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Journal of Electroanalytical Chemistry 534 (2002) 115–121

Journal of
Electroanalytical
Chemistry

www.elsevier.com/locate/jelechem

Electrochemical behaviour of some copper(II) salts in 20 wt.% propylene carbonate + ethylene carbonate: Standard potential of the Cu^{2+}/Cu system at 25 °C

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Received 23 April 2002; received in revised form 31 July 2002; accepted 9 August 2002

Abstract

The behaviour of $\text{Cu}(\text{ClO}_4)_2$, CuCl_2 and CuBr_2 in 20 wt.% propylene carbonate (PC) + ethylene carbonate (EC) has been studied by conductivity, potentiometry and voltammetry. The conductance behavior of copper(II) halides in 20 wt.% PC+EC is explained on the basis of the equilibrium $3\text{CuX}_2 \rightleftharpoons \text{Cu}^{2+} + 2\text{CuX}_3$ and $2\text{CuX}_2 \rightleftharpoons (\text{CuX}_2)_2$. A copper indicator electrode in conjunction with a $\text{Hg}/\text{HgCl}_2(\text{s})$ in 20 wt.% PC+EC reference electrode was used for the potential measurements. The results of the potentiometric measurements, combined with those of the conductance measurements, provided the standard potential, E° , of the reaction $\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$ versus SHE in 20 wt.% PC+EC at 25 °C, which is found to be 0.400 ± 0.002 V. Sampled dc and cyclic voltammetric measurements were also undertaken with these Cu(II) salts in 20 wt.% PC+EC using Pt working and counter electrodes and $\text{Hg}/\text{HgCl}_2(\text{s})$ in 20 wt.% PC+EC as the reference electrode. These voltammetric measurements yielded the standard potential value (0.394 ± 0.003 V vs. SHE) of the system, which is in agreement with the value obtained by the potentiometric method.

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Keywords: Propylene carbonate; Ethylene carbonate; Standard potential; Copper(II) salts

1. Introduction

Propylene carbonate (4-methyl-1,3-dioxolane-2-one) abbreviated as PC has long been recognized as an outstanding dipolar aprotic solvent for electrochemical studies [1]. It has a convenient liquid range (-49.2 – 241.7 °C). The physicochemical properties and some fundamental studies in PC have been briefly reviewed by Mukherjee [2]. Several types of investigations, like conductivity, potentiometry, transfer activities, complexation studies, etc. have been carried out in this solvent [3–11].

Although PC has been receiving increasing attention as an electrochemical solvent, less attention has been directed towards ethylene carbonate (1,3-dioxolane-2-one or EC) as a solvent [12] probably because of its high freezing point (37 °C). However, some fundamental

studies have been reported in EC+water mixtures [13,14] and in EC+PC mixtures [15,16]. Both PC and EC are dipolar aprotic solvents with large dipole moments and relatively high permittivities. The dipole moments of PC (4.94 D) and EC (4.93 D) are similar and the solvents are miscible with each other [17]. The 20 wt.% PC+EC solution has a relative permittivity of 87.2 at 25 °C, which is higher than that of PC (64.4 at 25 °C). This offers a special advantage over low dielectric media where ionic association often creates undesirable complications [2,18,19]. The present work was undertaken to examine the behaviour of copper(II) perchlorate, copper(II) chloride and copper(II) bromide through conductance, potentiometric and voltammetric measurements. A copper indicator electrode was used to study copper(II) salts in conjunction with a $\text{Hg}/\text{HgCl}_2(\text{s})$ in 20 wt.% PC+EC reference electrode [16]. The results of the potentiometric measurements are combined with those of the conductance measurements to obtain the standard potential, E° , of the reaction $\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$ versus SHE in 20 wt.% PC+EC at 25 °C. In

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addition, the value of the standard potential of this reaction has also been determined by voltammetric measurements using sampled dc and cyclic voltammetric (CV) techniques.

