^{2+} and Cl^-, respectively, $m^{\mathrm{o}} = 1$ mol kg^{-1}, A and B are Debye-Hückel constants calculated using literature data for the relative permitivity of the solvent,[5] I denotes the ionic strength of the solution, a is the ion-size parameter (taken to be 0.45 nm; Refs. 4 and 6), M is the molar mass of the solvent, $\Sigma_{\mathrm{x}}m(\mathrm{X})$ is the total molality of all the ionic species, C is the empirical parameter, while the remaining symbols have their standard meaning.

Determination of the E_m^{o} can be performed either by extrapolation of E' to $I \to 0$ or by the least-squares method.

To calculate $m(\mathrm{Cd}^{2+})$, $m(\mathrm{Cl}^-)$ and m(of the remaining ionic species) for each molality of $\mathrm{CdCl_2}$, it is necessary to consider the complexation reactions in these solvents

$$\mathrm{Cd}^{2+} + n\ \mathrm{Cl}^- = \mathrm{CdCl}_n{}^{(2-n)+}, \qquad (n = 1,\ 2,\ 3 \text{ and } 4) \tag{3}$$

or the literature data for the thermodynamic stability constants[4] of the formed complexes (K_n^{o}).

From these constants, the concentration stability constants K_n' have to be determined for each complex, *i.e.*

$$K_n' = ([\mathrm{CdCl}_n{}^{(2-n)+}]/c^{\mathrm{o}})/\{([\mathrm{Cd}^{2+}]/c^{\mathrm{o}})([\mathrm{Cl}^-]/c^{\mathrm{o}})^n\}, \tag{4}$$

where [X] is the concentration of ion X, and $c^{\mathrm{o}} = 1$ mol dm^{-3}.

The K_n^{o} constant is related to K_n' according to expression

$$K_n^{\mathrm{o}} = K'_n K_y, \tag{5}$$

where K_y denotes the relation of activity coefficients, *i.e.*

$$K_y = [y(\mathrm{CdCl}_n{}^{(2-n)+})]/\{[y(\mathrm{Cd}^{2+})][y(\mathrm{Cl}^-)]^n\}. \tag{6}$$

The thermodynamic constant is the true constant and it is only dependent on temperature, while K_n' depends also on the ionic strength of the solution according to equation

$$\log K_n' = \log K_n^{\mathrm{o}} + \Delta z^2 AI^{1/2}/(1 + BaI^{1/2}) + \Delta \mathrm{C}_n I/c^{\mathrm{o}}. \tag{7}$$

In this equation $\Delta z^2 = z^2(\mathrm{CdCl}_n^{(2-n)+}) - z^2(\mathrm{Cd}^{2+}) - nz^2(\mathrm{Cl}^-)$, $-\Delta C_n = C(\mathrm{CdCl}_n^{(2-n)+}) - C(\mathrm{Cd}^{2+}) - nC(\mathrm{Cl}^-)$, where z and C denote the charge and the empirical constant for each ion. Other symbols have already been explained.

The values for K_n° and for ΔC_n at 298.15 and 313.15 K are taken directly from Ref. 4, while at other temperatures the K_n° values were determined from the plot ln K_n° against T^{-1}, and the values of ΔC_n were obtained by interpolation.

The calculating method has already been described in detail,[1,2] so it is given here only in brief. Namely, for each molality of $\mathrm{CdCl_2}$, first the starting ionic strength was calculated according to equation $I = 3md$, where d is the solvent density taken from literature,[7] then the K_n' values were determined using equation (7), enabling calculation of the concentrations of all the ionic species present. The new ionic strength of the solution is now determined, as well as the new K_n' values, and the treatment is repeated until a satisfactory constancy of K_n' values is obtained. Accordingly, by the approximation procedure, we obtain the ionic strength containing the equilibrium concentrations of all the ionic species when K_n' values become constant.

