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Selective Liquid-Liquid Extraction of Lead Ions Using Newly Synthesized Extractant 2-(Dibutylcarbamoyl)benzoic Acid

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A new carboxylic acid extractant, named 2-(dibutylcarbamoyl)benzoic acid, is prepared and its potential for selective solvent extraction and recovery of lead ions from industrial samples was investigated. The slope analysis indicated that the lead ions are extracted by formation of 1:2 metal to ligand complexes. The effect of the parameters influencing the extraction efficiency including kind of the organic diluent, extractant concentration, type of the salt used for ionic strength adjustment, contact time and temperature was evaluated and discussed. Under optimized conditions (aqueous phase: 5 ml, initial lead concentration 1×10^{-4} M, pH 4, sodium chloride 0.1 M; organic phase: 5 ml dichloromethane, ligand concentration 0.05 M), a quantitative ($75.2 \pm 0.8\%$) and highly selective extraction of lead ions in the presence of zinc, nickel, cobalt and cadmium ions (each 1×10^{-4} M) was achieved, after 20 min. magnetically stirring of the phases, at 25 °C. The extracted lead ions were stripped from the organic phase by diluted nitric acid (0.1 M) solution. The proposed method was successfully applied for separation of lead from industrial samples. The study of the effect of temperature allowed evaluating the thermodynamic parameters of the extraction process of lead ions by the studied extractant into dichloromethane.

Keywords: Lead ions, Solvent extraction, Selective separation, Carboxylic acid extractant, Industrial samples

INTRODUCTION

Lead has been used by man for more than 5000 years. Its role in various industry demonstrates the economically importance of lead and lead alloys [1]. As instance this metal is used for large rechargeable batteries, pigments, rolled and extruded products, cable sheathing, alloys, shot and ammunition, radiation sheeting, stabilizer and pesticides production. Beside these industrial roles, lead is known as a toxic heavy metal [2]. This metal is a major environmental and public hazard, especially for infants and children. Accumulation of lead in the vital organs of humans and animals causes intense hematological damage, brain and central nervous damage, reproduction function damage, kidney malfunction and symptoms of anemia and muscle weakness [3,4]. Due to vast application of lead and adverse

impact of this element on the environment and living organisms, determination [5-7], the removal [8-10] and recovery [11-13] of this heavy metal from industrial effluents and contaminated environmental matrices form an important interest in various industrial and environmental studies.

Solvent extraction (liquid-liquid extraction) techniques as effective, simple, inexpensive, rapid and selective analytical method are widely used for separation, purification, and removal of different target metal ions [14,15]. These techniques are applicable to both trace and macro level separation of various metal ions. The selectivity and efficiency of solvent extraction processes are mainly controlled by the extractant used. The selection of an appropriate extractant allows achieving group separation or selective separation of trace elements with high efficiencies [16].

Application of acidic ligands used in solvent extraction

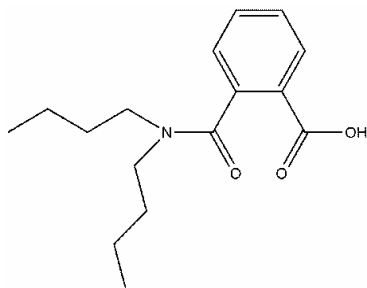
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processes offers the opportunity to tune the selectivity of the process by controlling the aqueous phase pH. Among the acidic ligands used in solvent extraction studies are carboxylic acid molecules. The properties of this type of extractants has been investigated in numerous studies reported [18-23].

Despite the potential of solvent extraction techniques for extraction-separation of metal ions, especially those based on the application of the acidic ligands, there are few investigations on the extraction of lead ions by these extractants. Among the acidic ligands used for solvent extraction of lead ions are dibenzopolyether dicarboxylic acid [24], carboxylic acid substituted calix[4]arenes [25,26] and phosphoric acid compounds [27,28].

Carbamoyl-carboxylic acid compounds [29-31] are a class of extractants in which suitable complexation ability of glycolamide binding groups is combined with the selective attitude of carboxylic acid functionalities *via* pH control of the aqueous phase. It is shown that these extractants are able to extract efficiently rare earth ions [29,30].