2. Theory

2.1. Conductivity data analysis

2.1.1. Copper(II) perchlorate

The method for evaluating the conductivity data of weakly associating non-symmetric electrolytes is that proposed by Fuoss and Edelson [20], which has been used previously by us [8] for the alkaline earth metal perchlorates in PC, and is used for the treatment of copper(II) perchlorate conductivity data in 20 wt.% PC+EC also. This treatment is based on the following equilibria:



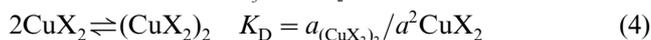
The equilibria leading to the neutral species $\text{Cu}(\text{ClO}_4)_2$ are neglected in this method. The results of the treatment in the form of a plot of Λ^* versus χ (Fuoss and Edelson plot) are shown in Fig. 1.

2.1.2. Copper(II) chloride and copper(II) bromide

The conductivity data of CuCl_2 and CuBr_2 in 20 wt.% PC+EC do not suggest a simple relation. On the contrary, they indicate strongly that these systems involve the unusual solution equilibria suggested by Pandey et al. [7]:



$$K_d = (a_{\text{Cu}^{2+}} + a_{\text{CuX}_3^-}^2) / a_{\text{CuX}_2}^3 \quad (4)$$



where X = Cl and Br. Assuming that the activity coefficients of all uncharged species are unity, Eqs. (3) and (4) can be written as:

$$K_d = [\text{Cu}^{2+}] [\text{CuX}_3^-] f_i f^2 / [\text{CuX}_2]^3 \quad (5)$$

$$K_D = [(\text{CuX}_2)_2] / [\text{CuX}_2]^2 \quad (6)$$

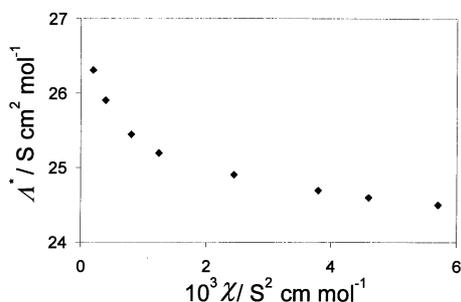


Fig. 1. Plot of Λ^* vs. χ for $\text{Cu}(\text{ClO}_4)_2$ in 20 wt.% PC+EC.

where f_i and f are the activity coefficients of Cu^{2+} and CuX_3^- , respectively. From the charge neutrality rule,

$$2[\text{Cu}^{2+}] = [\text{CuX}_3^-] \quad (7)$$

Now, on expressing $[\text{CuX}_2]$ and $[(\text{CuX}_2)_2]$ in terms of $[\text{Cu}^{2+}]$, according to Eqs. (5) and (6),

$$[\text{CuX}_2]^3 = 4[\text{Cu}^{2+}]^3 f_i f^2 / K_d \text{ or,}$$

$$[\text{CuX}_2] = (4f_i f^2 / K_d)^{1/3} [\text{Cu}^{2+}] \quad (8)$$

and

$$[(\text{CuX}_2)_2] = K_D [\text{CuX}_2]^2 \quad (9)$$

From the principle of mass balance, the total concentration, c_{CuX_2} , can be written as

$$c_{\text{CuX}_2} = [\text{Cu}^{2+}] + [\text{CuX}_3^-] + [\text{CuX}_2] + 2[(\text{CuX}_2)_2] \quad (10)$$

by substituting Eq. (7) in Eq. (10)

$$c_{\text{CuX}_2} = [\text{Cu}^{2+}] + 2[\text{Cu}^{2+}] + [\text{CuX}_2] + 2[(\text{CuX}_2)_2] \quad (11)$$

and on substituting Eqs. (8) and (9) in the above equation one gets

$$c_{\text{CuX}_2} = 3[\text{Cu}^{2+}] + (4f_i f^2 / K_d)^{1/3} [\text{Cu}^{2+}] + 2K_D [(4f_i f^2 / K_d)^{1/3} [\text{Cu}^{2+}]]^2 \quad (12)$$

and on rearrangement of Eq. (12), the total concentration, c_{CuX_2} , can be represented in terms of $[\text{Cu}^{2+}]$, and the constants K_d and K_D :

$$c_{\text{CuX}_2} = [\text{Cu}^{2+}] \times [3 + (4f_i f^2 / K_d)^{1/3} + 2K_D (4f_i f^2 / K_d)^{2/3}] \quad (13)$$

According to Eq. (13), for a series of assumed values of $[\text{Cu}^{2+}]$, it is possible to generate the corresponding values of c_{CuX_2} using $3[\text{Cu}^{2+}]$ as the ionic strength, activity coefficients f_i and f calculated from the Debye–Huckel equation and a given set of values for K_d and K_D .

