Journal of Molecular Liquids 231 (2017) 20–24

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Application of polyethylene glycol based aqueous two-phase systems for extraction of heavy metals

Afshin Hamta, Mohammad Reza Dehghani *

Thermodynamics Research Laboratory, School of Chemical Engineering, Iran University of Science and Technology, Narmak, Tehran 16846–13114, Iran

ARTICLE INFO

Article history:
Received 17 September 2016
Received in revised form 17 January 2017
Accepted 24 January 2017
Available online 26 January 2017

Keywords:
Aqueous two phase system
Heavy metal
PEG
Waste water treatment

ABSTRACT

In this work the partitioning behavior of Hg(II), Zn(II) and Co(II) was measured in a polyethylene glycol based aqueous two phase system (PEG–ATPS) containing Na_2CO_3 as a phase forming salt. The experiments were performed by mixing equal weights of 30% (*w*/w) PEG–6000 solution and 10% (*w*/w) Na_2CO_3 solution. The partitioning of ions was studied at various concentration of iodide as extracting agent, stock salt solution pH, temperature and initial metal ion concentration. The experimental results showed that extraction of metal ions mainly depends on concentration of iodide. In the other words the extraction of metal ions increases as the amount of iodide ions increases. It was observed that the extraction of mercury increases as pH increases, while in the case of zinc and cobalt it was insignificant meanwhile temperature has a minor effect on metal ions extraction. In this work the maximal extraction percentages of Hg(II), Zn(II) and Co(II) were obtained as 99.3%, 98.62% and 58.2%, respectively.

1. Introduction

Several kinds of metal ions such as lead, sodium, molybdenum, magnesium, zinc, titanium, manganese, chromium, iron, cobalt, cadmium, copper and mercury can be present in the wastewater of pulp and paper, plating and oil industries [1–3] that seep into groundwater. However, some of them are essential for our body but higher dose of any of them could potentially cause allergies and serious toxicity and may also lead to irrecoverable damage to the natural environment. Meanwhile, previous studies have shown that ions like Hg^{2+} [4], Bi^{3+} [5], Ni^{3+}, Cd^{2+} [6], Co^{2+} [7] and Pb^{2+} [8] can be toxic and have harmful effects on environment. It must be mentioned that mercury is extremely toxic and has dangerous effects on human health such as fatigue, irritability, loss of memory, and depression [9,10]. Considering above facts, heavy metal removal is a mandatory job from health and environmental point of view. Several methods such as chemical precipitation, ion–exchange, adsorption, membrane and liquid–liquid extraction (LLE) processing have been proposed for extraction of metal ions from wastewater [8,11]. Traditionally, organic solvents have been used for liquid–liquid extraction of species, while most of organic solvents are toxic, flammable and volatile [12–14]. Recently Aqueous Two–Phase Systems (ATPS) have been used for this purpose [12,15,16].

ATPS is a liquid–liquid extraction system that unlike the conventional organic solvent extraction, both phases are aqueous and consequently environmental friendly [17]. Actually, in this system both phases have high water content (about 70–90%) [18]. ATPSs are low in cost, nontoxic, nonflammable, biocompatible and recyclable [15,19,20]. ATPSs may be formed through mixing two incompatible polymers (Polymer/Polymer system) or by mixing an inorganic salt and a water soluble polymer (Polymer/Salt system) [15,21–24]. Due to the advantages of the polymer/salt systems over the polymer/polymer systems, such as low interfacial tension between two phases, low cost of materials, great selectivity and low viscosity, polymer/salt systems have been widely used for extraction of metal ions [12,25–30]. Because of high stability and low cost, polyethylene glycol (PEG) is one of the most extensively used polymers as a phase forming material for the metal ion extraction [28,31–33]. Nevertheless, there is lack of knowledge on theory of distribution behavior of metal ions in ATPS and consequently it is hard to predict the distribution coefficient [34,35], to the Best of our knowledge there is no mathematical model to predict or correlate the extraction of metal ions using ATPS. However, there are some models to correlate the partitioning of biomolecules in these systems [36–38]; as an example, recently Nazer et al. [39] studied the partitioning of pyrimidine single stranded oligonucleotide in ATPS composed of PEG and sodium sulfate.