Considering the ability of carbamoyl-carboxylic acids for extraction of rare earth ions, in this investigation a carboxylic acid extractant named 2-(dibutylcarbamoyl)benzoic acid was synthesized and characterized. This extractant was examined for the extraction of lead(II) ions from aqueous solutions containing multiple divalent metal ions. The effect of the aqueous phase pH, organic diluent, ligand concentration, temperature and salt in the presence of other ions has been investigated and discussed. The thermodynamic parameters of the extraction of lead into the organic phase were evaluated. The presented procedure was examined for the recovery of lead ions from two real samples.



Chemical structure of 2-(dibutylcarbamoyl)benzoic acid

EXPERIMENTAL

Reagents and Materials

Phthalic anhydride (Purum, Fluka, Switzerland), dibutylamine (Purum, Fluka, Switzerland), sodium sulfate anhydrous (Puriss, Fluka, Switzerland), cyclohexane (For analysis, Merck, Germany) and *n*-hexane (For analysis, Merck, Germany), were used for preparation of the extractant 2-(dibutylcarbamoyl)benzoic acid. The organic diluents dichloromethane (Laboratory reagent grade, Mojallali, Iran), carbon tetrachloride (Extra pure, Merck, Germany) and ethyl acetate (Extra pure, Merck, Germany) were washed twice with distilled water, for removing the stabilizers and saturation with water, before being used for the extraction experiments. The stock solutions of metal nitrates (1000 mg l^{-1}) were prepared by dissolving an appropriate amount of corresponding nitrate salts with deionized water containing 0.01 M nitric acid (For analysis, Merck, Germany). $\text{Pb}(\text{NO}_3)_2$ (For analysis, Merck, Germany), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Pure, Merck, Germany), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Purum, Fluka, Switzerland), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (For analysis, Merck, Germany), $\text{Cd}_3(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ (For analysis, Merck, Germany) were the salts used for preparing the stock solutions. These solutions were standardized by complex formation titration [32]. The working solutions were prepared by diluting the stock solutions with deionized water. The pH values of these solutions were adjusted with diluted hydrochloric acid (Extra pure, Mojallali, Iran) or sodium hydroxide (For analysis, Merck, Germany) solutions. Sodium chloride and sodium nitrate (For analysis, Merck, Germany) were used for adjusting the aqueous phase's ionic strength.

Apparatus

^1H NMR measurements were performed on a FT-Bruker (AVC 250 MHz) spectrometer and data were referenced relative to residual protonated solvent (7.26 ppm for CDCl_3). FT-IR spectrum was recorded on a Unicam (Matson 1000) spectrometer. A Varian (220AA) flame atomic absorption spectrometer (air/acetylene flame) was used for metal ions determinations. A Metrohm (model 780) digital pH meter equipped with a combined glass electrode was used for the pH adjustments. Separation of the phases was assisted by a centrifuge Heraeus (model Labofuge 300).

Synthesis of 2-(Dibutylcarbamoyl)benzoic Acid

Phthalic anhydride (4 g, 26.9 mmol) was dispersed in dichloromethane (40 ml). To this solution was slowly added dibutylamine (3.96 g, 29.6 mmol) dissolved in dichloromethane (10 ml). The mixture was magnetically stirred in an ice bath overnight. The resulted clear solution was washed four times with dionized water and dried with anhydrous sodium sulfate. The solvent was evaporated and the crude product was recrystlized in cyclohexane. The white crystals were washed repeatedly with *n*-hexane and dried in air. (6.5 g, 87% yield). The purity of the product was checked by thin layer chromatography. Characterization: FT-IR (KBr, cm^{-1}); 3424 (br) (O-H), 2959 (s), 2925 (s), 2860 (m), 1849 (w), 1788 (m), 1720 (s), 1633 (s), 1594 (vs), 1462 (s), 1422 (m), 1297 (w), 1257 (vs), 1074 (vs), 874 (m), 742 (w), 650 (s), 583 (w), 534 (w). ^1H NMR; CDCl_3 , $\delta = 0.95$ (6H, t, CH_3), 1.06 (4H, m, $\text{CH}_3\text{-CH}_2$), 4, 1.68 (4H, m, $\text{N-CH}_2\text{-CH}_2$), 2.96 (4H, $\text{CH}_2\text{-N}$), 7.29-7.60 (3H, m, CHAr), 8.04 (1H, d, CH-C-COOH), 11.15 (1H, br s, -COOH) ppm. ^{13}C NMR; 125.77 MHz, CDCl_3 , $\delta = 13.54$ (CH_3), 19.77 ($\text{CH}_3\text{-CH}_2$), 28.74 ($\text{CH}_3\text{-CH}_2\text{-CH}_2$), 44.53 (N-CH_2), 126.79, 127.11, 128.56, 131.08, 133.05 and 139.28 (C-Ar), 169.69 (CON), 171.00 (COOH) ppm.