2.1.3. Calculation of Λ_C

The molar conductance, Λ_C , for any given salt concentration, c_{CuX_2} , can be obtained from the equilibrium concentration of all relevant ionic species and available estimates of their mobilities:

$$\Lambda_C = \frac{\sum c_i \lambda_i}{c_{\text{CuX}_2}} \quad (14)$$

or simply

$$\Lambda_C = \frac{[\text{Cu}^{2+}] \lambda_{\text{Cu}^{2+}} + [\text{CuX}_3^-] \lambda_{\text{CuX}_3^-}}{c_{\text{CuX}_2}} \quad (15)$$

where $\lambda_{\text{Cu}^{2+}}$ and $\lambda_{\text{CuX}_3^-}$ are the molar conductivities of Cu^{2+} and CuX_3^- , respectively.

Combining Eqs. (7) and (13) one can rewrite Eq. (15) as:

$$A_C = \frac{[\text{Cu}^{2+}]\lambda_{\text{Cu}^{2+}} + [\text{CuX}_3^-]\lambda_{\text{CuX}_3^-}}{[\text{Cu}^{2+}][3 + (4f_i^2/K_d)^{1/3} + 2K_D(4f_i^2/K_d)^{2/3}]} \quad (16)$$

which, on further simplification, becomes

$$A_C = \frac{\lambda_{\text{Cu}^{2+}} + [\text{CuX}_3^-]\lambda_{\text{CuX}_3^-}}{[3 + (4f_i^2/K_d)^{1/3} + 2K_D(4f_i^2/K_d)^{2/3}]} \quad (17)$$

Finally, Eq. (17) is used to calculate the molar conductance of CuCl_2 and CuBr_2 solutions in 20 wt.% PC + EC for a given salt concentration. A series of plots of $\log A_0$ versus $-\log c_{\text{CuX}_2}$ were constructed with different sets of values K_d and K_D over an assumed range of $[\text{Cu}^{2+}]$ using $3.12 \text{ S cm}^2 \text{ mol}^{-1}$ (twice the limiting molar conductivity of $1/2 \text{ Cu}^{2+}$ ions in 20 wt.% PC + EC as obtained in the present work) for $\lambda_{\text{Cu}^{2+}}$. Values of 13.0 and $11.72 \text{ S cm}^2 \text{ mol}^{-1}$ were found for $\lambda_{\text{CuX}_3^-}$ as half of $\lambda_{\text{Cl}^-}^0$ and $\lambda_{\text{Br}^-}^0$, respectively (unpublished work from our lab), in 20 wt.% PC + EC at 25°C . The mobility of the CuX_3^- species is reduced to half on association of X^- with CuX_2 species. The particular set of values of K_d and K_D , which proves the best fit with the experimental plot of interest is finally accepted as representative for a given system.

2.2. Potentiometric studies

The determination of the standard potential, $E_{\text{Cu}^{2+}/\text{Cu}}^\circ$, in 20 wt.% PC + EC was based on the measurements of the cell:

$\text{Cu}/\text{CuX}_2/\text{HgCl}_2(\text{s})$ in 20 wt.% PC + EC/Hg

(where $\text{CuX}_2 = \text{Cu}(\text{ClO}_4)_2$, CuCl_2 and CuBr_2 solutions in 20 wt.% PC + EC)

The emf, E , of the cell can be expressed as

$$E = E_{\text{ref.}} + E_j - [E_{\text{Cu}^{2+}/\text{Cu}}^\circ + (0.05916/n)\log a_{\text{Cu}^{2+}}] \quad (18)$$

where $E_{\text{ref.}}$ is the potential of the reference electrode and E_j is any liquid-junction potential that may be involved. The value of the sum $E_{\text{ref.}} + E_j$ is referred to as $E'_{\text{ref.}}$.

