# Thermodynamic determination of solvation potentials of various metal chlorides by (1,4-dioxane + water) mixtures through EMF measurements

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## ARTICLE INFO

## ABSTRACT

The EMF data of different metal chlorides (2:1 electrolytes) were obtained by using a cell [$M_X$ Hg|$MCl_2$ ($m$)|AgCl–Ag] at two temperatures. Stock solutions of metal chlorides ($CoCl_2$, $CuCl_2$ and $ZnCl_2$) were prepared by weight in 1,4-dioxane–aqueous mixtures. There was a significant change in the EMF values with change of metal chloride, its concentration and solvents composition. The standard electrode potential ($E^\circ$) values of the above cell were calculated from the measured EMF of these mixtures. The standard thermodynamic functions ($\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$) and respective transfer parameters of $MCl_2$ from water to 20, 45 and 70% dioxane–water mixtures were also evaluated. Equilibrium dissociation constants ($K_1$ and $K_2$) as well as the degrees of dissociation ($\alpha_1$ and $\alpha_2$) were obtained by iterative procedures. The data were analyzed in terms of solute–solvent interactions depending on standard and transfer thermodynamic parameters and mean activity coefficients ($\gamma_\pm$) of electrolytes.

## 1. Introduction

Various cycloethers (1,4-dioxane, 1,3-dioxane, THF, etc.) are widely used as solvents in different fields such as chemical synthesis, solvent extraction and reliable liquid chromatography. Even at room temperature these cycloethers are miscible with water at any composition and their physicochemical properties such as dielectric constant, density, viscosity, EMF, etc., can be continuously varied by changing mixing molar ratios. Thus aqueous mixtures of the cycloethers are more frequently used as solvents than pure liquids. It has been considered from the molecular structures that an important reason why these cycloethers are completely mixed with water at any composition might be hydrogen bonding between the oxygen atoms of the cycloether molecules and protons of water molecules. In fact, Gutman's donor numbers ($D_N$) [1] of 1,4-dioxane (14.8) and THF (20.0) are comparable with water (18.0) while Mayer–Gutman's acceptor numbers ($A_N$) [1] of formers (10.8 and 8.0, respectively) are much smaller than that of latter (54.8). Thus the cycloether molecules can play as a proton acceptor but not proton donor.

Many investigations have so far been performed on cycloether–water mixtures by using various methods, such as thermodynamic techniques, infrared [2], NMR [3], and Raman [4] spectroscopy, dielectric relaxation [5,6] and computer simulations [7] suggested the mixing states of cycloether–water mixtures. Recently Takamuku et al. [8] have investigated the structures of 1,4-dioxane–water mixtures over the whole concentration range of dioxane at 25 °C by LAXS, mass spectrometry, and NMR relaxation. These results showed that the structures of 1,4-dioxane–water mixtures changed with dioxane mole fraction as: at less than 0.1 mole fraction, hydrogen bonded network of water predominated in the mixtures, in a very narrow range of 0.1–0.3 mole fraction of dioxane small aggregates of water and 1,4-dioxane molecules were formed, and an ordered structure of 1,4-dioxane was observed as for pure liquid in the mixtures over a wide range of concentration greater than 0.3 mole fraction. A local solvent structure study on 1,4-dioxane–water binary mixtures by total isotropic Rayleigh light scattering method was carried out by Wu et al. [9] at 546 nm using a conventional fluorometer. From the analysis of their studies, it was concluded that local structure of the mixed solvent changes at three specific compositions, $X_{dio}$ = 0.13, 0.3 and 0.7, respectively.

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Bester-Rogac et al. [10] measured electric conductivities of dilute magnesium sulfate solutions in binary mixtures of 1,4-dioxane with water up to 50 wt% of dioxane at temperatures from 5 to 35 °C and calculated standard Gibbs energy, enthalpy and entropy of the ion-pairing process from the temperature dependence of the ion-association constants. The EMF of M–amalgam cells [11,12] (M = Li, Cs) has been measured as a function of molality (up to 0.8) of metal halide in (methanol + water), (acetonitrile + water) and (1,4-dioxane + water) solvent mixtures at 25 °C. The respective standard molal potential differences ($E°$) have been determined with the relevant activity coefficients. Analysis of the primary medium effects on metal halides showed always unfavorable transfer from water to water + organic solvent. Eysseltova et al. [13] have studied the solubility of NaCl and KCl at 25 °C in 1,4-dioxane–water mixtures for the determination of the immiscibility boundary for phase equilibrium. In sodium chloride system an area of two liquid phases occurs, whereas with potassium chloride only a smooth solubility curve exists. Alkali metal halide solutions in 1,4-dioxane–water mixtures were investigated in the framework of Monte Carlo simulations on the Born–Oppenheimer level with classical interaction site models (ISM) by Krienke et al. [14]. The structure of the solvent as well as solvation and association of ions were studied in detail. Preferential and selective solvation was shown in the solvation shell of sodium and chloride ions. Pure 1,4-dioxane and 1,4-dioxane–water mixtures were also investigated in the framework of Monte Carlo (MC) simulations on the molecular Born–Oppenheimer (BO) level with classical interaction site models (ISM) by Ahn-Ercan et al. [15]. Dielectric constants were calculated within the Monte Carlo simulations and by integral equation theories. The EMF measurements at 298 K were reported by Gregory et al. [16] for galvanic cells with flowing liquid junctions in which one-half cell contained an aqueous electrolyte solution and the other contained the same electrolyte in 1,4-dioxane–water mixtures of varying composition. The electrolytes (HCl, NaCl, KCl and CsCl) were studied in the dioxane–water system using silver–silver chloride electrodes in each half-cell. The solvation characteristics of the dioxane–water system were discussed and compared with those in methanol–water and DMF–water solvent systems. Gibbs functions for transfer of divalent metal cations ($Cu^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Hg^{2+}$, $Zn^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$) from water to water–methanol mixtures using potentiometry, polarography and solubility measurements were calculated by El Marackchi et al. [17]. The enthalpies of transfer of Co(II) ion in several aqueous–organic and organic mixed solvents were analyzed by means of the theory of preferential solvation by Kamienska-Piotrowicz [18]. Their results provided the quantitative description of preferential solvation of the ion and of its effect on interactions between solvent molecules. The mean number of molecules of one component of the mixture in the solvation sphere of Co(II) ion vs. solvent composition was determined. Thermodynamic study of cadmium chloride in aqueous mixtures of 2-butanol from potential difference measurements was carried out by Tomas et al. [19]. By using standard molal potential differences ($E°$), they calculated standard thermodynamic quantities ($\Delta G°$, $\Delta H°$ and $\Delta S°$), mean molal activity coefficients ($\gamma_\pm$) and the standard thermodynamic functions of transfer of $CdCl_2$ ($\Delta_t G°$, $\Delta_t H°$ and $\Delta_t S°$) from water to the examined aqueous mixtures of 2-butanol.