Acid Dissociation Constant of 2-(Dibutylcarbamoyl)benzoic Acid

The acid dissociation constant of the prepared extractant was determined in mixed water/ethanol (70/30) solvent by potentiometric titration with sodium hydroxide at constant ionic constant (0.1 M NaCl) and 25 °C. The pK_a value of 2-(dibutylcarbamoyl)benzoic acid was determined as 5.91 ± 0.02 . The corresponding value for acetic acid was found to be 5.15 ± 0.02 in the same mixed solvent. These values show the higher acidic strength of the studied extractant in comparison with that of acetic acid.

Solvent Extraction Experiments

Solvent extraction experiments were carried out in stoppered glass tubes immersed in a thermostated water bath (25.0 ± 0.1 °C) using equal volumes (5 ml) of the aqueous and organic phases. The ionic strength of the aqueous phases was adjusted by sodium chloride (0.1 M) and the pH of the aqueous phases was controlled by addition of hydrochloric acid or sodium hydroxide

solutions. It was confirmed that the extraction equilibrium was reached after 20 min. under continuous magnetically stirring the phases. After separation of the phases, the equilibrium pH was determined. The metal concentrations remained in the aqueous phase and that in the organic phase, after stripping with nitric acid solution (0.1 M), were determined by FAAS. The metal ion stripping from organic phase was realized by contacting equal volumes of organic phase and 0.1 M nitric acid for 20 min. under continuous magnetically stirring.

RESULTS AND DISCUSSION

Distribution of the Studied Ligand

Lipophilic nature is a decisive parameter for selecting a ligand in solvent extraction processes. In order to investigate this characteristic of the studied ligand, its distribution between dichloromethane and aqueous phase (0.1 M NaCl) as a function of aqueous phase pH, in the range 1-10, was investigated (Fig. 1). In the investigated pH range 85-100% of 2-(dibutylcarbamoyl)benzoic acid is remained in the organic phase. Although these results show suitable lipophilic nature of the studied extractant, a lower distribution of the ligand at the lower pH values than 6, can be attributed to the protonation of its amide group. However as the metal concentration is very lower than the extractant used throughout the study, it can be practically considered that the concentration of the ligand in the organic phase equals to its initial concentration.

Competitive Extraction of Pb(II), Zn(II), Ni(II), Co(II) and Cd(II) Ions

In order to evaluate the binding ability and the selectivity of the studied extractant towards Pb(II), Zn(II), Ni(II), Co(II) and Cd(II) ions, the extraction of these ions from their mixtures (1×10^{-4} M each) by 2-(dibutylcarbamoyl)benzoic acid dissolved in dichloromethane as a function of the aqueous phase pH was performed (Fig. 2). The results show an excellent selectivity of the studied extractant towards lead ions among the examined heavy metals.

