ROSELAINE CALZAVARA DA CUNHA

EXTRAÇÃO DE COBALTO, NÍQUEL, FERRO E MERCÚRIO EMPREGANDO SISTEMA AQUOSO BIFÁSICO NA PRESENÇA DE CONCOMITANTES

Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Agroquímica, para obtenção do título de DoctorScientiae.

VIÇOSA
MINAS GERAIS – BRASIL
2015

Ficha catalográfica preparada pela Biblioteca Central da Universidade Federal de Viçosa - Câmpus Viçosa

T
Cunha, Roselaine Calzavara da, 1975-
C972e Extração de cobalto, níquel, ferro e mercúrio empregando
2015 sistema aquoso bifásico na presença de concomitantes /
Roselaine Calzavara da Cunha. – Viçosa, MG, 2015.
xii, 59f. : il. (algumas color.) ; 29 cm.

Orientador: Maria do Carmo Hespanhol da Silva.
Tese (doutorado) - Universidade Federal de Viçosa.
Inclui bibliografia.

1. Processos químicos. 2. Extração (Química). 3. Separação (Tecnologia). 4. Sistemas aquosos bifásicos. 5. Química ambiental. 6. Mercúrio. 7. Cobalto. 8. Níquel. 9. Ferro. I. Universidade Federal de Viçosa. Departamento de Química. Programa de Pós-graduação em Agroquímica. II. Título.

CDD 22. ed. 660.2842

ROSELAINE CALZAVARA DA CUNHA

EXTRAÇÃO DE COBALTO, NÍQUEL, FERRO E MERCÚRIO EMPREGANDO SISTEMA AQUOSO BIFÁSICO NA PRESENÇA DE CONCOMITANTES

Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Agroquímica, para obtenção do título de *DoctorScientiae*.

APROVADA:*09 de dezembro de 2015.*

Antônio Augusto Neves

Carlos Roberto Bellato

LeonardusVergutz

Letícia Malta Costa

Maria do Carmo Hespanhol da Silva

(Orientadora)

Ao meu filho, João, que alegra ainda mais a minha vida e me revigora a cada dia.

Ao meu esposo, Sávio,o seu apoio, dedicação e amor foram fundamentais para conclusão deste trabalho e a quem amo muito!

Dedico

Agradecimentos

À Deus, que me fortalece e dá coragem para prosseguir na minha caminhada.

À minha mãe, Oraci, que mesmo distante fisicamente, estará sempre presente em meu coração.

Ao meu esposo, Sávio, por seu amor incondicional e apoio em todos os momentos da minha vida.

À minha família, pai, irmãos, cunhados, sobrinhas e sobrinhos que se preocuparam e sempre me incentivaram.

As minhas amigas, Luciana, Pamela e Renata, por todos os consolos e palavras de conforto nos momentos mais oportunos.

À orientadora, Profª. Maria do Carmo Hespanhol da Silva pela orientação, incentivo, paciência e por todas as contribuições à minha vida profissional.

Aoco-orientador, Prof. Luis Henrique Mendes da Silva, pelas sugestões e discussões.

Aos Profs. Antônio Augusto Neves, Carlos Roberto Bellato, LeonardusVergutz e Letícia Malta Costapela participação nesta defesa.

AoLuis Felipe, Pamela e Vivianne pelo grande auxílio na realização dos experimentos.

Aos amigos do QUIVECOM pela boa convivência.

À Universidade Federal de Viçosa, e em especial ao Departamento de Química, pela oportunidade na realização deste trabalho.

Ao Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPQ) e a Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) pela concessão da bolsa de estudos.

Ao Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) e Instituto Nacional de Ciências e Tecnologias Analíticas Avançadas (INCTAA) pelo auxílio financeiro.

Biografia

Roselaine Calzavara da Cunha, filha de Ralph Calzavara e OraciBolotariCalzavara, nasceu em 27 de abril de 1975, na cidade de Bicas, Minas Gerais.

Em março de 1994 ingressou no curso de Química da Universidade Federal de Juiz de Fora (UFJF), diplomando-se com o título de Licenciatura e Bacharelado em fevereiro de 2000.

Em agosto de 2008, iniciou o mestrado em Química Analítica no Programa de Pós-graduação em Agroquímica na Universidade Federal de Viçosa, obtendo seu título em julho de 2010.

Em março de 2011 iniciou o doutorado em Química Analítica no Programa de Pós-graduação em Agroquímica na Universidade Federal de Viçosa, submetendo-se à defesa de tese em dezembro de 2015.

Sumário

Lista de figuras

Lista de tabelas

Resumo

CUNHA, Roselaine Calzavara da, D.Sc., Universidade Federal de Viçosa, dezembro de 2015. **Extração de cobalto, níquel, ferro e mercúrio empregando sistema aquoso bifásico na presença de concomitantes.** Orientadora: Maria do Carmo Hespanhol da Silva. Co-orientadores: Luis Henrique Mendes da Silva eLuisAntonioMinim.