The Eq. (18) can be rewritten as

$$E_{\text{ref.}} - E_{\text{Cu}^{2+}/\text{Cu}}^\circ = E + 0.02958\log a_{\text{Cu}^{2+}} \quad (19)$$

In order to calculate $E_{\text{Cu}^{2+}/\text{Cu}}^\circ$ from the emf of the cell using Eq. (19), knowledge of the activity of Cu^{2+} for a given concentration of the copper salt is required, which was obtained from conductivity data.

In the case of $\text{Cu}(\text{ClO}_4)_2$ in 20 wt.% PC + EC, the total salt concentration corresponding to an arbitrary value of $[\text{Cu}^{2+}]$ can be calculated on the basis of equilibria (1) and (2), from which one can write K_{A_1} and K_{A_2} as:

$$K_{A_1} = \frac{a_{\text{CuClO}_4^+}}{a_{\text{Cu}^{2+}} + a_{\text{ClO}_4^-}} = \frac{[\text{CuClO}_4^+]}{[\text{Cu}^{2+}]f_i[\text{ClO}_4^-]} \quad (20)$$

$$K_{A_2} = \frac{a_{\text{Cu}(\text{ClO}_4)_2}}{a_{\text{CuClO}_4^+} + a_{\text{ClO}_4^-}} = \frac{[\text{Cu}(\text{ClO}_4)_2]}{[\text{CuClO}_4^+][\text{ClO}_4^-]f} \quad (21)$$

From the charge neutrality rule

$$[\text{ClO}_4^-] = 2[\text{Cu}^{2+}] + [\text{CuClO}_4^+] \quad (22)$$

which can be written further as

$$[\text{ClO}_4^-] = 2[\text{Cu}^{2+}]/\{1 - K_{A_1}[\text{Cu}^{2+}]f_i\} \quad (23)$$

and from the principle of mass balance, the total salt concentration, $c_{\text{Cu}(\text{ClO}_4)_2}$, can be given as

$$c_{\text{Cu}(\text{ClO}_4)_2} = [\text{Cu}^{2+}] + [\text{CuClO}_4^+] + [\text{Cu}(\text{ClO}_4)_2] \quad (24)$$

Now using Eqs. (20) and (21) one can write

$$[\text{CuClO}_4^+] = K_{A_1}[\text{Cu}^{2+}][\text{ClO}_4^-]f_i \quad (25)$$

and

$$[\text{Cu}(\text{ClO}_4)_2] = K_{A_1}K_{A_2}[\text{Cu}^{2+}][\text{ClO}_4^-]^2f_i^2 \quad (26)$$

Substituting Eqs. (25) and (26) into Eq. (24); one gets

$$c_{\text{Cu}(\text{ClO}_4)_2} = [\text{Cu}^{2+}] + K_{A_1}[\text{Cu}^{2+}][\text{ClO}_4^-]f_i + K_{A_1}K_{A_2}[\text{Cu}^{2+}] \times [\text{ClO}_4^-]^2f_i^2 \quad (27)$$

where K_{A_1} is equal to 17.25, as obtained from treatment of conductivity data of $\text{Cu}(\text{ClO}_4)_2$ in 20 wt.% PC + EC by the Fuoss and Edelson method and K_{A_2} is taken as unity because of complete dissociation as assumed in the conductance-data treatment.

The equilibrium concentration of ClO_4^- can be calculated for a range of assumed values of $[\text{Cu}^{2+}]$ from Eq. (23), which also determines the ionic strength ($I = 3[\text{Cu}^{2+}]$), and thus the activity coefficients f and f_i can be obtained. Now, substituting the assumed value of $[\text{Cu}^{2+}]$ and the corresponding values of $[\text{ClO}_4^-]$, f , f_i and K_{A_1} in Eq. (27), one can calculate the total concentration, $c_{\text{Cu}(\text{ClO}_4)_2}$. Thus the arbitrary value of $a_{\text{Cu}^{2+}}$ corresponding to the total salt concentration can be obtained.

