Preparation of New Copper (II) – PVC Membrane Sensor Based on Phenyl Disulfide

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Abstract:

Membrane of phenyl disulfide as an ionic membrane carrier in poly (vinyl chloride) (PVC) based matrix have been used for preparing Copper selective electrode. The electrode exhibits according to Nernst equation response for Cu^{2+} ions over a wide concentration range from 1.0×10^{-6} to 1.0×10^{-1} M with a slope equal to 29.2 mV/decade, r=0.9988 and a detection of limit 4.4×10^{-7} M. The response time measured was 8 second. It was found to be selective and useable within the pH range of (2.0-7.0) and the temperature equal to 293 K to 303 K. The lifetime of membrane sensor prepared could be used for at least 3 months. The electrode was successfully used as an indicator electrode in potentiometric titration of Copper ions with EDTA.

الخلاصة :

غشاء الناقل الايوني phenyl disulfide في قالب البولي (فنيل كلورايد) (PVC) استخدم لتحضير قطب النحاس الانتقائي . أظهر القطب استجابة حسب معادلة نيرنست لايونات Cu^{2+} ضمن مدى تراكيز تراوحت بين (1.0×10^{-1}-1.0×10^{-6}) مولاري وبميل مقداره 29.2 decade\mV وقيمة r تساوي 0.9988 وحد تحسس مقداره 4.4×10^{-7} مولاري . وكان زمن الاستجابة 8 ثواني . تم إيجاد الانتقائية ومدى الدالة الحامضية المناسبة والتي تراوحت ما بين (2.0-7.0) ودرجة الحرارة مساوية الى (293-303) كلفن. وكان العمر الزمني للغشاء المحضر ثلاثة اشهر . وتم استعمال القطب بنجاح كقطب دليل في التسحيح الجهدي لايونات النحاس مع EDTA .

Keywords: Copper selective electrode, membrane, sensor, response time, lifetime, potentiometric titration.

Introduction:

For ecological assessments and comprehension the dissemination of pollutants environmental monitoring of heavy metals is of great importance (1). Copper is one of the heavy metals that need precise control in the environment that has a biological action at low doses (1 mg/kg) and a toxic effect when ingested in larger quantities (3 – 4 mg/kg) (2,3). While, copper deficiency causes anemia(4). Copper could catalyze oxidation of fatty acid chains, exerting a deleterious influence on shelf life and nutritional value (5). That's why, having an efficient and fast method for the determination of this ion is necessary. Various instrumental techniques and methods such as plasma mass spectrometry (6), flame photometry (7), voltammetry (8), UV-Vis spectrometry (9), atomic absorption spectrometry (10), chromatography (11) and flow injection (12), are developed for the copper(II) quantification. However, these techniques are long-time, expensive, and require sample pretreatment and specialized persons for manipulation. On the other hand, because of simplicity, wide dynamic range and fast response of the ion-selective electrodes (ISEs) the analytical procedures that overcome the above described obstructions are provided. In comparison with the other types of ISEs, (e.g. glass, single crystal, or precipitate based electrode materials), the modern solvent polymer membrane based devices represent a generic approach to chemical sensing (13).
Potentiometric measurements with copper ion selective electrode allow the direct determination of free Cu^{2+} ion concentration in aqueous samples. Ion-selective electrodes (ISEs) based on ionophores are widely used (14-25) and plasticized poly (vinyl chloride) (PVC) membrane ISEs based on several kinds of neutral carriers. An important requirement for preparation of an ion selective

sensor is that membrane electroactive material should have high lipophilicity and strong affinity for a target metal ion and poor affinity to the others (26). It is well known that coordination abilities of ligands, containing sulfur atoms, are very selective to the transition metal ions (27,28). Some Cu(II) selective sensors based on macrocyclic, non-macrocyclic carriers such as thioethers, dithiocarbamates, thiohydrazone, thiosemicarbazone, calixarenes and Schiff bases have been described (29-41). However, most of these show some limitations in their working activity range, selectivity, response time, pH range and lifetime. Thus, the development of reliable sensing ion selective sensors for copper ions is therefore, of considerable importance for environment and human health. To improve the analytical selectivity, it is essential to search novel carrier compounds that would interact with copper ion with high selectivity.