O objetivo deste trabalho foi estudar a partição dos íons metálicos Hg(II), Fe(III), Co(II) e Ni(II) utilizando novos sistemas aquosos bifásicos (SABs). Para estudar o comportamento de extração do Hg(II) foram utilizados os SABs constituídos por PEO1500 + $Na_3C_6H_5O_7$ + H_2O, PEO1500 + Na_2SO_4+ H_2O, L35 + $Na_3C_6H_5O_7$ + H_2O, L35 + Na_2SO_4+ H_2O e L64 + $Na_3C_6H_5O_7$ + H_2O. A influência da composição do SAB e a presença de íons cloreto, assim como o efeito do eletrólito, pH, comprimento da linha de amarração (CLA) do SAB na porcentagem de extração (%E) foram investigados. O íon Hg(II) foi extraído quantitativamente para a fase rica em macromolécula utilizando o SAB constituído por PEO1500 + $Na_3C_6H_5O_7$ + H_2O em pH = 1,00 e 0,225 mol kg^{-1} do extratante KCl mesmo na presença dos concomitantes Fe(III), Co(II), Cr(III), Zn(II), Cd(II), Cu(II), Ni(II) e Pb(II). Este sistema foi utilizado para separação do Hg(II) presente em amostras de bateria, resíduos de indústria de cloro-soda e lâmpadas fluorescentes com %E ≥ (92,3 ± 5,2) %. O comportamento de extração dos íons metálicos Fe(III), Co(II) e Ni(II) foram estudados aplicando os SABs L64 + NaSCN + H_2O, L64 + KSCN + H_2O, L64 + NH_4SCN + H_2O, F68 + KSCN + H_2O sem a utilização de extratantes. Os efeitos da composição do SAB, pH, natureza do eletrólito, concentração do metal, o balanço hidrofóbico/hidrofílico e o tamanho da macromolécula foram avaliados. Sendo a separação dos íons metálicos influenciada pelo pH do meio e o tamanho da macromolécula. Utilizando o SAB L64 + NH_4SCN + H_2O no CLA 28,93 % (m/m) em pH 3,00 foi possível separar Co(II) de Ni(II) e em pH = 6,00, Ni(II) de Fe(III). Em pH = 12,0, o Fe(III) pode ser separado de Co(II) e Ni(II) devido a formação de $Fe(OH)_3$ que é insolúvel no meio.

Abstract

CUNHA, Roselaine Calzavara da, D.Sc., Universidade Federal de Viçosa, December, 2015. **Extraction of cobalt, nickel, iron and mercury using aqueous two-phase system in the presence of concomitants.**Adviser: Maria do Carmo Hespanhol da Silva. Co-Advisers: Luis Henrique Mendes da Silva andLuisAntonioMinim.

The objective of this work was study the partition of the metal ions Hg(II), Fe(III), Co(II) and Ni(II) using new aqueous two-phase systems (ATPS). Tostudytheextractionbehaviorof Hg(II), ATPSconsistingPEO1500 + $Na_3C_6H_5O_7$ + H_2O, PEO1500 + Na_2SO_4+ H_2O, L35 + $Na_3C_6H_5O_7$ + H_2O, L35 + Na_2SO_4+ H_2O e L64 + $Na_3C_6H_5O_7$ + H_2Owereused. The influence of ATPS composition and the presence of chloride ions, as well as the effect of the electrolyte, pH, tie-line length (TLL) of the ATPSin the percentage of extraction (%E) were investigated. The ion Hg(II) was quantitatively extracted into the macromolecule-rich phase using ATPS comprisingPEO1500 + $Na_3C_6H_5O_7$ + H_2O at pH = 1.00 and 0.225 mol kg^{-1}KClextractant even in the presence of concomitant Fe(III), Co(II), Cr(III), Zn(II), Cd(II), Cu(II), Ni(II) andPb(II). This system was used for separation of the Hg(II) present in battery, chlor-alkali industry residues, and fluorescent lamps samples with %E ≥ (92.3 ± 5.2) %. The extraction behavior of metal ions Fe(III), Co(II) and Ni(II) were studied by applying the ATPSL64 + NaSCN + H_2O, L64 + KSCN + H_2O, L64 + NH_4SCN + H_2O, F68 + KSCN + H_2O without the use of extractants.The effects of the composition of ATPS, pH, electrolyte nature, metal concentration, the hydrophobic/hydrophilic balance and size of the macromolecule were evaluated. Since the separation of metal ions influenced by the pH and the size of the macromolecule. Using ATPSL64 + NH_4SCN + H_2O inTLL 28.93 % (m/m) at pH 3.00 was possible to separate Co(II) and Ni(II) and at pH 6.00, Ni(II) of the Fe(III). At pH = 12.0, Fe(III) may be separated from Co(II) and Ni(II) due to the formation of $Fe(OH)_3$ which is insoluble at medium pH.