Similarly, the values of $a_{\text{Cu}^{2+}}$ for various concentrations of CuCl_2 and CuBr_2 can be generated on the basis of Eq. (12) after incorporating the values of K_d and K_D (as obtained from conductivity data for CuCl_2 in 20 wt.% PC + EC in Section 2.1.2) and the activity coefficient f and f_i . The results of such activity calculations for the copper salts are organized in the form of plots of $-0.02958\log a_{\text{Cu}^{2+}}$ versus $-\log c_{\text{CuX}_2}$.

In the present approach, the emf–concentration data are organized in the form of E versus $-\log c_{\text{CuX}_2}$ plots and compared with the respective generated plots of $-0.02958\log a_{\text{Cu}^{2+}}$ versus $-\log c_{\text{CuX}_2}$. The comparison is made at four different concentrations. The sum of the observed emf, E , of the cell and the calculated value of $0.02958\log a_{\text{Cu}^{2+}}$ for a given total salt concentration, c_{CuX_2} , would be a measure of $(E'_{\text{ref.}} - E_{\text{Cu}^{2+}/\text{Cu}}^\circ)$. From the knowledge of $E'_{\text{ref.}} = 0.383 \text{ V}$ versus SHE in 20 wt.% PC + EC at 25°C [16], it is possible to calculate $E_{\text{Cu}^{2+}/\text{Cu}}^\circ$ versus SHE in 20 wt.% PC + EC at 25°C .

2.3. Voltammetric studies

The voltammetric behavior of copper(II) perchlorate, copper(II) chloride and copper(II) bromide has been investigated in 20 wt.% PC+EC by sampled dc (SDC), differential pulse voltammetry (DPV) and cyclic voltammetry (CV). A three-electrode assembly comprising a microplatinum working electrode (area = 9.13×10^{-3} cm²), a platinum counter electrode and Hg/HgCl₂ (s) in 20 wt.% PC+EC reference electrode was used for the study.

The sampled dc voltammograms for these copper salts in 20 wt.% PC+EC consisted of one reduction wave. The half-wave potential, $E_{1/2}$, values for all three salts are very close to each other with an average value of 0.095 V versus the Hg/HgCl₂(s) in 20 wt.% PC+EC reference electrode. The differential pulse voltammograms (DPV) recorded for the solutions of copper salts in 20 wt.% PC+EC in the concentration range 3×10^{-4} – 5×10^{-3} M, gave linear plots of peak current versus concentration. The cyclic voltammograms showed well-defined cathodic and anodic peaks.

The plots of $\log(I/I_d - I)$ versus E_{app} were found to be linear, indicating that the process is diffusion controlled. The half-wave potential, $E_{1/2}$, in SDC and the peak potential, E_p , in DPV are found to have the following relation:

$$E_{1/2} = E_p + \Delta E/2 \quad (28)$$

(ΔE = pulse amplitude)

The following equation [21] was used to calculate the standard electrode potential, E° , using the obtained value of $E_{1/2}$:

$$E_{1/2} = E^\circ + (RT/nF)\ln(D_R/D_O)^{1/2} \quad (29)$$

where D_R and D_O are the diffusion coefficients of the reduced and oxidised species, respectively. As D_R is unity, D_O is calculated from the CV curve parameters using the Randles and Sevcik equation. This D_O value is then substituted into Eq. (29) to give E° of the system.

3. Experimental

3.1. Solvents and reagents

The purification of PC and EC and the preparation of the 20 wt.% PC+EC mixture were carried out as described elsewhere [15,16].

Copper(II) perchlorate was prepared by dissolving copper(II) carbonate (E. Merck) in a slight excess of 70% perchloric acid (Loba-GR). On evaporation of this solution, crystals of hydrated copper perchlorate separated out, which were recrystallised thrice with con-

ductivity water and dried in a vacuum oven to obtain anhydrous copper perchlorate.

Copper(II) bromide and copper(II) chloride were prepared by a standard procedure [22].