In this work, sulphur-containing ligands have received continuous attention as a platform for the construction of a number of selective and efficient electrodes, the use of phenyl disulfide (PD) as an ionophore are reported in the construction of a Copper(II)-PVC membrane electrode and studied the characteristic and properties of selective electrode.

Experimental Part:

1- Materials:

Reagent grade *o*-nitrophenyl octyl ether (*o*-NPOE), dibutyl phthalate (DBP), dioctyl phthalate (DOP), tri-*n*-butylphosphate (TBP), acetophenone (AP), benzyl acetate (BA), phenyl disulfide (PD), tetrahydrofuran (THF) and high relative molecular weight PVC. The nitrate salts of the cations used (all from Merck) were of the highest purity available. (0.1 M) stock solutions were prepared by dissolving metal nitrates in double distilled water. The working solutions of different concentration were prepared by diluting stock solutions. The pH adjustments were made by the addition of HNO_3 or NaOH diluted solutions.

2- Apparatus:

All potentiometric measurements were carried out with the following assembly:

Ag | AgCl(satd.) | KCl(satd.) | internal solution (1.0×10^{-1} *M* $Cu(NO_3)_2$) *| PVC membrane | test solution | KCl(satd.) |* Hg_2Cl_2*(satd.) | Hg*

A pH-inolab 720 pH/mV meter was used for the potential and the pH measurements.

3- Preparation of Membrane and Electrodes:

The general procedure to prepare the PVC membrane was to mix thoroughly 3.0 mg of ionophore (PD), 60 mg of plasticizer (*o*-NPOE), 30 mg of powdered PVC and 10.0 mg of $Cu(NO_3)_2$ in 9 mL of THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A pyrex tube (8-10 mm) was dipped into the mixture for about 5 second so that a nontransparent membrane of about 0.5 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 12 h. The tube was then filled with internal filling solution (0.1 M $Cu(NO_3)_2$). The electrode was finally conditioned by soaking in 0.5 M $Cu(NO_3)_2$ solution for 48 h. A silver/ silver chloride wire was used as an internal reference electrode; it is shown in Figure 1.

4- Selectivity:

The selectivity coefficient ($K_{Cu,J}$) of the electrode towards different cationic species (J^{n+}) was determined using the mixed solution method (42, 43). The mixed solution method was used according to the following equation:

$$K^{Pot}_{Cu,J}\, a_J^{(1/Zj)} = a_{Cu}(anti\log\frac{E_2 - E_1}{RT/F}) - a_{Cu}$$

Where E_1 is the potential of a known volume of solution containing Cu^{2+} ions at (1×10^{-5} M) of a_{Cu}, E_2 is the potential of the Cu^{2+} solution with a known volume of interfering ions at (1×10^{-4}-1×10^{-1}) M. R is the gas constant, T is the temperature in Kelvin, and F is Faraday’s constant.

Results and Discussion:

Phenyl disulfide (PD) it is shown in Figure 2, the ionophore used to construct a membrane for potentiometric measurements (44,45). The results are summarized in (Table 1). Several plasticizers including *o*-NPOE, DBP, DOP, TBP, AP and BA, which are often used with PVC membrane electrodes, were evaluated. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the inophore molecules and the state of ligands (46), it is expected to play an important role in determining the ionselective characteristics. As it is seen from Table 1, among different plasticizers examined, (*o*-NPOE) results in the best sensitivity, it is shown in Figure 3(a,b). The dependence of the electrode response (slope and detection limit) on the amount of carrier was also examined and is shown in Figure 4. In spite of these considerations, a carrier content of 3.0 mg was chosen as the optimum condition (No. 4, Table 1), because the surface condition of the PVC membrane deteriorated as a result of decreasing and increasing the carrier content (1.0 and 4.0 mg, respectively). The plasticizer/PVC ratio of 1.0-3.0 was examined. The membranes prepared with a plasticizer/PVC ratio of about 2.0 were found to have the best sensitivity (47,48), with a slope of 29.2 mV per decade over a wide concentration range (Figure 5).

1- The concentration range, the slope and detection limit:

The electromotive force (emf) response of the proposed Cu^{2+} sensor (prepared under optimal membrane ingredients) indicates a rectilinear range from $1.0x10^{-6}$ to $1.0x10^{-1}$ M. The slope of the calibration curve was 29.2 mV/decade. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration curve, was $4.4x10^{-7}$M.