Introdução

O crescimento econômico e o avanço tecnológicogeram uma demanda por produtos de alta tecnologia fazendo com que diversos equipamentos eletroeletrônicosfossem substituídos rapidamente.Isto tem levado a um consumo maior de matéria-prima, bem como aumento na poluição, devido a maior quantidade de resíduos gerados. Em consequência disso, cresce a preocupação com o descarte de materiais desta natureza.

Um novo desafio para a comunidade acadêmica surgiu: como recuperar metais desses resíduos, de maneira econômica e ambientalmente segura? Iniciaram-se investigações voltadas para o desenvolvimento de técnicas de extração e/ou separação de metais. A extração líquido–líquido(ELL) ou extração por solvente (ES)foi uma das primeiras metodologias a ser empregadapara separação e enriquecimento de metais, sendo utilizada não só para aplicações analíticas, como também, para aplicações industriais (Wellenset al., 2012; Shibukawa et al., 2001). A vantagem da ES em relação a outras metodologias de separação é a capacidade de extrair diversos metais, devido a possibilidade do uso de diferentes solventes e/ou extratantes. Entretanto, a ES utiliza solventes orgânicos, os quais são imiscíveis em água, tóxicos, voláteis, inflamáveis e perigosos ao ambiente e à saúde humana (Song et al., 2013). Desta maneira, este sistema de extração torna-se inconveniente para o desenvolvimento de tecnologias de extração ambientalmente seguras (Ventura et al., 2011).

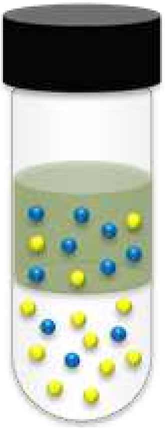
Uma alternativa estratégica para a extração e/ou separação de metais é a utilização do sistema aquoso bifásico (SAB), que por ser constituído por compostos atóxicos, biodegradáveis, recicláveis e de baixo custoatende aos princípios da Química Verde, além de ser economicamente atrativo.

Sistema Aquoso Bifásico (SAB)

OSABé um sistema constituído predominantemente por água. Este sistema pode ser obtido pela combinação de soluções aquosas,em diferentes composiçõesde eletrólito e polímero (Reschkeet al., 2014), dois polímeros (Monteiro et al., 2014; Machado et al., 2012)ou dois eletrólitos(Bridges et al., 2007), que se tornam parcialmente imiscíveis sobre algumas condições termodinâmicas específicas como concentração, temperatura e pressão(De Lemos et al., 2013; Silverio et al., 2010).

Em geral, para sistemas constituídos por polímero, sal e água, a fase superior (FS) é rica em polímero e a fase inferior (FI) rica em eletrólito, como exibido pelaFig.1.

COMPOSIÇÃO GLOBAL
[PEO1500] = 31,48 % (m/m)
[$ZnSO_4$] = 10,45 % (m/m)
[H_2O] = 58,07 % (m/m)



FASE SUPERIOR
[PEO1500] = 47,21 % (m/m)
[$ZnSO_4$] = 0,57 % (m/m)
[H_2O] = 52,22 % (m/m)

FASE INFERIOR
[PEO1500] = 2,18 % (m/m)
[$ZnSO_4$] = 28,49 % (m/m)
[H_2O] = 69,33 % (m/m)

Fig.1. Composição do sistema formado por poli(óxido de etileno) 1500 + sulfato de zinco + água a 25 ºC (de Lemos et al., 2011).

Para representação da composição química das duas fases, em equilíbrio termodinâmico, normalmente utilizam-se diagramas de fases retangulares. Este diagrama (Fig1) é representado por um sistema cartesiano em que a concentração de polímero encontra-se no eixo das ordenadas e a concentração de eletrólito no eixo das abscissas, sendo as concentrações dos constituintes do sistema expressos em porcentagem mássica, % (m/m).