The obtained equilibrium concentrations of all the ionic species were then expressed as molalities, and using equation (2) the value of E_m° of the cell and its standard deviation were determined using the least-squares method. In Table II, these values are given together with the data for the aqueous medium.

TABLE II

Standard e.m.f. of the cell: Cd(Hg) (l, satd.) |$\mathrm{CdCl_2}$ (m) in t-butanol – water mixtures ($w_{t\text{-BuOH}}$ = 0%, 10%, 30%, 50%) | AgCl | Ag at different temperatures

$\frac{T}{\mathrm{K}}$	$\frac{E_m^\circ}{\mathrm{V}}$	$\frac{10^3\,s(E_m^\circ)}{\mathrm{V}}$	$\frac{E_m^\circ}{\mathrm{V}}$	$\frac{10^3\,s(E_m^\circ)}{\mathrm{V}}$	$\frac{E_m^\circ}{\mathrm{V}}$	$\frac{10^3\,s(E_m^\circ)}{\mathrm{V}}$	$\frac{E_m^\circ}{\mathrm{V}}$	$\frac{10^3\,s(E_m^\circ)}{\mathrm{V}}$
	w = 0%[a]		w = 10%		w = 30%		w = 50%	
293.15	0.57550	0.06	0.55765	0.18	0.52052	0.19	0.47047	0.12
298.15	0.57346	0.08	0.55583	0.22	0.51861	0.21	0.46637	0.14
303.15	0.57150	0.07	0.55395	0.18	0.51663	0.22	0.46310	0.22
308.15	0.56933	0.09	0.55153	0.19	0.51408	0.23	0.45901	0.28
313.15	0.56728	0.14	0.54930	0.16	0.51176	0.20	0.45512	0.39

[a] Calculated from E values in Ref. 1, and constants K_n° in Ref. 6.

The values of E_m° from the above table can be expressed in dependence on temperature in the range from 293.15 to 313.15 K by the following relations

$$E_m^\circ\ (w=0\%)/\mathrm{V}=0.63577-1.30\times10^{-5}\ T/\mathrm{K}-65.71\times10^{-8}\ T^2/\mathrm{K}^2, \quad (8)$$

$$E_m^\circ\ (w=10\%)/\mathrm{V}=0.32407+193.59\times10^{-5}\ T/\mathrm{K}-388.57\times10^{-8}\ T^2/\mathrm{K}^2, \quad (9)$$

$$E_m^\circ\ (w=30\%)/\mathrm{V}=0.28523+196.69\times10^{-5}\ T/\mathrm{K}-397.14\times10^{-8}\ T^2/\mathrm{K}^2, \quad (10)$$

$$E_m^\circ\ (w=50\%)/\mathrm{V}=0.58860-68.29\times10^{-6}\ T/\mathrm{K}-114.29\times10^{-8}\ T^2/\mathrm{K}^2. \quad (11)$$

The standard e.m.f. of the cell and its temperature coefficient ($\mathrm{d}E_m^\circ/\mathrm{d}T$), which is derived from equations (8) – (11), served to calculate the standard thermodynamic quantities Δ_rG°, Δ_rH° and Δ_rS° for the cell reaction (1) by applying the usual relations. The values for 298.15 K are given in Table III. The deviations were calculated from the standard deviation for E_m°.

TABLE III

Standard thermodynamic quantities for cell reaction (1) in *t*-butanol – water mixtures ($w_{t\text{-BuOH}}$ = 0%, 10%, 30%, 50%) at 298.15 K

w	Δ_rG°/kJ mol^{-1}	Δ_rH°/kJ mol^{-1}	Δ_rS°/J K^{-1} mol^{-1}
0%	–110.66 ± 0.02	–133.95 ± 0.07	–78.1 ± 0.2
10%	–107.26 ± 0.04	–129.17 ± 0.10	–73.5 ± 0.3
30%	–100.08 ± 0.04	–123.16 ± 0.24	–77.4 ± 0.8
50%	–90.00 ± 0.03	–133.14 ± 0.54	–144.7 ± 1.8

