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Thermodynamic transfer study of various metal chlorides from water to formamide and dimethylformamide by EMF measurements

Manjula Spah[a,*], Dal Chand Spah[b], Jong Jin Park[b], Ho-Jun Song[b], Kwinam Park[c], Jin-Won Park[b]

[a] Department of Chemistry, Yonsei University, Seoul 120 749, South Korea
[b] Department of Chemical Engineering, Yonsei University, Seoul 120 749, South Korea
[c] Gyeonggi Daejin Technopark, San 11-1 Sundan-dong, Pocheon City Gyeonggi-do, South Korea

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ABSTRACT

Cell potentials (EMF) were measured at two different temperatures (303.15 and 313.15 K) of three different metal chlorides ($CoCl_2$, $CuCl_2$ and $ZnCl_2$) on the cell M_X Hg|MCl_2 (m) in solvent S = W, FD and DMF|AgCl–Ag, where W = water, FD = formamide and DMF = dimethylformamide. For $ZnCl_2$, the investigations were carried out at 313.15 K only. Stock solutions of metal chlorides were prepared by weight in pure solvents (W, FD and DMF) and further varied the concentration by adding more of pure solvents to these stock solutions. There was a significant change in EMF values with a change of concentration of electrolyte and metal ion. This change of EMF was associated with the change of ion–solvent interactions and was explained on the basis of kinetics of electrode processes. The standard electrode potentials (E°) values of the above cell were calculated in W, FD and DMF. Further the E° values were used to compute standard molar Gibbs free energy of transfer (ΔG°_{tr}) and other thermodynamic parameters of transfer (ΔH°_{tr}, ΔS°_{tr}) of MCl_2 from W to FD and DMF. Equilibrium constants (K_1 and K_2) as well as the degrees of dissociation (α_1 and α_2) for two step dissociation of metal chlorides in these solvents were obtained by iterative procedures. The data were analyzed in terms of the standard thermodynamic functions and standard transfer thermodynamic parameters depending on electrolytes and their concentration, nature of solvents and temperature to interpret the solute–solvent interactions.

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1. Introduction

An ion–solvent interaction is an important tool in the hands of chemical engineers for the design and simulation of various models/programs of industrial use. Knowledge of ion–solvent interactions has a vital role to play for separation of various components in petroleum refinery, solvents use in paints and emulsions industry, medicine industry, cosmetics industry and so on. So, the role of electrolytes (metal-halides) in various pure solvents and their mixtures to study the ion–solvent interactions is of immense importance. Solvating tendency of an ion in a solvent depends among other things, on electron pair donation by solvent (measured by Gutmann donor number [1,2]) and acceptance of electrons by cation (as indicated by electron pair acceptance polarity index [3], structural [4] (categorized by stiffness, openness and ordering) and self-association characteristics of solvent molecules. If solvating tendency of an ion in any solvent is the net effect of the formation of definite solvates [5] and further solvation of an ion in any solvent involves its transfer from its ideal standard state to its standard state in solution [4a], so the solute particles should undergo drastic change in their internal degrees of freedom. And hence the thermodynamic quantities of transfer do not truly reflect the solute–solvent interactions.

Therefore, the study of thermodynamic quantities of transfer would be a good measure of solute–solvent interactions only if a solute is transferred from one solvent to another solvent [4b]. In that situation, the knowledge of thermodynamic quantities of transfer from water to another solvent should yield meaningful insight into the influence of ion–ion, ion–solvent and solvent–solvent interactions on the dissolution behavior of a solute in water in the presence of a co-solvent. The extra thermodynamic tetraphenylarsonium tetraphenylborate assumption [6] has been applied in order to calculate the contribution [6] from individual ions. The Gibb's free energies of transfer have been calculated from standard electrode potentials determined potentiometrically. The Cu (II) ion which is regarded as a borderline acceptor, is strongly solvated by DMSO, pyridine and liq. NH_3, but is weakly solvated by methanol and acetonitrile. The solvation pattern of the Cu (I) ion is significantly different from that of Cu (II). So, the Cu (I) ion, a soft electron pair acceptor, is strongly solvated by acetonitrile and the other soft donor solvents like pyridine, tetrahydrothiophene and liq. NH_3.

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* Corresponding author. Tel.: +82 2 2123 2636; fax: +82 2 364 7050.
E-mail address: manju_dc@yonsei.ac.kr (M. Spah).

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Potential difference measurements have been done to examine the thermodynamic stability [7] of copper (I) ion and to study halide-complex formation [7] in propylene carbonate. The hydrated Cu (I) ion is unstable in water, and in the absence of ligands responsible for the stabilization of its monovalent state, it disproportionate to copper (II) and metallic copper. In some aprotic solvents, copper (I) is more solvated than copper (II) and this causes drastic changes in the relative stabilities of both the oxidation states. A complex formation between a metal ion and any ligand competes with the solvating power of all other species involved.

The enthalpies [8] of transfer of Co (II) ions from pure to mixed solvents in several aqueous-organic and organic mixed solvents were analyzed by means of the theory of preferential solvation [9]. The results provided the quantitative description of preferential solvation of the ion and its effect on interactions between solvent molecules. They [8] also enabled to compare the solvating properties of various mixtures. Generally, the mean composition of the solvating sphere differs from that of mixed solvents, so the ion is preferentially solvated by one of the solvent components. Considerable insight into the solvation studies from thermodynamic data provided a theory of preferential solvation that was presented for the first time in 1983 by de Valera et al. [9].