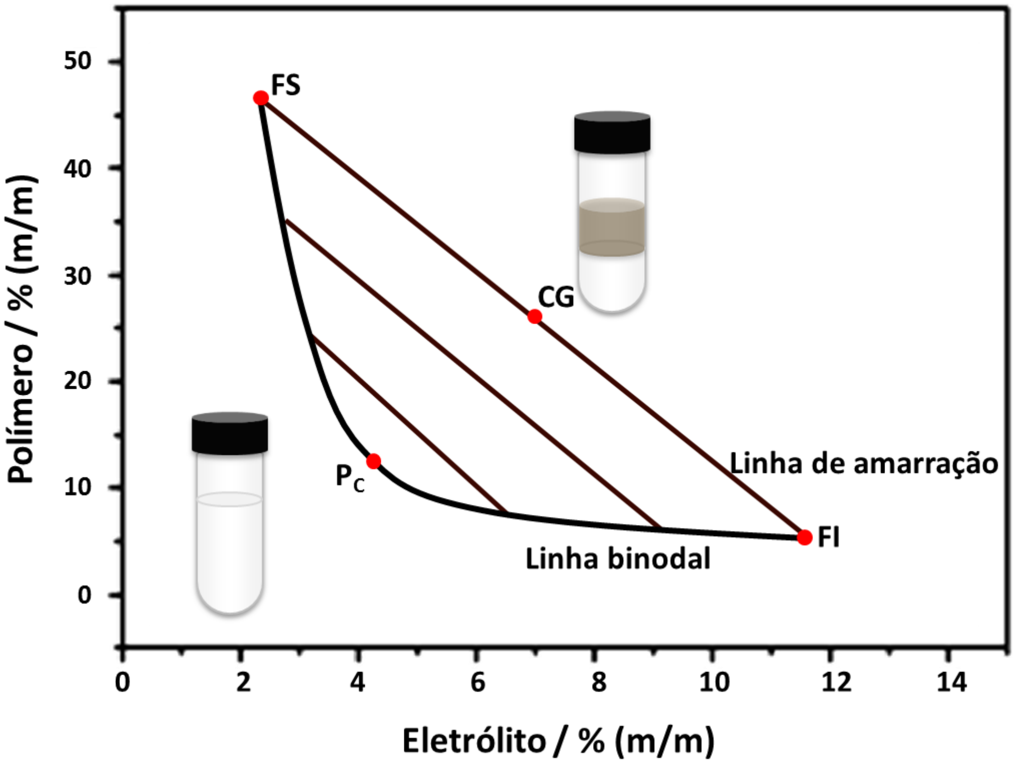


Fig1. Diagrama de fases em coordenadas retangulares para SAB constituído por polímero e eletrólito.

Através deste diagrama obtemos informações que auxiliam na obtenção de SAB e potencializam a separação e/ou pré-concentração da espécie de interesse. Assim, o diagrama é constituído pela linha binodal (FS – Pc – FI) que separa a região monofásica da região bifásica indicando em quais concentrações de polímero e eletrólito há formação de sistemas homogêneo ou heterogêneo. A localização da linha binodal sofre deslocamento em função do tipo e massa molar do polímero, a natureza química do eletrólito, a temperatura e o pH do meio. Para sua obtenção normalmente são empregadas titulações turbidimétricas e análise da composição das fases (da Silvaet al., 2006).

Além disso, no diagrama são representadas as linhas de amarração que são segmentos de reta que unem os pontos FS a FI e fornecem a composição de polímero e eletrólito das duas fases, em equilíbrio. A composição global, representada pelo ponto CG, fornece um sistema com propriedade termodinâmica extensiva (como por exemplo o volume), das FS e FI iguais, quando a CG se situa no ponto médio da linha de amarração (LA). Entretanto, deslocando-se sobre uma mesma LAobtêm-se fases(superiores ou inferiores), que em equilíbrio,possuem uma mesma propriedade termodinâmica intensiva (densidade, volume molar, entalpia molar, etc.), porém as propriedades termodinâmicas extensivas são distintas (massa, volume, etc.) (da Silvaet al., 2006).

Um parâmetro importante envolvendo a linha de amarração é o seu comprimento (CLA). Este parâmetro indica a diferença entre as propriedades intensivas entre as fases, ou seja, quanto maior o CLA, maior a diferença de composição entre as fases, promovendo maior eficiência de extração da espécie de interesse (da Silvaet al., 2006). Sendo assim, para avaliar a eficiência de separação da espécie entre sistemas é importante que os CLAs sejam próximos para efeito de comparação.

O CLA é um valor numérico que mede a distância entre os pontos FS e FI e é calculado com o auxílio da Eq.(1), em que e são as concentrações de polímero e e as concentrações de eletrólito, nas fases superiores e inferiores, respectivamente.

$$\boldsymbol{CLA} = \sqrt{\left(\boldsymbol{C_P^{FS}} - \boldsymbol{C_P^{FI}}\right)^{2} + \left(\boldsymbol{C_E^{FS}} - \boldsymbol{C_E^{FI}}\right)^{2}} \tag{1}$$

Diminuindo continuamente o CLA obtêm-se o ponto crítico (Pc). Neste ponto,teoricamente existiria distinção entre as fases no sistema, porémcom propriedades termodinâmicas intensivas iguais.