From the table it can be seen that the spontaneity (Δ_rG°) of reaction (1), or the possible electrical work of the cell, decreases continuously with the increase of *t*-butanol content in the mixed solvent, which is conditioned by the decrease of its relative permitivity. Analogy was established with the mixtures 2-propanol – water[2] and acetone – water.[3] The exothermity of the reaction (Δ_rH°), however, decreases up to 30 mass per cent *t*-butanol, and then it increases. This discontinuity was also observed with the 2-propanol – water mixtures, while with acetone – water mixtures, we found a continuous exothermic increase with an increasing content of acetone in the mixture. Finally, starting from 10 mass per cent *t*-butanol, Δ_rS° begins to decrease with an increase of its content in the mixture; the same effect was also observed with 2-propanol – water mixtures, while there is a continous decrease with acetone – water mixtures. Evidently, there is an analogy in the behaviour of the organic component in the mixture with an alcohol group relative to the component with a keto group.

The stoichiometric activity coefficients $\gamma_\pm$ of cadmium chloride for each molality were calculated by means of the Nernst equation applied to the cell reaction (1)

$$E = E_m^\circ - (RT\,/\,2F)\ \ln\ \{4[(m\,/\,m^\circ)\gamma_\pm]^3\}, \quad (12)$$

provided that Cd chloride complexes were not formed 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 shown in Table IV.

TABLE IV

Mean activity coefficients $\gamma_{\pm}$ of $CdCl_2$ at different molalities in *t*-butanol – water mixtures ($w_{t\text{-BuOH}}$ = 10%, 30%, 50%) at 298.15 K

w	m/mol kg^{-1}					
	0.002	0.005	0.007	0.01	0.015	0.02
10%	0.691	0.535	0.488	0.442	0.395	0.364
30%	0.514	0.373	0.331	0.292	0.253	0.229
50%	0.258	0.173	0.149	0.128	0.107	0.094

The data from the table indicate that in each solvent $\gamma_{\pm}$ decreases with an increase in $CdCl_2$ molality, and for each molality with an increase of *t*-butanol content in the solvent, or with a decrease of its relative permitivity. This is in agreement with the Debye-Hückel theory.

It should be mentioned that an analogy was found with 2-propanol – water and acetone – water solutions; however, from Figure 1 we can see that at the same relative permitivity, the nature of the organic component in the solvent becomes prominent. Namely, the figure presents the dependencies of $\gamma_{\pm}$ on the relative permitivity ($\gamma_{\pm}$ against ε_r^{-1}) for $m(CdCl_2)$ / mol kg^{-1} = 0.005, 0.01 and 0.02 for the aqueous medium, of the mixtures 2-propanol – water, acetone – water and *t*-butanol – water. It is seen that the activity coefficients, at the same relative permitivity, are the highest with *t*-butanol – water mixtures, and the lowest with acetone – water mixtures, and that this difference is smaller with the solvents containing an alcohol component. Obviously, this is related to the degree of complexation, since in Ref. 4 it was established that, at the same relative permitivity, the highest stability constants of Cd chloride complexes are found in acetone – water mixtures, and the lowest in *t*-butanol – water mixtures, and that there is a smaller difference between solvents containing an alcohol component.

Finally, the standard thermodynamic quantities were calculated for $CdCl_2$ transfer from water to *t*-butanol – water mixtures. The standard Gibbs energy change was calculated according to the relation

$$\Delta_t G^{\circ} = 2F[(E_x^{\circ})_w - (E_x^{\circ})_s], \tag{13}$$

where $(E_x^{\circ})_w$ and $(E_x^{\circ})_s$ denote the standard e.m.f. of the cell in aqueous medium and in a mixed solvent on a mole-fraction scale, and they are