2- The effect of internal solution:

The influence of the concentration of internal solution on the potential response of the Cu^{2+} ion-selective electrode was studied. The concentration of copper nitrate was changed from $1.0x10^{-1}$ to $1.0x10^{-3}$ M and the emf-pCu plot was obtained. It was found that the variation of the concentration of internal solution does not any significant difference in the electrode's potential response, except for an expected change in the intercept of the resulting near-Nernstein plots. A 0.1 M concentration of the reference solution is quite appropriate for smooth functioning of the system (Figure 6).

3- Response time and stability:

Optimum conditioning time for the membrane sensor in a 0.5 M $Cu(NO_3)_2$ solution is 48 h. It then generates stable potentials when placed in contact with Cu^{2+} solutions. The response time measured was less than 8 s for Cu^{2+} concentrations $1.0x10^{-2}$ M. It is noteworthy that the equilibrium potentials essentially remained constant for more than 4 min, after which only a very small divergence within the resolution of the pH meter was recorded the membrane sensor prepared could be used for at least 3 months (lifetime) without any measurable divergence.

4- The effect of pH:

One of the ions present in aqueous solution is the hydrogen ion. It interferes, in many instances, with the functioning. In view of this, it is necessary to find the optimum pH range where the electrode without interference from the hydrogen ions. pH dependence of the membrane electrode works has been tested by using 0.01 M and 0.001M Cu^{2+} solutions over a pH range (1-10) (Fig.7). pH was adjusted by the addition of small drops of nitric acid (0.1 M) or sodium hydroxide (0.1 M). The potentials stay constant from pH 2.0 to 7.0. The observed increase in the potential at low pH values indicates that the ionophore responds to the hydronium ions and a drift in potential is observed which is due to the formation of $Cu(OH)_2$ at pH greater than 7 (49).

4- The effect of temperature:

The effect of temperature on the membrane electrode work has been tested by using 0.01 M and 0.001M Cu^{2+} solutions over a temperature range (278 K -323 K) (Fig.8). Temperature was adjusted by heating the solution (5 K) and measurement stability of electrode work. The potentials stay constant from temperature 293 K to 313 K, because of the stability of complex in this range of temperatures (44).

5- *Selectivity:*

The important parameter of many potentiometric ion is response to the primary ion in the presence of the other ions presence in solution, which is expressed in terms of the potentiometric selectivity constant ($K_{Cu,J}$). The values obtained for selectivity coefficients by the mixed solutions method with a mixed concentration of interference metal ion (J^{n+}) with an activity of aqueous 0.1 M solution of $Cu(NO_3)_2$ and interfering ions at ($1x10^{-4}$-$1x10^{-1}$) M, are given in (Table 2). It can be seen from these values that the electrode is characterized by a high selectivity towards copper ions with respect to alkali, alkaline earth, transition and heavy metal ions (41).

Analytical Application:

The proposed copper membrane electrode was found to work well under laboratory conditions. The sensor has been used as an indicator electrode in the titrimetric determination of copper ions. A 20 mL solution of $1.0x10^{-3}$ M Cu^{2+} was titrated against $1.0x10^{-2}$ M EDTA and the change in potential was noted and plotted in Figure 9. The titration plot obtained at pH 4.0 is of sigmoid shape and the end point corresponds to 1:1 stoichiometry of Cu–EDTA complex. Thus, the sensor can be used to determine copper by potentiometric titration (13).

Conclusion:

A PVC-membrane electrode for Cu^{2+} ions based on (PD) as ionophore, was investigated. The optimized formulation of the membrane (*i.e*. 3.0 mg PD, 30 mg PVC, 60 mg (*o*-NPOE), 10.0 mg $Cu(NO_3)_2$ resulted in a linear concentration range of $1.0x10^{-6}$-$1.0x10^{-1}$ M with a slope of 29.2 mV/decade, r=0.9988 and a limit of detection of $4.4x10^{-7}$ M. The fast response time, wide linear range, fair selectivity coefficients and long lifetime of the proposed sensor are advantageous over most of the reported Cu^{2+} selective electrodes. The proposed electrode can be used successfully as a sensor in potentiometric titrations.