Aplicação de sistemas aquosos bifásicos

A descoberta do sistema aquoso bifásico foi em 1896 por Beijerinck, em que foi verificada a incompatibilidade ao misturar soluções aquosas de gelatina e ágar ou gelatina e amido solúvel, a uma dada temperatura e concentração. Após um período de repouso esta mistura tornava-se turva ocorrendoa separação do sistema em duas fases, líquidas e límpidas. O sistema heterogêneo obtido era constituído de FI enriquecida em ágar (amido) e a FS em gelatina, sendo o componente águapredominante em ambas as fases (Beijerinck, 1910; Beijerinck, 1896a;Beijerinck, 1896b).

Entretanto, a potencialidade doSAB só foi comprovada, na década de 50,por Per-ÅkeAlbertssonem processos debiosseparação (Albertsson, 1986). A purificação de biomoléculas complexas utilizando os SABs possui muitas vantagens, em virtude da predominância de água no sistema, evitando a sua desnaturação e perda de atividade biológica (Claudio et al., 2012).

Porém, mesmo com a aplicação satisfatória dos SABs na partição de biopartículas,estes sistemas só foram introduzidos para a extração de íons metálicos, em meados da década de 80, com o trabalho de Zvarovaet al. (1984)em que foi avaliado o comportamento de extração de íons metálicos na ausência ou presença de agentes extratores solúveis em água.

O poli(óxido) de etileno (PEO) é o mais utilizado polímero em estudos de particionamento em sistemas aquosos bifásicos, principalmenteaqueles constituídos por PEO + sal devido a elevada seletividade, baixa viscosidade, baixo custo e rápida separação de fases (Zafarani-Moattar e Nasiri, 2010). Entretanto, estes sistemas são limitados devido a sua natureza hidrofílica,restringindo a extração apenas de espécies solúveis em água.

Com o objetivo de ampliar a utilização de SABs para extração de diferentes espécies, tanto hidrofílicas quanto hidrofóbicas, novos SABsconstituídos por copolímeros triblocos,formados por unidadesde óxido de etileno (EO) e óxido de propileno (PO) simbolizado por $(EO)_x(PO)_y(EO)_x$,foram obtidos (da Silva et al., 2005). Estes copolímeros, a uma determinada concentração e temperatura, sofrem o processo de auto-organização e formam micelas,constituídas por uma coroa hidrofílica formada por EO e um núcleo hidrofóbico formado por PO. Portanto, devido à natureza do núcleo, é possível solubilizar os compostos de caráter hidrofóbico (Rodrigues et al., 2008).

Os sistemas aquosos bifásicos são, portanto, uma técnica promissora e tem sido aplicado com sucesso na separação, determinação e pré-concentração de biopartículas (Pimentel et al., 2013;Luechau et al., 2010; Azevedo et al., 2009; Rosa et al., 2007), corantes (Mageste et al., 2012;Mageste et al., 2009) e metais (Rodrigues et al., 2013;de Lemos et al., 2012; Patrício et al., 2011; Bulgariu e Bulgariu, 2011;Lacerda et al., 2009).

Devido à potencialidade de aplicação dos SABs para separação de íons metálicos torna-se necessário o estudo de diversos parâmetros comopH do meio reacional, composição do sistema, hidrofobicidade do polímero e natureza do eletrólito que constitui o sistema, com o objetivo de compreender e promover alterações significativas no comportamento de partição do analito de interesse.

Referências Bibliográficas

Albertsson, P.A. Partition of Cell Particles and Macromolecules, 3rd ed., John Wiley & Sons, New York, **1986**.

Azevedo, A.M.; Rosa, P.A.J.; Ferreira, I.F.; Pisco, A.M.M.O.; de Vries, J.; Visser, T.J.; Aires-Barros, M.R. Affinity-enhanced purification of human antibodies by aqueous two-phase extraction. *Separation and Purification Technology*, **2009**, 65 (1), 31-39.

Beijerinck, M. W. UeberEmulsionsbildungbei der VermischungwässerigerLösungengewissergelatinierenderKolloide.*ZeitschriftfürChemie und Industrie der Kolloide*, **1910**, 7 (1), 16-20.

Beijerinck, M.W. ÜbereineEigentümlichkeit der löslichenStärke.*ZentralblBakteriolParasitenkdInfektionskr*, **1896a**, 2 (2), 698-699.

Beijerinck, M.W. ÜbereineEigentümlichkeit der löslichenStärke.*ZentralblBakteriolParasitenkdInfektionskr*, **1896b**, 2 (2), 627.

Bridges, N. J.; Gutowski, K. E.; Rogers, R. D., Investigation of aqueous biphasic systems formed from solutions of chaotropic salts withkosmotropic salts (salt-salt ABS).*Green Chemistry*,**2007**, 9 (2), 177-183.

Bulgariu, L.; Bulgariu, D. Extraction of gold(III) from chloride media in aqueous polyethylene glycol-based two-phase system. *Separation and Purification Technology*, **2011**, 80 (3), 620-625.