For 2:1 electrolytes [10], the activity coefficients of Ba^{2+}, Ca^{2+} and Mg^{2+} ions were calculated using values of the mean ionic activity coefficients of the salts. At low electrolyte concentration, the activity coefficients of the metal ions are smaller than that of anion, but at higher concentration this trend is reversed. The interest in mixed solvents [11] with water as a component is still great. Insight into the properties of such a solvent mixture can be obtained indirectly through its effect on the electro kinetic and thermodynamic behavior of the dissolved electrolyte. Recent literature shows that a significant role in assessing the thermodynamics of electrolytes in mixed solvents can be attributed to the measurements of potential difference of reversible galvanic cells [12,13]. Such measurements provide fundamental thermodynamic quantities for the cell reaction, such as the appropriate standard electrode potentials, the corresponding standard thermodynamic functions (ΔG°, ΔH° and ΔS°) and the transfer functions of electrolyte from water to the solvents/mixed solvents along with the mean activity coefficients and solvating numbers. Though the 2:1 electrolytes generally get ionize in water and other solvents as [14]: $\mathrm{M\ X_2} \leftrightarrow (\mathrm{MX})^+ + \mathrm{X}^-$; $(\mathrm{MX})^+ \leftrightarrow \mathrm{M}^{2+} + \mathrm{X}^-$, yet very few equilibrium constant data are available in medium other than water. Again, as lower amides are suitable model compounds [15] of proteins, the dissolution behavior of 2:1 electrolytes in W, and lower amides should be of considerable biochemical interest. These considerations led us to study the solvating behavior of metal chlorides in aqueous and non-aqueous solvents. That is why for our present investigations, we selected three 2:1 metal chlorides of Mn–Zn series ($CoCl_2$, $CuCl_2$ and $ZnCl_2$) each in three solvents: W, FD and DMF. The potential measurements as a function of m of each electrolyte in all the three solvents at two different temperatures were thought appropriate to study the change of ion–solvent interactions with concentration and temperature. The measured EMF data were used to calculate standard cell potential (E°) which could further be utilized to evaluate thermodynamic transfer functions ($\Delta G^\circ_{\mathrm{tr}}$, $\Delta H^\circ_{\mathrm{tr}}$ and $\Delta S^\circ_{\mathrm{tr}}$) to throw light on the ion–solvent interactions.

2. Experiment

2.1. Sample preparation

FD (BDH, AR grade, 98%) and DMF (Loba, AR grade, 99%) were purified as described earlier [16]. De-ionized double distilled water (from all glass apparatus) was used for preparing stock solutions. Cupric chloride dihydrate (Loba, AR grade, 98%) was dehydrated [17] by heating it in an oven at 130 °C for 18 h. The anhydrous $CuCl_2$ was found by complexometric determination [18] of its copper content to contain 98.5% of $CuCl_2$. Cobalt chloride (Loba, AR grade, 98%) was also dehydrated [17] by keeping it in the oven at 118 °C for 18 h. The anhydrous $CoCl_2$ was found by complexometric determination [18] of its cobalt contents to contain 97.6% of cobalt chloride. $ZnCl_2$ (Loba, AR grade, 97%) was dehydrated by keeping it in an oven at 110 °C for overnight. The zinc chloride salt was found to contain 96.8% pure $ZnCl_2$ by complexometric determination [18] of its zinc content.

2.2. Preparation of electrodes

(a) For the preparation[19] 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 [19] 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 amalgam.

(c) The liquid zinc-amalgam (2–3% zinc) was prepared [20] 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 1 N 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 particles. These solids could be used to enhance the zinc concentration of amalgam that had lost some zinc during use.

(d) The AgCl–Ag electrode was prepared [21] by anodic polarization of Ag-electrode at a current density of 0.4 mA cm^{-2} in 0.1 N HCl for 30 min and kept in distilled water. To get reproducible results we found it necessary to have a uniform current density over the electrode during the entire electrolysis process.

2.3. Potential difference measurements

The stock solutions of metal chlorides were prepared from weighed amounts of metal chlorides and solvents. Concentrations of these solutions of metal chlorides in W, FD and DMF were prepared near 0.01 m. Required sets of solutions were obtained by mass dilution of the stock solutions. The nitrogen gas was passed through the cell intermittently to displace dissolved oxygen from the solution. The EMF values of all these solutions were measured twice at each concentration to check the reproduce-ability. EMF in the concentration range from 0.01 to 0.001 m was obtained with a vernier potentiometer (Osaw, India) coupled with a spot reflecting galvanometer (Toshniwal, India) to an accuracy of ±0.01 mV. The EMF was measured (after attaining thermal equilibrium) with the cell (I), which is represented as

$$\mathrm{M}_X\ \mathrm{Hg}\,|\,\mathrm{M\ (II)\ Cl_2}\ (m)\ \text{in W or solvent S}\,|\,\mathrm{AgCl{-}Ag\ cell} \qquad (1)$$

Molar Gibb's free energy of transfer ($\Delta G^\circ_{\mathrm{tr}}$) of MCl_2 from W to S (FD and DMF) were evaluated from measured EMF of the cell (I) without liquid junction.

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