Tetraethylammonium perchlorate was prepared by adding a slight excess of perchloric acid (70% Loba-GR) to tetraethylammonium hydroxide (Sisco). The precipitate was washed several times with water to obtain the filtrate free from acid. The product thus obtained was recrystallised twice from water and dried in vacuum and used as supporting electrolyte.

Mercury used for the preparation of the reference electrode was triply distilled under reduced pressure. The stock solutions of Cu(ClO₄)₂, CuCl₂ and CuBr₂ in 20 wt.% PC+EC were analyzed for copper by standard EDTA titrations. Stock solutions were prepared by dissolving weighed amounts of the substance in the desired volume of solvent at room temperature. In conductance measurements, working solutions were prepared by adding aliquots of stock solutions to a known volume of the solvent using a microliter syringe burette. The transfer of solutions and other manipulations were carried out with minimum exposure to air.

3.2. Procedures

3.2.1. Conductivity measurements

All conductivity measurements were made in a conventional way using a dip-type cell (Cell constant 1.080 cm⁻¹) at 25 ± 0.05 °C. A Toshniwal digital conductivity meter type CLO 1.10A was used in the measurements. All reported conductivities refer to a frequency of 200 Hz; and no significant change in conductivities was found on using a different frequency (3 KHz). All molar conductivities have been calculated after correcting for the solvent conductance.

3.2.2. Potential measurements

3.2.2.1. Cu²⁺ indicator electrode. A platinum wire (1.5 cm long, 16 gauze) sealed into a Pyrex glass tube was cleaned by treating with hot aqua regia and then electroplated with copper by electrolyzing 0.1 M copper(II) perchlorate solution at a low current density using a platinum anode encased in a glass frit. The plated electrodes, which were usually prepared in batches of 5–6 electrodes at a time under the same conditions, were washed over 2 days by repeatedly suspending them in fresh conductivity water to leach out the last traces of the plating solution. The electrodes were stored in conductivity water until use. They were rinsed thoroughly with conductivity water and then with reagent-grade C₃H₆O followed by air-drying before placing in the experimental solution.

Table 1
Results of conductivity measurements for $\text{Cu}(\text{ClO}_4)_2$, CuCl_2 and CuBr_2

$c_{\text{Cu}(\text{ClO}_4)_2}/\text{mM}$	$\Lambda_c/\text{S cm}^2 \text{ mol}^{-1}$	$c_{\text{CuCl}_2}/\text{mM}$	$\Lambda_c/\text{S cm}^2 \text{ mol}^{-1}$	$c_{\text{CuBr}_2}/\text{mM}$	$\Lambda_c/\text{S cm}^2 \text{ mol}^{-1}$
0.318	50.911	0.134	5.231	0.254	3.463
0.634	49.542	0.333	5.083	0.654	3.458
1.258	47.615	0.659	4.798	0.912	3.409
2.024	46.936	0.978	4.691	1.295	3.390
3.072	44.987	1.292	4.685	1.924	3.362
4.521	43.617	1.599	4.582	2.785	3.285
7.261	41.096	2.020	4.506	4.091	3.244
9.808	39.090	3.054	4.217	5.787	3.110
13.310	36.965	4.125	4.001	8.618	3.090
19.363	34.989	6.057	3.802	10.551	2.958
22.821	34.021	8.701	3.806	14.052	2.818

3.2.2.2. *Reference electrode.* The preparation and use of the $\text{Hg}/\text{HgCl}_2(\text{s})$ in 20 wt.% PC+EC reference electrode are given in our earlier article [16].

An Equip-Tronics digital potentiometer model EQ DGS was used for the emf measurements. As a general procedure, the emfs were noted after every 2–3 min for all the cells over a period of about 20 min; the reported potentials are averages of the last two readings which normally agreed to ± 0.5 mV or better. The measured cell potentials were reproducible to ± 2 mV.