Claudio, A.F.M.; Ferreira, A.M.; Freire, C.S.R.; Silvestre, A.J.D.; Freire, M.G.; Coutinho, J.A.P.Optimization of the gallic acid extraction using ionic-liquid-based aqueous two-phase systems. *SeparationandPurification Technology*, **2012**, 97, 142-149.

Da Silva, M.C.H.; da Silva, L.H.M.; Paggioli, F.J.; Coimbra, J.S.R.; Minim, L.A. Sistema aquoso bifásico: uma alternativa eficiente para extração de íons. *Química Nova*, **2006**, 29, 1332-1339.

Da Silva, L.H.M.; da Silva, M.D.H.; Mesquita, A.F.; do Nascimento, K.S.; Coimbra, J.S.R.; Minim, L.A. Equilibrium phase behavior of triblock copolymer plus salt plus water two-phase systems at different temperatures and pH.*Journal of Chemical and Engineering Data*, **2005**, 50 (4), 1457-1461.

De Lemos, L.R., Campos, R.A., Rodrigues, G.D., da Silva, L.H.M., da Silva, M.C.H. Green separation of copper and zinc using triblock copolymer aqueous two-phase systems. *Separation and Purification Technology*,**2013**, 115, 107-113.

De Lemos, L.R., Santos, I.J.B., Rodrigues, G.D., da Silva, L.H.M., da Silva, M.C.H. Copper recovery from ore by liquid-liquid extraction using aqueous two-phase system. *Journal Hazardous Materials*, **2012**, 237-238, 209-214.

De Lemos, L.R.; Patrício, P.R.; Rodrigues, G.D.; de Carvalho, R.M.M.; da Silva, M.C.H.; da Silva, L.H.M. Liquid-liquid equilibrium of aqueous two-phase systems composed of poly(ethylene oxide) 1500 and diferente electrolytes ($(NH_4)_2SO_4$, $ZnSO_4$ and K_2HPO_4): Experimental and correlation. *Fluid Phase Equilibria*, **2011**, 305, 19-24.

Lacerda, V.G., Mageste, A.B., Santos, I.J.B., da Silva, L.H.M., da Silva, M.D.H. Separation of Cd and Ni from Ni–Cd batteries by an environmentally safe methodology employing aqueous two-phase systems. *Journal Power Sources*, **2009**, 193, 908-913.

Luechau, F.; Ling, T.C.; Lyddiatt, A. Two-step process for initial capture of plasmid DNA and partial removal of RNA using aqueous two-phase systems. *ProcessBiochemistry*, **2010**, 45 (8), 1432-1436.

Machado, F.L.C.; Coimbra, J.S.D.; Zuniga, A.D.G.; da Costa, A.R.; Martins, J.P.Equilibrium Data of Aqueous Two-Phase Systems Composed of Poly(ethylene glycol) and Maltodextrin. *Journal of Chemical and Engineering Data*, **2012**, 57 (7), 1984-1990.

Mageste, A.B.; Senra, T.D.A.; da Silva, M.C.H.; Bonomo, R.C.F.; da Silva, L.H.M. Thermodynamics and optimization of norbixin transfer processes in aqueous biphasic systems formed by polymers and organic salts. *Separation and Purification Technology*, **2012**, 98, 69-77.

Mageste, A.B.; de Lemos, L.R.; Ferreira, G.M.D.; da Silva, M.D.H.; da Silva, L.H.M.; Bonomo, R.C.F.; Minim, L.A. Aqueous two-phase systems: an efficient, environmentally safe and economically viable method for purification of natural dye carmine. *Journal of Chromatography A*, **2009**, 1216 (45), 7623-7629.

Monteiro, E.S.; Pessoa, P.A.; Meirelles, A.J.A.Liquid-Liquid Equilibrium of Aqueous Biphasic Systems Containing Ethylene Oxide-Propylene Oxide Block Copolymers and Maltodextrins.*Journal of Chemical and Engineering Data*, **2014**, 59 (7), 2310-2319.

Patricio, P.D.; Mesquita, M.C.; Da Silva, L.H.M.; Da Silva, M.C.H. Application of aqueous two-phase systems for the development of a new method of cobalt(II), iron(III) and nickel(II) extraction: A green chemistry approach. *Journal Hazardous Materials*, **2011**, 193, 311- 318.

Rodrigues, G.D.; de Lemos, L.R.; da Silva, L.H.M.; da Silva, M.C.H. Application of hydrophobic extractant in aqueous two-phase systems for selective extraction of cobalt, nickel and cadmium. *Journal of Chromatography*, **2013**, 1279, 13-19.

Rodrigues, G.D.; da Silva, M.D.H.; da Silva, L.H.M.; Paggioli, F.J.; Minim, L.A.; Coimbra, J.S.D. Liquid-liquid extraction of metal ions without use of organic solvent. *Separation and Purification Technology*, **2008**, 62 (3), 687-693.