In order to have a deep understanding on separation mechanism, knowledge about the effects of various parameters is really helpful. In this regard, Shibukawa et al. [12] found that Zn(II) and Co(II) can be extracted using ATPS containing PEG–4000, Na_2SO_4 and SCN^- as extracting agent. Laura and Dumitru Bulgariu [29] demonstrated that Zn(II) can be extracted by PEG–rich phase in a PEG/$(NH_4)_2SO_4$ system containing SCN^-. It was also shown that iodide ion is not useful for extraction of Zn(II) [26]. Previous works showed that extraction of Co(II)

---

* Corresponding author.
E-mail address: m_dehghani@iust.ac.ir (M.R. Dehghani).

http://dx.doi.org/10.1016/j.molliq.2017.01.084
0167-7322/

can be increased by increasing pH through using small amount of PAN[1], TAN[2], PAR[3] or TAR[4] in a system containing PEG and $(NH_4)_2SO_4$ [40]. Recently, Cu(II) ions have been successfully extracted from aqueous media using ATPS containing PEG2000 and sodium sulfate [41]. Moreover, Santos et al. [42] investigated the recovery of calcium using ATPS. In the continuation of previous works, in this work the partitioning of Co^{+2}, Zn^{+2} and Hg^{+2} is studied in ATPS containing PEG–6000, Na_2CO_3 and KI as extracting agent. Due to the high solubility of Na_2CO_3 in water and strong salting–out effect of carbonate ($\Delta G_{hyd}^{CO_3^{2-}} = -1315^{Kj}/_{mol}$) [43], Na_2CO_3 was used as the phase forming salt, consequently PEG solution was separated into two aqueous phases in the presence of Na_2CO_3. The effect of parameters like amount of extracting agent, pH of stock salt solution and temperature are studied on the extraction efficiency. We hope this technique finds considerable application for biocompatible decontaminations of the toxic heavy metals from wastewater streams.

2. Experimental

2.1. Materials and chemicals

Polyethylene glycol with average molecular mass of 6000 (PEG–6000) was purchased from Merck and was used in this study without any modification. The water content of PEG–6000 was neglected. $Na_2CO_3 \cdot H_2O$ (purity 99%), NaOH (purity 97%), zinc nitrate (purity 98%), cobalt(II) nitrate (purity 99%) and mercury(II) chloride (purity 99.5%) were also purchased from Merck Ltd. Potassium iodide (KI) was obtained from Sinchem (Japan). All chemicals were of analytical grade of quality and were used as received without further purification. Double distilled water was used in all experiments.

2.2. Equipment

The concentrations of metal ions were measured using an atomic absorption spectrometer (Shimadzu AA–6200) with an accuracy of ±0.001 ppm. A digital pH meter combined with a glass electrode (Sartorius professional meter, PP–50) with uncertainty of ±0.1 was used for measurement of pH values. The composition of mixtures was calculated by mass using an analytical balance (Precisa, XT 220A, Switzerland) with $\pm 1 \times 10^{-4}$gr accuracy. The temperature of the ATPS was adjusted to the desired temperature by a water bath (LAUDA Alpha RA 8, Germany) with an uncertainty of ±0.1 K.