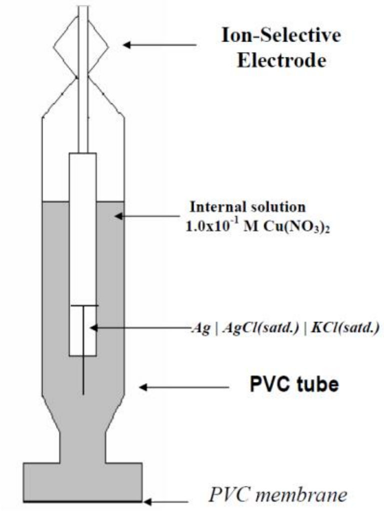

Figure 1. Structure of Copper Selective Electrode

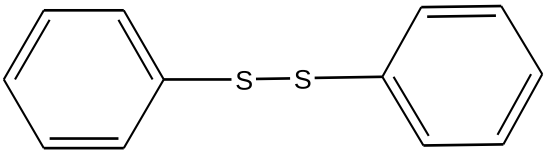

Figure 2. Structure of Phenyl Disulfide (PD)

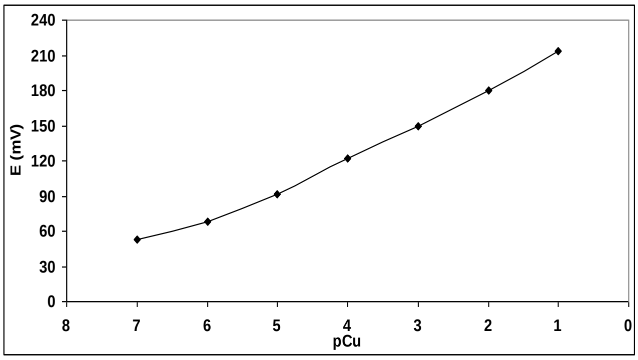

Figure 3 (a). Calibration Curve of Structure of Copper Selective Electrode

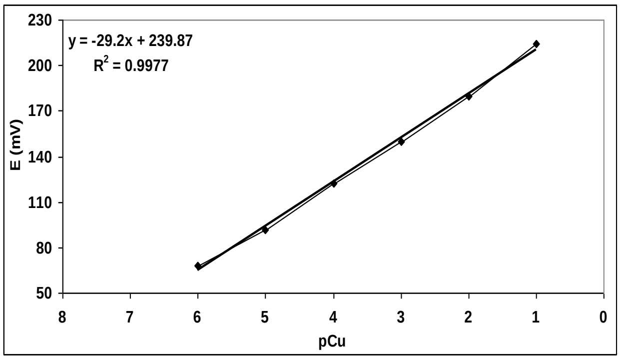

Figure 3 (b). Slope and r value of Structure of Copper Selective Electrode

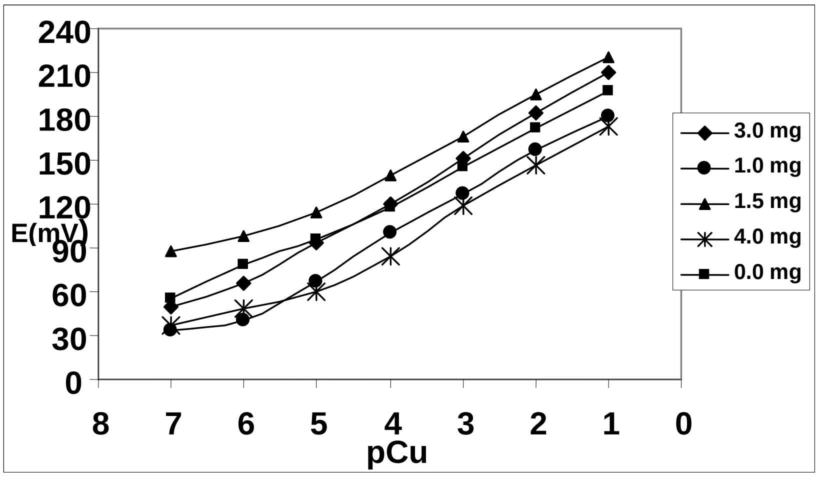

Figure 4. Effect of the content of (PD) on the response of the membrane

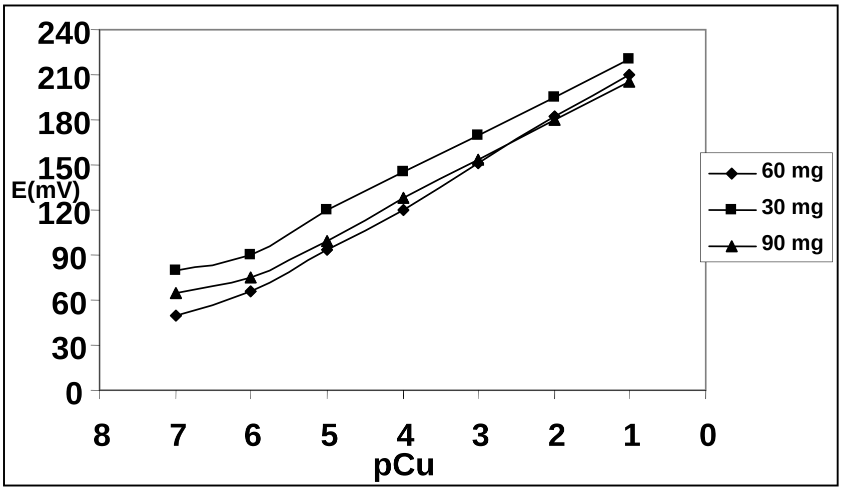

Figure 5. Effect of the content of (*o*-NPOE) on the response of the membrane

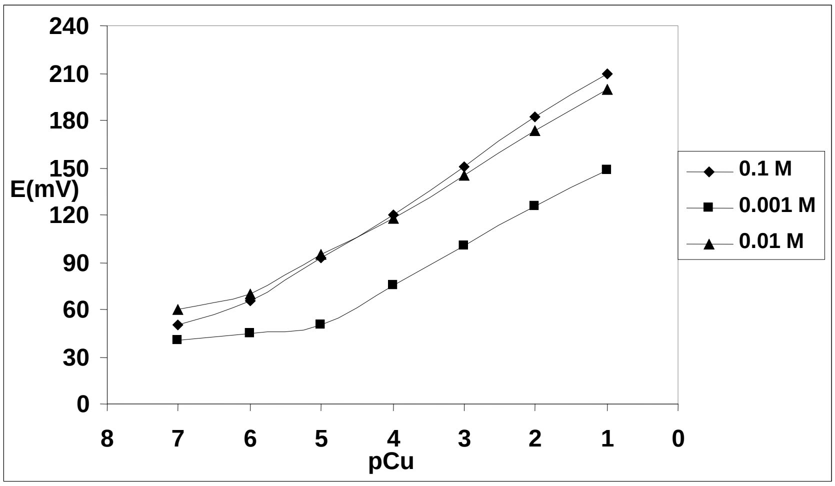