3.2.3. Voltammetric measurements

The voltammetric system used for the studies was an EG&G 264 A system with a model 303 electrode assembly and x–y chart recorder RE 0089 supplied by Princeton Applied Research (PAR) USA. The system has the capabilities for sampled dc, differential pulse voltammetry and CV. A three-electrode cell comprising platinum working and counter electrodes and a $\text{Hg}/\text{HgCl}_2(\text{s})$ in 20 wt.% PC+EC reference electrode was used for the measurements.

A voltammogram of the solution containing the supporting electrolyte was run before every experiment and the analyte concentration in the experimental solution was achieved by adding aliquots from a stock solution of the analyte prepared in the supporting electrolyte solution. All test solutions were purged with dry nitrogen for at least 10–12 min to remove oxygen.

4. Results and discussion

The conductivity data analysis for a $\text{Cu}(\text{ClO}_4)_2$ solution in 20 wt.% PC+EC according to the Fuoss and Edelson method resulted in a plot Λ^* versus χ (Fig. 1). From this plot, the derived values of the limiting equivalent conductance, Λ_o , and the first step association constant, K_A , for $\text{Cu}(\text{ClO}_4)_2$ in 20 wt.% PC+EC are $\Lambda_o = 26.25 \text{ S cm}^2 \text{ mol}^{-1}$ and $K_A = 17.25$, respectively. The association constant ($K_A = 98.53$) in pure PC [7] is higher than in this medium as its relative permittivity is lower than that of this mixture. It can

Table 2
Evaluation of the standard potential of the reaction $\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$ in 20 wt.% PC+EC vs. SHE at 25 °C

CuX_2	$-\log c_{\text{CuX}_2}/\text{mM}$	$-0.02958 \log a_{\text{Cu}^{2+}}/V$ calculated	E/V experimental	$E_{\text{Cu}^{2+}/\text{Cu}}^\circ/\text{V}$ vs. SHE
Copper perchlorate	2.0	0.0565	0.0415	0.3976
	2.5	0.0725	0.0570	0.3981
	3.0	0.0885	0.0730	0.3981
	4.0	0.1200	0.1040	0.3986
	Average $E^\circ = 0.3981 \pm 0.0005$			
Copper chloride	2.0	0.0595	0.0445	0.3976
	2.5	0.0740	0.0580	0.3986
	3.0	0.0885	0.0715	0.3996
	4.0	0.1170	0.0990	0.4006
	Average $E^\circ = 0.3991 \pm 0.0015$			
Copper bromide	2.0	0.0595	0.0405	0.4016
	2.5	0.0740	0.0550	0.4016
	3.0	0.0890	0.0705	0.4011
	4.0	0.1180	0.1000	0.4006
	Average $E^\circ = 0.4012 \pm 0.0006$			

be seen from Fig. 1 that the plot is non-linear as the concentration increases. This is because of the failure of the approximation used in the treatment. The value reported for K_A is obtained from the tangent in the region of x values before the divergence from a straight line. The value of $\lambda_{\text{Cu}^{2+}}^0$ is calculated by using $\lambda_{\text{ClO}_4^-}^0 = 24.69$ [15] and is found to be $1.56 \text{ S cm}^2 \text{ mol}^{-1}$.

The conductivity data for the three copper salts are given in Table 1. An examination of these data reveals that there is not much change in the conductivity of the copper halides with increase in concentration and also that the values are low compared to those of the perchlorate salt. This indicates that the copper halides behave as weak electrolytes in this medium. Hence, the conductivity data were treated by considering the equilibria involving complicated dissociation and dimer formation (Section 2.1.2). The results on conductivity measurements of CuCl_2 in the form of $\log A_c$ versus $-\log c_{\text{CuX}_2}$ are given in Fig. 2, along with the best-fit plot generated by the present treatment. The values of K_d and K_D for CuCl_2 are 0.19 and 160 and for CuBr_2 , 0.039 and 28, respectively. The almost exact correspondence between the experimental and calculated plots of $\log A_c$ versus $-\log c_{\text{CuX}_2}$ (Fig. 2) suggest the reliability of the proposed equilibria (Eqs. (3) and (4)) and the validity of the representation of the salt system by the equilibrium constant K_d and dimerization constant K_D . The effect of relative permittivity is seen here too. For example, in pure PC [7], the values of K_d and K_D for CuCl_2 are 0.015 and 600, respectively; i.e. lower the relative permittivity, the lower is the dissociation and the higher is the dimerization.