Reschke, T., Brandenbusch, C., Sadowski, G. Modeling aqueous two-phase systems: I. Polyethylene glycol and inorganic salts as ATPS former. *Fluid Phase Equilibria*,**2014**, 368, 91-103.

Rosa, P.A.J.; Azevedo, A.M.; Aires-Barros, M.R. Application of central composite design to the optimisation of aqueous two-phase extraction of human antibodies.*Journal of Chromatography A*, **2007**, 1141 (1), 50-60.

Shibukawa, M.; Nakayama, N.; Hayashi, T.; Shibuya, D.; Endo, Y.; Kawamura, S. Extraction behaviour of metal ions in aqueous polyethylene glycol-sodium sulphate two-phase systems in the presence of iodide and thiocyanate ions. *AnalyticaChimicaActa*, 2001, 427, 293-300.

Silverio, S.C.; Rodriguez, O.; Teixeira, J.A.; Macedo, E.A. Solute partitioning in polymer-salt ATPS: The Collander equation. *Fluid Phase Equilibria*, **2010**, 296 (2), 173-177.

Song, X.; Ye, M.; Tang, X.; Wang, C. Ionic liquids dispersive liquid–liquid microextraction and HPLC-atomic fluorescence spectrometric determination of mercury species in environmental waters.*Journal of Separation Science*, **2013**, 36, 414-420.

Ventura, S.P.M.; Sousa, S.G.; Freire, M.G.; Serafim, L.S.; Lima, A.S.; Coutinho, J.A.P. Design of ionic liquids for lipase purification. *Journal of Chromatography B*, **2011**, 879 (26), 2679-2687.

Wellens, S.; Thijs, B.; Binnemans, K. An environmentally friendlier approach to hydrometallurgy: highly selective separation of cobalt from nickel by solvent extraction with undiluted phosphonium ionic liquids. *Green Chemistry*, **2012**, 14 (6), 1657-1665.

Zafarani-Moattar, M.T.; Nasiri, S. (Liquid plus liquid) and (liquid plus solid) equilibrium of aqueous two-phase systems containing poly ethylene glycol di-methyl ether 2000 and di-sodium hydrogen phosphate.*Journal of Chemical Thermodynamics*, **2010**, 42 (9), 1071-1078.

Zvarova, T.I.; Shkinev, V.M.; Vorobeva, G.A.; Spivakov, B.Y.; Zolotov, Y.A. Liquid-liquid-extraction in the absence of usual organic-solvents - application of 2-phase aqueous systems based on a water-soluble polymer. *MikrochimicaActa*, **1984**, 3 (5-6), 449-458.

Objetivos

Objetivo geral

O objetivo deste trabalho éampliar o conhecimento e aplicação do sistema aquoso bifásicoconstituído por macromolécula, eletrólito e água.

Objetivos específicos

Para o íon metálico Hg(II):

- estudaros SABs PEO1500 + $Na_3C_6H_5O_7$ + H_2O, PEO1500 + Na_2SO_4+ H_2O, L35 + $Na_3C_6H_5O_7$ + H_2O, L35 + Na_2SO_4+ H_2O eL64 + $Na_3C_6H_5O_7$ + H_2O com o auxílio de KCl como extratante na separação seletiva de Hg(II);
- verificar a influência dos parâmetros: composição do SAB, presença dos íons cloreto,efeito da macromolécula e eletrólito formador do sistema, pH, comprimento da linha de amarração e a influência de íons metálicos (Fe(III), Co(II), Cr(III), Zn(II), Cd(II), Cu(II), Ni(II) e Pb(II) na %E do mercúrio;
- separarmercúrio de amostras sintéticas de bateria do tipo botão, lâmpadas ede efluentes de indústria cloro-soda.

Para os íons Fe(III), Co(II) e Ni(II):

- estudar os SABs L64+ NaSCN +H_2O, L64+KSCN+H_2O, L64+NH_4SCN+H_2O, F68 + KSCN + H_2O e PEO1500 + KSCN + H_2O, sem o auxílio deextratantepara separação destes íons metálicos;
- avaliar a influência dos parâmetros: composição do SAB, pH, natureza do eletrólito,balanço hidrofóbico/hidrofílico e tamanho da macromolécula na extração dos íons metálicospara a fase com predominância de polímero.