Figure 6. Effect of the internal solution on the response of the membrane

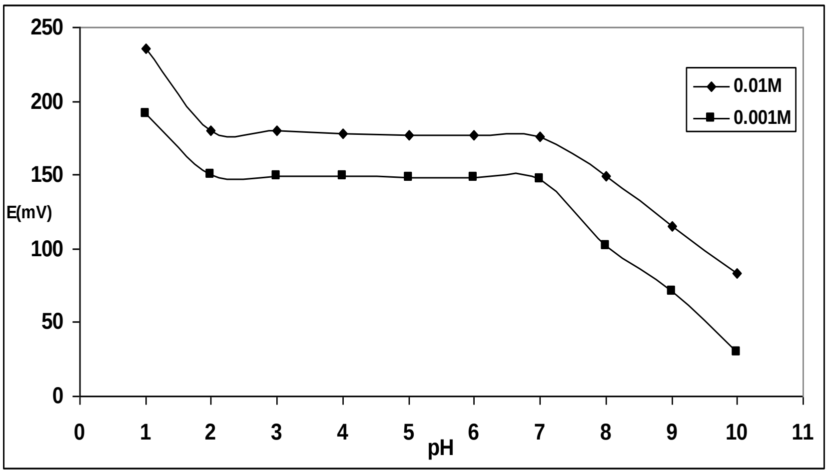

Figure 7. Effect of pH on the response of Copper Selective Electrode

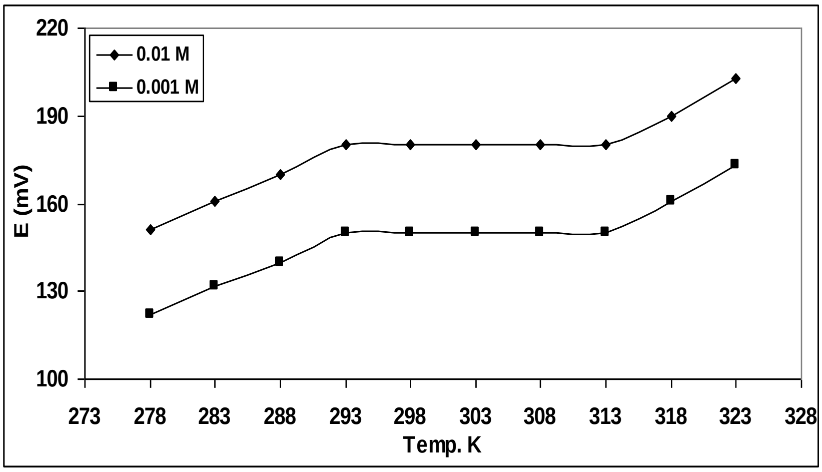

Figure 8. Effect of temperature on the response of Copper Selective Electrode

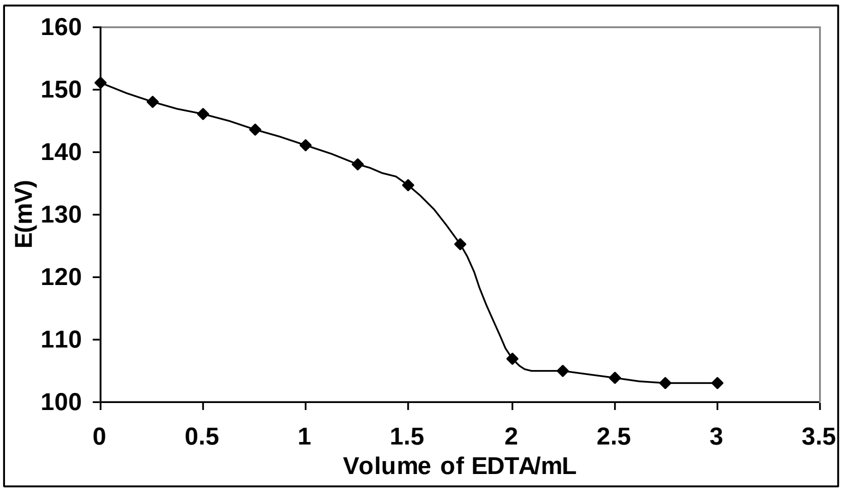

Figure 9. Potentiometric titration plot of (1.0×10^{-3}M) Cu^{2+} solution (20 mL) with EDTA (1.0×10^{-2} M)

Table 1. Optimization of the membrane ingredients

Electrode No.	Composition (mg)								Slope mV/decade
	PD	PVC	*o*-NPOE	DBP	DOP	TBP	AP	BA	
1	0.0	30	60	-	-	-	-	-	23.8
2	1.0	30	60	-	-	-	-	-	25.9