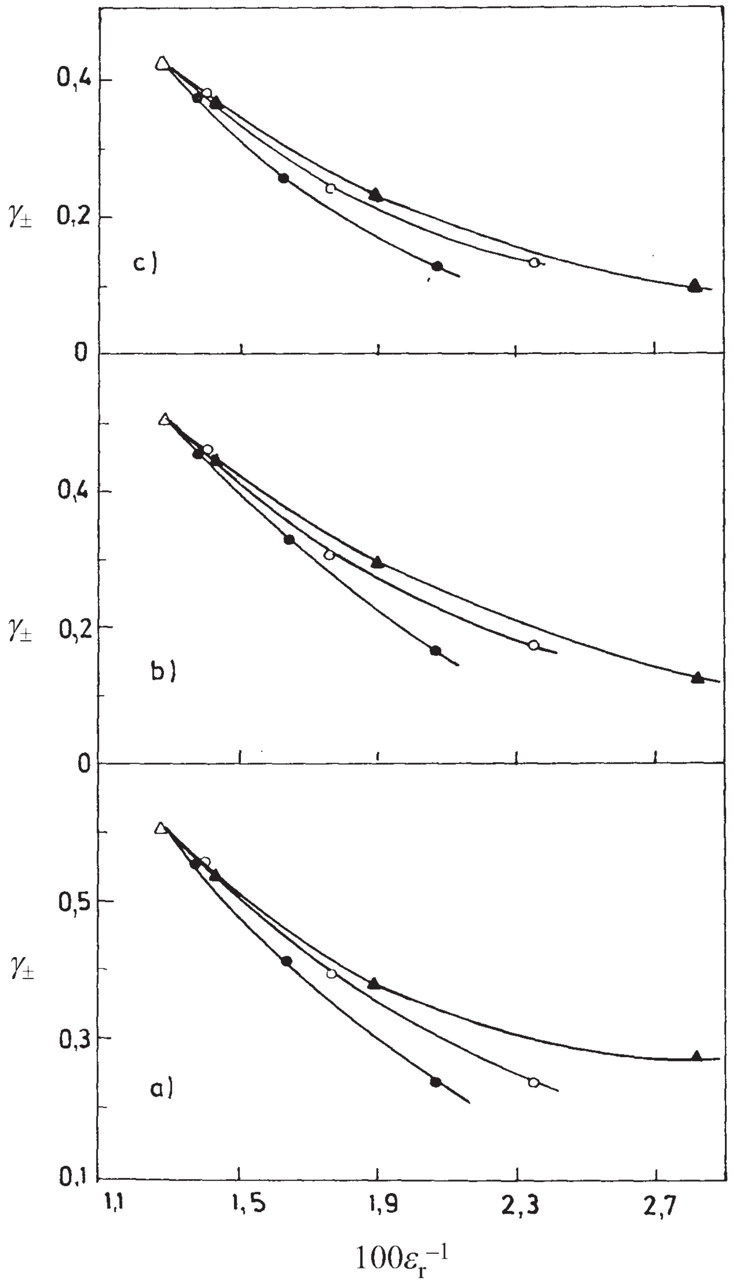

Figure 1. Variation of $\gamma_\pm$ with ε_r^{-1} at 298.15 K for $m(CdCl_2)$ / mol kg^{-1}: a) 0.005, b) 0.01 and c) 0.02 in: aqueous solution (Δ) (Ref. 2), acetone – water (●) (Ref. 3), 2-propanol – water (O) (Ref. 2) and t-butanol - water (▲) mixtures.

calculated from E_m° (Table II) using the known relation.[8] For the investigated temperature range, we obtained the following dependencies for $\Delta_t G^\circ$

$$\Delta_t G^\circ\ (w = 10\%)/\text{J mol}^{-1} = 59126 - 371.33\ T/\text{K} + 61.20 \times 10^{-2}\ T^2/\text{K}^2, \quad (14)$$

$$\Delta_t G^\circ\ (w = 30\%)/\text{J mol}^{-1} = 67120 - 385.09\ T/\text{K} + 63.41 \times 10^{-2}\ T^2/\text{K}^2, \quad (15)$$

$$\Delta_t G^\circ\ (w = 50\%)/\text{J mol}^{-1} = 8568 + 224.51 \times 10^{-2}\ T/\text{K} + 88.22 \times 10^{-3}\ T^2/\text{K}^2. \quad (16)$$

From these relations the temperature dependencies for entropy ($\Delta_t S^\circ$) and enthalpy of transfer ($\Delta_t H^\circ$) were obtained by known equations. The values for temperature at 298.15 K are given in Table V. The deviations were determined from the standard deviations for E_m° in the water medium and in the mixed solvent.