Characterization of the Extracted lead Complexes

The pH dependency of the extraction lead ions by 2-

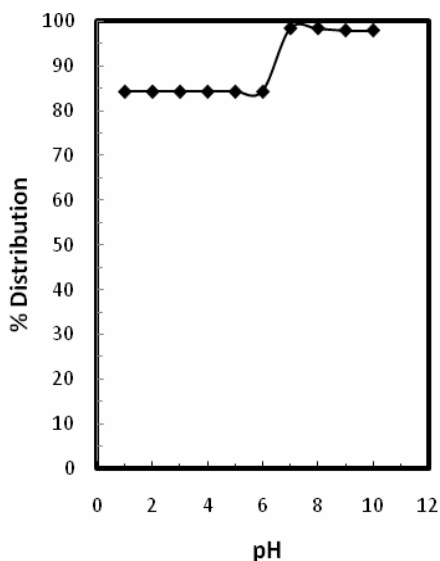


Fig. 1. Distribution of extractant 2-(dibutylcarbamoyl) benzoic acid between dichloromethane and 0.1 M sodium chloride aqueous solution as a function of pH, at 25 °C. Initial concentration of the extractant was 1×10^{-3} M.

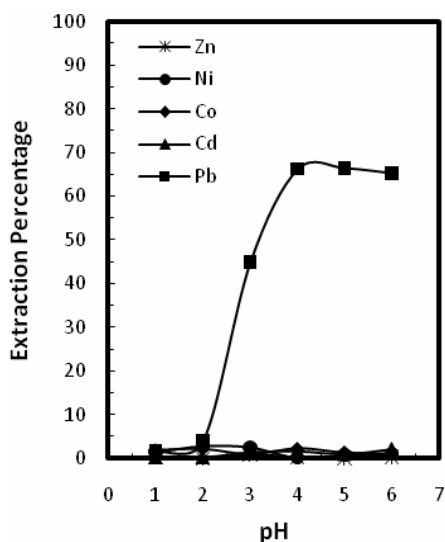
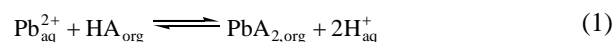


Fig. 2. Results of the competitive extraction of Pb(II), Co(II), Cd(II), Zn(II) and Ni(II) ions (1×10^{-4} M) from sodium chloride (0.1 M) solutions by 2-(dibutylcarbamoyl)benzoic acid (1×10^{-2} M) as a function of aqueous phase pH, at 25 °C.

(dibutylcarbamoyl)benzoic acid can be attributed to a cation exchange mechanism for the extraction process. This allows suggesting the corresponding extraction reaction equilibrium by Eq. (1):



where HA is 2-(dibutylcarbamoyl)benzoic acid, the subscripts 'aq' and 'org' denote 'aqueous' and 'organic' phase, respectively, in which the species are present. The extraction equilibrium constant (K_{ex}) is defined as:

$$K_{\text{ex}} = \frac{[\text{PbA}_{2,\text{org}}][\text{H}_{\text{aq}}^{+}]^2}{[\text{Pb}^{2+}]_{\text{aq}}[\text{HA}]_{\text{org}}^2} \quad (2)$$

The metal concentrations in the organic phase are much lower than that of the initial ligand concentration. It means initial metal concentration equals its equilibrium concentration,

$$[\text{HA}]_{0,\text{org}} \approx [\text{HA}]_{\text{org}} \quad (3)$$

Considering this assumption and by introducing the distribution ratio,

$$D = \frac{[\text{PbA}_{2,\text{org}}]}{[\text{Pb}^{2+}]_{\text{aq}}} \quad (4)$$

the logarithmic expression of Eq. (2) is:

$$\log D = \log K_{\text{ex}} + 2 \log [\text{HA}]_{0,\text{org}} + 2\text{pH} \quad (5)$$

The conventional analysis of $\log D$ vs. pH (Fig. 3) and $\log D$ vs. $\log [\text{HA}]_{0,\text{org}}$ provide the stoichiometry of the extracted lead species. The slopes were in agreement with a 1:2 metal to ligand ratio for the extracted complexes, and confirm the assumed extraction equilibrium shown by Eq. (1). The logarithm of the evaluated apparent extraction equilibrium constant has been calculated to be $-4.89 (\pm 0.03)$.