Investigations of electrochemical behavior of binary electrolytes (MX or $MX_2$) in water or (water + organic solvent) mixtures faces the problem of availability of pertinent electrodes reversible to the $M^+$ or $M^{2+}$ cations. To this purpose, the metal–amalgam electrodes of the flowing dilute–amalgam type, which were systematically studied lends best credence. In the domain of electrochemical thermodynamics, the studies of the general reversible cell: $M_X$ Hg|$MCl_2$ ($m$) in $Z$|AgCl–Ag (where $M$ stands for any metal, $MCl_2$ for metal chloride, $m$ for molality of electrolyte and $Z$ for aqueous–solvent

mixtures) have received a lot of attention due to their importance which extends to the related areas of electro-analysis and metal corrosion. The organic solvent chosen for the present study was 1,4-dioxane which is a non-polar and aprotic. In fact, a knowledge of such fundamental thermodynamic quantities as the standard electromotive force ($E°$) of cell with the related classical functions ($\Delta G°$, and so forth) for the cell reaction, together with the primary medium effects and solvation numbers, as well as the mean activity coefficients ($\gamma_\pm$) for the pertinent electrolytes, is indispensable even for investigations outside the realm of thermodynamics, for example, studies of ionic transference parameters through concentration cells with transference.

In the present work, we extended our former investigations [20] of 2:1 electrolytes ($CoCl_2$, $CuCl_2$ and $ZnCl_2$) in dilute solutions of pure solvents (W, FD and DMF) to mixed solutions of organic solvent and water. Precise EMF measurements of $MCl_2$ in 1,4-dioxane–water mixtures (by mass) were carried out at two temperatures. Then using measured EMF data ($E$), we calculated the mean activity coefficient ($\gamma_\pm$) and standard cell potential ($E°$) of electrolytes, and further computed these values to get the standard thermodynamic as well as standard transfer thermodynamic functions from water to aqueous mixtures of 1,4-dioxane.

## 2. Materials and methods

### 2.1. Materials

1,4-Dioxane (Loba, AR Grade) was refluxed with sodium metal as suggested by McGlashan and Rastogi [21], and then fractionally distilled. De-ionized double distilled water (from all glass apparatus) was used for preparing stock solutions. The stock solutions of 20, 45 and 70% dioxane–water mixtures were prepared by weight percent method. Cupric chloride dihydrate (Loba, AR grade, 98%) was dehydrated [22] by heating it in an oven at 130 °C for 18 h. The anhydrous $CuCl_2$ was found (by complexometric determination [23] of its copper content) to contain 98.5% of $CuCl_2$. Cobalt chloride (Loba, AR grade, 98%) was also dehydrated [22] by keeping in an oven at 118 °C for 18 h. The anhydrous $CoCl_2$ was found (by complexometric determination [23] of its cobalt contents) to contain 97.6% of cobalt chloride. $ZnCl_2$ (Loba, AR grade, 97%) was also dehydrated by keeping it in an oven at 110 °C for overnight. The zinc chloride was found to contain 96.8% pure $ZnCl_2$ (by complexometric determination [23] of its zinc content).

### 2.2. Preparation of metal–amalgams

(a) For the preparation [24] of cobalt–amalgam, 94.44 g of $CoSO_4$ was dissolved in 125 ml of distilled water, and 75 ml of mercury was amalgamated at a current of 200 mA for 10 h in a 200 ml beaker (electrolysis of mercury) making Hg-pool as cathode and platinum electrode of area 1.5 cm$^2$ as anode. Constant current was supplied by stabilized power supply.

(b) The copper–amalgam was prepared [24] by vigorous shaking of as much of freshly prepared atomic copper with distilled mercury as could keep the percentage of Cu(II) in the amalgam below 0.0042%. Under these conditions the EMF of copper–amalgam electrode was reported to be independent of the amount of copper in the amalgam.

(c) The liquid zinc–amalgam (2–3% zinc) was prepared [25] from 4.0 g of zinc. The zinc was degreased with ether, thoroughly washed with dilute $H_2SO_4$ placed in a 100 ml flask and heated on a water bath together with 200 g (14.8 ml) of mercury and 2 ml of 1N $H_2SO_4$. The zinc dissolved completely in about 20 min and the liquid amalgam was washed repeatedly with very dilute $H_2SO_4$, cooled and separated in a dropping funnel from solid