TABLE V

Standard thermodynamic quantities for the transfer of $CdCl_2$ from water to *t*-butanol – water mixtures ($w_{t\text{-BuOH}}$ = 10%, 30%, 50%) at 298.15 K

w	$\Delta_t G^\circ$/kJ mol^{-1}	$\Delta_t H^\circ$/kJ mol^{-1}	$\Delta_t S^\circ$/J K^{-1} mol^{-1}
10%	2.82 ± 0.02	4.73 ± 0.12	6.4 ± 0.4
30%	8.67 ± 0.01	10.76 ± 0.27	7.0 ± 0.9
50%	17.08 ± 0.05	0.71 ± 0.56	–54.9 ± 1.9

The data from table show that the transfer process is non-spontaneous, the more so with the higher content of *t*-butanol in the mixed solvent. An analogy was found also with the transfer process in 2-propanol – water and acetone – water mixtures. The transfer of $CdCl_2$ in 10 and 30 mass per cent *t*-butanol is accompanied by increasing enthalpy and entropy, while in 50 mass per cent the increase in enthalpy is negligible and there is a decrease in entropy. With transfer to the mixtures with 10 and 30 mass per cent 2-propanol there is an increase in enthalpy, while the enthalpy decreases in 50 mass per cent. As for entropy, the transfer in 10 mass per cent is a positive value, while the transfer to 30 and 50 mass per cent results in its decrease. In contrast, the transfer of $CdCl_2$ in all the investigated acetone – water mixtures results in a decrease of both enthalpy and entropy.

Consequently, there is an analogy for enthalpy and entropy with $CdCl_2$ transfer from water to 2-propanol – water and *t*-butanol – water mixtures, respectively. It can therefore be said also here that lower amounts of *t*-butanol in water promote its three-dimensional structure, and so the ions have a more destructive effect on its structure in a mixed solvent than in water; hence, $\Delta_t H^\circ$ and $\Delta_t S^\circ$ have positive values. With higher amounts of alcohol, however, the effect is opposite, so that $\Delta_t H^\circ$ and $\Delta_t S^\circ$ are negative values.

It should be mentioned that a similar trend of changes in $\Delta_t H^o$ and $\Delta_t S^o$ was found also with the transfer of KCl, KBr and KI electrolytes in *t*-butanol – water mixtures, which is summed up in Table VI. Gibbs energy of transfer was obtained from the e.m.f. measurements of the cell,[9,10] the transfer enthalpy from calorimetric measurements,[11,12] while $\Delta_t S^o$ was calculated by the standard relation.

TABLE VI

Standard thermodynamic quantities for the transfer of KCl, KBr and KI from water to *t*-butanol – water mixtures ($w_{t\text{-BuOH}}$ = 10%, 20%, 30%, 40%) at 298.15 K

w	$\Delta_t G^o$/kJ mol^{-1}	$\Delta_t H^o$/kJ mol^{-1}	$\Delta_t S^o$/J K^{-1} mol^{-1}	Ref.
		KCl		
10%	1.77	2.82	3.5	
20%	3.48	7.72	14.2	$\Delta_t G^o$ (9)
30%	4.98	8.72	12.5	$\Delta_t H^o$ (11)
40%	6.56	7.64	3.6	
		KBr		
10%	1.50	2.82	4.4	
20%	2.90	6.65	12.6	$\Delta_t G^o$ (10)
30%	4.31	6.78	8.3	$\Delta_t H^o$ (12)
40%	5.86	5.10	–2.5	
		KI		
10%	1.18	3.59	8.1	
20%	2.12	6.51	14.7	$\Delta_t G^o$ (10)
30%	2.82	4.65	6.1	$\Delta_t H^o$ (12)
40%	3.87	1.88	–6.7	

In conclusion, it can be said that an insight into the structure of mixed *t*-butanol – water solvents can be gained on the basis of establishing the enthalpy and entropy for the transfer of type 2-1 and type 1-1 electrolytes.