Effect of Type and Concentration of Electrolyte on the Extraction of Lead Ions

The effect of two different electrolytes, *i.e.* sodium chloride and sodium nitrate in the concentration range 0.1-

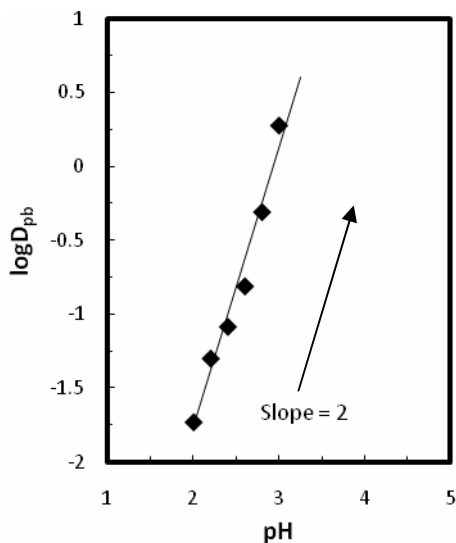


Fig. 3. Results of the extraction of lead ions (1×10^{-4} M) from sodium chloride (0.1 M) solutions by 2-(di butylcarbamoyl)benzoic acid in dichloromethane as a function of aqueous phase pH, at 25 °C.

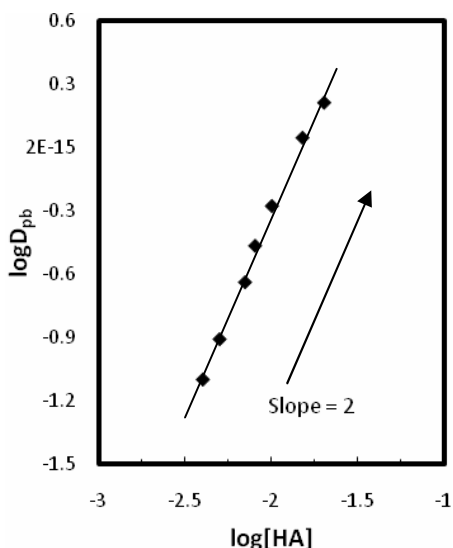


Fig. 4. Results of the extraction of lead ions (1×10^{-4} M) from sodium chloride (0.1 M) solutions by 2-(di butylcarbamoyl)benzoic acid (1×10^{-4} - 5×10^{-2} M) as a function of ligand concentration at pH 4 and at 25 °C.

0.5 M on the extraction of lead ions (initial concentration 1×10^{-4} M) from aqueous solutions adjusted at pH 4 by dichloromethane solution of the studied ligand was investigated. The results are given in Fig. 5. Higher extraction percentage of lead ions in the presence of sodium nitrate with respect to that found in the presence of sodium chloride can be attributed to the formation of stable chloro-complexes of lead in the aqueous phase in the presence of the latter salt [33]. The results show that the presence of sodium nitrate in the investigated concentrations does not affect the extraction efficiency of the ligand towards lead ions.

Effect of Diluent on the Extraction Process

An important parameter affecting the extraction process is the organic diluent used. In order to examine this effect, the extraction of lead ions into dichloromethane, carbon tetrachloride and ethyl acetate solutions of the ligand were assessed. The results (Fig. 6) reveal that the highest extraction efficiency can be achieved by using dichloromethane as diluent.

Stripping of Lead Ions from Organic Phase

The stripping of a metal extracted into an organic phase in solvent extraction process is environmentally and economically important. However, this point is critical for analyzing the amount of extracted metal ions because many of the conventional organic diluents cannot be used directly for introduction to the analytical instruments such as flame atomic absorption spectroscopy. Hydrochloric acid and nitric acid (0.01-0.5 M) were tested for the stripping of the lead ions extracted into the organic phase. It was found that a quantitative ($98.8 \pm 0.7\%$ with respect to the extracted values) stripping of lead ions from 5 ml of the loaded organic phase can be stripped by the same volume of 0.1 M nitric acid solution, after 20 min. magnetically stirring the phases.