3	1.5	30	60	-	-	-	-	-	26.2
4	3.0	30	60	-	-	-	-	-	29.2
5	4.0	30	60	-	-	-	-	-	25.7
6	3.0	30	30	-	-	-	-	-	26.4
7	3.0	30	90	-	-	-	-	-	27.2
8	3.0	30	-	60	-	-	-	-	27.1
9	3.0	30	-	-	60	-	-	-	26.5
10	3.0	30	-	-	-	60	-	-	25.8
11	3.0	30	-	-	-	-	60	-	24.3
12	3.0	30	-	-	-	-	-	60	22.9

Table 2. Selectivity coefficients of various interfering ions

Interfering ion	Log $K_{Cu,J}$	Interfering ion	Log $K_{Cu,J}$
H^+	-3.27	Ba^{2+}	-2.53
Li^+	-3.02	Fe^{2+}	-2.16
Na^+	-2.78	Co^{2+}	-2.48
K^+	-2.75	Ni^{2+}	-2.44
Cs^+	-2.47	Cd^{2+}	-2.71
Ag^+	-2.43	Mg^{2+}	-2.67
NH_4^+	-2.85	Zn^{2+}	-2.92
Tl^+	-2.12	Hg^{2+}	-2.95
Ca^{2+}	-2.56	Pb^{2+}	-2.76

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