2.3. Methods

Sodium carbonate monohydrate was dried before use in an oven at 115 °C for 24 h. The compositions were defined on a weight basis. The experiments were carried out by batch process for each metal ion. To form the ATPS, stock solutions of PEG–6000 (30% *w*/w) and Na_2CO_3 (10% *w*/w) were prepared. The solutions of metal ions (Co(II), Zn(II) and Hg(II)) were prepared by dissolving of suitable quantity of solid salts in water. To obtain adequate volume of sample solution, the experiments were carried out in 15 ml scale test tubes by mixing 5 g of PEG–6000 solution with 5 g of Na_2CO_3 solution at different pH values (10.5, 11.5 and 12.5). The effect of extracting agent amount on extraction of Co(II), Zn(II) and Hg(II) ions was studied by adding different amount of KI to the system. The system was equilibrated by mixing manually for a few seconds; after that, 1 ml of metal ions solution (Co(II), Zn(II) and Hg(II)) with concentration of 0.02 grL^{-1} was added to the system and was shaken for 10 min. The solutions were placed in a thermostatic water bath at the desired temperature for 24 h in order to achieve thermal equilibrium. Then two phases were separated with glass Pasteur pipette and were placed into separated tubes. The upper phase was appropriately diluted and concentration of metal ions in both phases was determined by atomic absorption spectrophotometry (AAS).

The extraction percentages (*%E*) were calculated having AAS results by Eq. (1).

$$\%E = \frac{(C)_{up}}{(C)_{total}} \times 100 \quad (1)$$

In order to investigate the extraction efficiency of metal ions, the distribution coefficient in each system was calculated as follows:

$$D = \frac{(C)_{up}}{(C)_{bottom}} \quad (2)$$

Accordingly:

$$D = \frac{\%E}{100-\%E} \quad (3)$$

where $(C)_{up}$ and $(C)_{bottom}$ are the solute concentration in the upper and bottom phase respectively, and $(C)_{total}$ is the total solute concentration.

3. Results and discussion

In Table 1, the extraction percentage of Hg, Zn^{+2}, Co^{+2} at 25 °C and pH = 11.5 in the absence of extracting agent are presented. It can be seen that in the absence of extracting agent the metal ions remain in the lower phase and the extraction of species is negligible. Our finding is compatible with previous works which show most of metal ions remain in the salt–rich phase and cannot be extracted without extracting agent [44,45]. This result shows that there is not affinity between metal ions and PEG molecules. Meanwhile the results show that Hg(II) has the highest extraction percentage compared to Co(II) and Zn(II) (Table 1).

These results can be referred to the ΔG_{hyd} of mercury (−1760 Kj/mol), cobalt (−1915 Kj/mol) and zinc(−1955 Kj/mol) [43]; less negative Gibbs free energy of hydration means higher affinity to polymer phase. In the other words, it can be referred to complex formation of metal ions with CO_3^{2-}, which is accumulated in the bottom phase according to Eq. (4).

$$M^{2+}{}_{(aq)} + xCO_3^{2-}{}_{(aq)} \rightleftarrows M(CO_3)_x^{2-2x}{}_{(aq)}$$
$$K^{\theta}_{M(CO_3)_x^{2-2x}} = \frac{\gamma_{M(CO_3)_x^{2-2x}}\left[M(CO_3)_x^{2-2x}\right]}{\gamma_{M^{2+}}\left[M^{2+}\right].\gamma_{(CO_3)^{2-}}\left[(CO_3)^{2-}\right]^x} \quad (4)$$

K^{θ} refers to the equilibrium constant of complex formation. The metal–carbonate complexes in the bottom and top phases are in equilibrium; therefore the distribution ratio of metal ions can be given by Eq. (5).

$$M(CO_3)_x^{2-2x}{}_{(aq),B} \rightleftarrows M(CO_3)_x^{2-2x}{}_{(aq),T}$$
$$K_{M(CO_3)_x^{2-2x}} = \frac{\left[M(CO_3)_x^{2-2x}\right]_T}{\left[M(CO_3)_x^{2-2x}\right]_B} \quad (5)$$

Table 1
The extraction percentage of metal ions in the absence of iodide ion, in the aqueous PEG–6000 + Na_2CO_3 two–phase system, pH = 11.5, temperature = 25 °C.

Metal ion	Hg(II)	Co(II)	Zn(II)
E%	12.86	3	0.5

---

[1] 1-(2-pyridylazo)-2-naphthol.
[2] 1-(thiazolylazo)-2-naphthol.
[3] 4-(2-pyridylazo)-resorcinol.
[4] 4-(2-thiazolylazo)-resorcinol.