Selected Extraction Conditions of Lead Ions and Stability of the Organic Phase

Based on the above mentioned results, the extraction of lead ions (initial concentration 1×10^{-4} M) from the 0.1 M sodium chloride aqueous solution adjusted at pH 4 into a

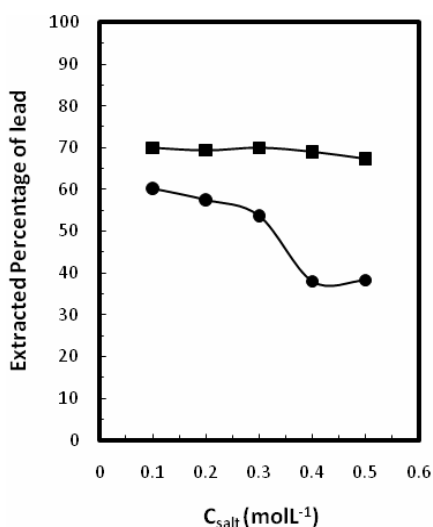


Fig. 5. Results of the extraction of lead ions (initial concentration 1×10^{-4} M) in the presence of 0.1-0.5 M sodium chloride (●) and sodium nitrate (■) adjusted at pH 4 by dichloromethane solution of 2-(dibutylcarbamoyl)benzoic acid (1×10^{-2} M), at 25 °C.

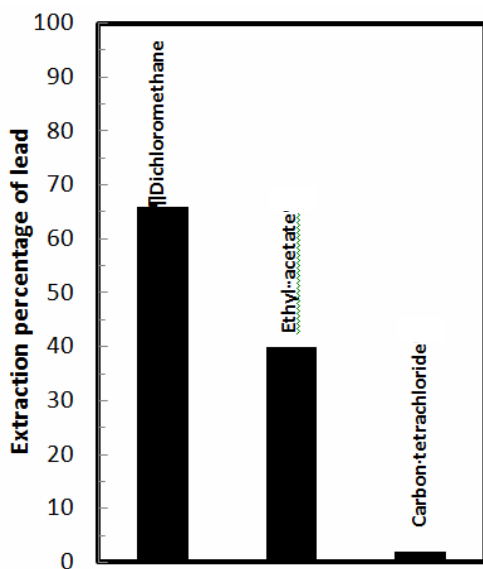


Fig. 6. Extraction percentage of lead ions (initial concentration 1×10^{-4} M) from 0.1 M sodium chloride aqueous solution adjusted at pH 4 by 2-(dibutylcarbamoyl)benzoic acid (1×10^{-2} M) in dichloromethane, ethyl acetate and carbon tetrachloride, at 25 °C.

dichloromethane solution of 2-(dibutylcarbamoyl)benzoic acid (5×10^{-2} M) was performed. The results of three independent extraction experiments show an efficient extraction $75.2 \pm 0.8\%$ of the lead ions.

The possibility to reuse the stripped organic phase in subsequent extraction experiments was checked by repeating four times the extraction of lead ions (1×10^{-4} M) from 0.1 M sodium chloride solution by the same organic phase (5×10^{-2} M of the ligand in dichloromethane). An average of $73.5 \pm 1.1\%$ extraction value of lead ions has been found, revealing a good stability of the organic phase.

Thermodynamics of the Extraction Process

In order to determine the thermodynamic parameters of the extraction process of lead ions from 0.1 M sodium chloride solution by the investigated extractant, a series of extraction experiments in different temperature (283-303 K) was performed.

The free-energy change (ΔG°) for the extraction equilibrium is calculated from the extraction constant K_{ex} by Eq. (6):

$$\Delta G^\circ = -RT \ln K_{ex} \quad (6)$$

and is related to the enthalpic and entropic changes (ΔH° and ΔS°) through the Gibbs-Helmholtz equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

Combining Eqs. (6) and (7) gives Eq. (8) which describes the temperature dependence of K_{ex} :

$$\ln K_{ex} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

The analysis of the variation of the evaluated extraction equilibrium as a function of inverse temperature (Fig. 7) allows calculating ΔG° (21.2 kJ mol^{-1}), ΔH° (99.2 kJ mol^{-1}), and $T\Delta S^\circ$ (78.1 kJ mol^{-1}) values, at 298 K. These values reveal that the process is endothermic and is controlled by positive entropy changes.