Acknowledgement. – This work was supported by the Ministry of Science and Technology of the Republic of Croatia (Project No. 011008).

REFERENCES

1. M. Višić and I. Mekjavić, *J. Chem. Thermodyn.* **21** (1989) 139–145.
2. M. Višić and I. Mekjavić, *Croat. Chem. Acta* **66** (1993) 479–488.
3. M. Višić and I. Mekjavić, *ibid.* **69** (1996) 27–36.
4. M. Višić, R. Tomaš, and I. Mekjavić, *ibid.* **72** (1999) 55–70.
5. G. Åkerlöf, *J. Am. Chem. Soc.* **54** (1932) 4125–4139.

6. M. Višić, A. Jadrić, and I. Mekjavić, *Croat. Chem. Acta* **66** (1993) 489–498.
7. K. Bose, A. K. Das, and K. K. Kundu, *J. Chem. Soc., Faraday Trans. I* **71** (1975) 1838–1848.
8. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworth, London, 1965, p. 353.
9. M. M. Elsemongy and A. A. Abdel-Khalek, *Thermochim. Acta* **158** (1990) 107–114.
10. D. Feakins, P. J. McCarthy, and T. A. Clune, *J. Chem. Soc., Faraday Trans. I* **84** (1988) 4213–4218.
11. Y. Pointud, J. Juillard, L. Avedikian, J. P. Morel, and M. Ducros, *Thermochim. Acta* **8** (1974) 423–431.
12. Y. Pointud and J. Juillard, *J. Chem. Soc., Faraday Trans. I* **73** (1977) 1907–1912.

SAŽETAK

Termodinamička svojstva kadmijeva klorida u 10, 30 i 50%-tnim smjesama *t*-butanol – voda na osnovi mjerenja elektromotorne sile

Renato Tomaš, Marija Višić i Ivica Mekjavić

Mjerena je EMS članka: Cd(Hg)(l,zas.) | $CdCl_2$ (m), smjesa t-butanol – voda |AgCl| Ag s masenim udjelom t-BuOH od 10, 30 i 50%, u temperaturnom području (293,15 – 313,15) K u intervalu po 5 K i u području molalnosti $CdCl_2$ (0,002 – 0,02) mol kg^{-1}. Iz tih vrijednosti uz uporabu literaturnih podataka za konstante stabilnosti kloridnih kompleksa Cd određene su za pojedine temperature standardne EMS članka (E_m°). Dobivene vrijednosti poslužile su za izračunavanje standardnih termodinamičkih veličina ($\Delta_r G^\circ$, $\Delta_r H^\circ$ i $\Delta_r S^\circ$) za reakciju članka, prosječnih koeficijenata aktiviteta $CdCl_2$, kao i standardnih termodinamičkih veličina ($\Delta_t G^\circ$, $\Delta_t H^\circ$ i $\Delta_t S^\circ$) za prijenos $CdCl_2$ iz vode u proučavana miješana otapala. Sve dobivene vrijednosti uspoređene su s vrijednostima za smjese 2-propanol – voda i aceton – voda, a vrijednosti za $\Delta_t H^\circ$ i $\Delta_t S^\circ$ uspoređene su također s onima za prijenos elektrolita KCl, KBr i KI u smjese t-butanol – voda. Vrijednosti za entalpiju i entropiju prijenosa su omogućile uvid u strukturu smjesa t-butanol – voda.