The emf–concentration data of CuBr_2 in the form of E versus $-\log c_{\text{CuX}_2}$ plots and the corresponding calculated plots of $-0.02958 \log a_{\text{Cu}^{2+}}$ versus $-\log c_{\text{CuX}_2}$ are shown in Fig. 3. Similar plots were obtained for $\text{Cu}(\text{ClO}_4)_2$ and CuBr_2 . It is evident from these figures that the plots of E versus $-\log c_{\text{CuX}_2}$ are linear over the concentration range studied and overall consistent agreement between the experimental and the corresponding calculated plots is obtained. Hence, this provides further verification of the overall reliability of

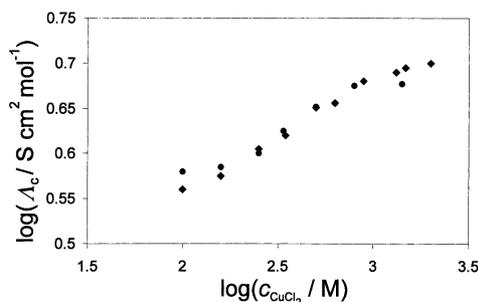


Fig. 2. Experimental (●) and calculated (◆) plot of $\log A_c$ vs. $-\log c_{\text{CuCl}_2}$.

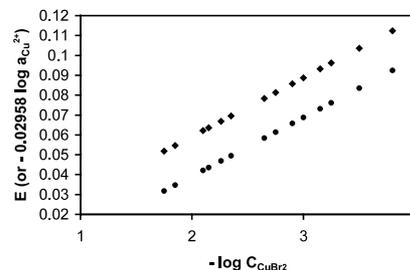


Fig. 3. Experimental (●) and calculated (◆) plot of E (or $-0.02958 \log a_{\text{Cu}^{2+}}$) vs. $-\log c_{\text{CuBr}_2}$.

Table 3

Summary of cyclic voltammetric results obtained for copper perchlorate, copper chloride and copper bromide in 20 wt.% PC+EC

Parameters	$\text{Cu}(\text{ClO}_4)_2$	CuCl_2	CuBr_2
Concentration/mM	5.104	2.229	1.553
E_{pc}/V	0.01	-0.04	-0.02
E_{pa}/V	0.35	0.34	0.36
E_f/V	0.17	0.19	0.19
$I_{\text{pc}}/\mu\text{A}$	10.0	2.8	3.0
$I_{\text{pa}}/\mu\text{A}$	18.0	4.3	4.8
$E_{\text{Cu}^{2+}/\text{Cu}}$ vs. SHE	0.394	0.390	0.397

the solution equilibria proposed. Table 2 gives the average values of $E_{\text{Cu}^{2+}/\text{Cu}}^0$ obtained for $\text{Cu}(\text{ClO}_4)_2$, CuCl_2 and CuBr_2 salts in 20 wt.% PC+EC by the potentiometric method. The plots of $\log(I/I_d - I)$ versus E_{app} as obtained by SDC were found to be linear, indicating that the process is diffusion controlled. A summary of the results obtained by CV is given in Table 3.

The comparison of the standard potential, E° , values obtained by the potentiometric and voltammetric methods is given in Table 4. The values are seen to be in good agreement with each other, indicating the consistency and reliability of both the methods.

Finally, the overall average value of $E_{\text{Cu}^{2+}/\text{Cu}}^0$ is found to be $0.397 \pm 0.003 \text{ V}$ versus SHE in 20 wt.% PC+EC at 25°C .

Table 4

Summary of the standard potential, E° , of the reaction $\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}(\text{s})$ by potentiometry and voltammetry in 20 wt.% PC+EC

Method	E° vs. SHE in 20 wt.% PC+EC		
	$\text{Cu}(\text{ClO}_4)_2$	CuCl_2	CuBr_2
Potentiometry	0.398	0.399	0.401
Voltammetry	0.394	0.390	0.397

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