Selected Conditions and Application of the Method

The synthesized ligand was used for extraction of lead

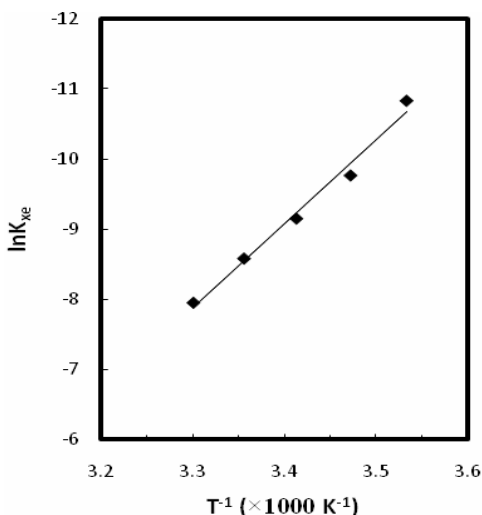


Fig. 7. The plot of $\ln K_{ex}$ of the extraction of lead ions by 2-(dibutylcarbamoyl)benzoic acid in dichloromethane as a function of the inverse of temperature.

from ore of Angoran zinc mine (Zanjan Province, Iran) and a leach cake sample of a zinc production plant. One gram of each sample was dissolved in 10 ml of hydrochloric acid (6 M) and heated for 60 min. The samples were filtered and diluted to 100 ml with distilled water. The results of the analysis of these solutions are given in Table 1. In order to examine the ability of the proposed method for recovery of the lead contents in the prepared samples, 5 ml of the samples adjusted at pH 4 was contacted with 5 ml of dichloromethane solution of 2-(dibutylcarbamoyl)benzoic acid. The phases were stirred magnetically for 20 min. After phase engagement and separation of the phases, the organic phase was stripped with diluted nitric acid (0.1 M). The amounts of metal ions measured in the stripped solution are given in Table 1. The results show the proposed method can be satisfactory used for recovery and concentration of lead ions from the examined real samples.

It is noteworthy that, zinc, nickel, cobalt and cadmium ions were selected as possible interfering ions on the

Table 1. Application of the Procedure for Recovery of Lead from Real Samples^a

Sample	Metal ion	Concentration in (mg l^{-1})		Recovery (%)	[Pb]/[M] ratio in	
		Leached solution	Stripped solution		Leached solution	Stripped solution
Angoran ore	Pb	15.1	10.0	66.3 (± 2.0)	-	-
	Zn	3.4	0.03	1.4 (± 0.3)	4.4	333.3
	Ni	2.0	0.05	2.5 (± 0.5)	7.6	200.0
	Cd	1.5	0.02	3.2 (± 0.3)	10.1	500
	Co	1.2	0.03	4.0 (± 0.2)	12.6	333.3
Leach cake	Pb	21.5	13.6	63.3 (± 1.6)	-	-
	Zn	37.5	1.5	4.0 (± 0.3)	0.6	9.1
	Ni	1.0	0.02	2.0 (± 0.4)	21.5	680.0
	Cd	2.0	0.06	3.0 (± 0.3)	10.8	226.7
	Co	1.6	0.05	3.0 (± 0.2)	13.4	272.0

^aExperimental conditions: see the text; results of three independent experiments.

extraction efficiency of lead ions, because they are the main associated metal ions in the investigated real samples.

CONCLUSIONS

A new carbamoyl-carboxylic acid extractant named 2-(dibutylcarbamoyl)benzoic acid was readily synthesized by using low cost chemicals, which justifies its use in fundamental as well as industrial investigations. This extractant showed a very selective attitude towards lead ions with respect to some other associated metal ions Zn(II), Ni(II), Co(II) and Cd(II). It was shown that the extracted lead complexes have a stoichiometry of 1:2 (metal to ligand). Under optimized conditions *i.e.* aqueous phase: 5 ml, 1×10^{-4} M of lead ions, sodium chloride 0.1 M, pH 4; organic phase: 5 ml, 2-(dibutylcarbamoyl)benzoic acid in dichloromethane, and by 20 min. stirring, ~75% of lead ions was extracted. The proposed method was successfully applied for recovery of lead from real samples.

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