CAPÍTULO 1

Green recovery of mercury from domestic and industrial waste

1.1. Abstract

Recovery of mercury from effluents is fundamental for environmental preservation. A new, green method was developed for separation of mercury from effluent containing different metals. The extraction/separation of Hg(II) was studied using aqueous two-phase system (ATPS) comprising by polyethylene oxide (PEO1500) or triblock copolymers (L64 or L35), electrolyte (sodium citrate or sodium sulfate) and water in the presence or absence of chloride ions. The extraction behavior of the Hg(II) for the macromolecule-rich phase (MRP) is affected by the following parameters: amount of added extractant, pH, and the nature of the electrolyte and macromolecule of the ATPS. The ATPS of PEO1500 + sodium citrate + H_2O (pH 1.00 and 0.225 mol kg^{-1}KCl) produced the highest Hg(II) %E = (92.3 ± 5.2) %. Under the same conditions, excellent separation factors ($1.54 \times 10^2 – 3.21 \times 10^{10}$) for recovery of mercury in the presence of co-existing metals were obtained. Efficient and selective extraction of Hg(II) from domestic and industrial synthetic effluents was achieved using this ATPS.

Keywords: Mercury;Aqueous two-phase system; Liquid-liquid extraction; Green chemistry; Waste.

1.2. INTRODUCTION

Mercury is considered one of the most dangerous elements [1] due to its high toxicity and bioaccumulative effect [2,3], and is listed as a priority pollutant by the US Environmental Protection Agency (EPA). Mercury occurs in different physical and chemical forms, where the mercuric ion (Hg^{2+}) is predominant and exerts high cell toxicity. Mercury in the environment may be derived from natural or anthropogenic sources [4-6], including the industrial production of chlor-alkali, pulp and paper, batteries, and fluorescent lamps [7].

Ion exchange [8], precipitation [9], electrolysis [10], adsorption [11,12], membrane separation [13], and solvent extraction [14] have been developed as strategies to minimize environmental mercury discharge. Solvent extraction (SE) is quite attractive because the number of analytes to be separated can be increased by changing the solvent and extractant. However, SE is not environmentally safe as it requires organic solvents that are often toxic and/or flammable [15-17]. A system employing a liquid phase at thermodynamic equilibrium without the presence of organic solvents is a strategic substitute for the classic SE. Thus, the aqueous two-phase system (ATPS) is an interesting alternative because it consists mainly of water with small amounts of polymers, salts, or ionic liquids, which conform well to the requirements of Green Chemistry [18]. ATPS has been used quite effectively in the recovery and purification of metals [19-26]; however, studies of mercury recovery using ATPS are still incipient.

Rogers and Griffin [27] studied the partitioning behavior of mercury using PEG5000 + $(NH_4)_2SO_4$ + H_2O ATPS. Metal partitioning into the polymer-rich phase occurred after the formation of complexes with halides in the following order $Cl^- < Br^- < I^-$. Larger distribution coefficients were obtained with the use of NaI, where the distribution coefficients were greater than 907 for the PEO5000, 40 % (m/m), + $(NH_4)_2SO_4$, 3.5 mol L^{-1}, ATPS.

Roy and Lahiri [28] separated Hg(I), Hg(II), and methylmercury using an ATPS formed by PEG4000 and electrolytes (Na_2SO_4, K_2CO_3, Na_3PO_4, or NaOH). Extraction of the electrolyte-rich phase (ERP) consisting of sodium sulfate yielded 100 % recovery of Hg(I) and Hg(II) and 80 % methylmercury. Lahiri and Roy [29] showed too, in other paper, high Hg radionuclides extraction was obtained when a PEO4000 + Na_2SO_4 + H_2O ATPS was used to extraction.

These studies demonstrate the potential of ATPS for extraction of mercury into the polymer-rich phase. However, no studies of mercury separation in relation to other metals have been presented.

This study assesses the extraction of Hg(II) in ATPSs in the presence of various metals (Cr(III), Fe(III), Co(II), Cd(II), Cu(II), Ni(II), Pb(II), Mn(II), and Zn(II)). The effects of the presence of chloride ions, presence different macromolecules and electrolyte in the system, pH, and the tie-line length (TLL) on mercury extraction are investigated. The PEO1500 + sodium citrate + H_2O ATPS system is applied to separation of mercury from three different synthetic wastes: fluorescent lamps, button-type battery (Zn-air), and the chlor-alkali industrial effluent.

1.3. MATERIAL AND METHODS

1.3.1. Chemicals

All reagents were of analytical grade. Poly(ethylene oxide), PEO1500, with an average molar mass of 1,500 g mol^{-1}, and H_2O_2 were purchased from Synth (Brazil); the triblock copolymers: $(HO\text{-}(EO)_{11}(PO)_{16}(EO)_{11}\text{-}H)$, denoted L35, with an average molar mass of 1,900 g mol^{-1} and $(HO\text{-}(EO)_{13}(PO)_{30}(EO)_{13}\text{-}H)$, denoted L64, with an average molar mass of 2,900 g mol^{-1}, HNO_3, KCl, and ($CrCl_3.6H_2O$ were purchased from Aldrich (USA). $FeCl_3.6H_2O$, $HgCl_2$, $CuSO_4.5H_2O$, $MnSO_4.H_2O$, $Pb(NO_3)_2$, $Ni(NO_3)_2.4H_2O$, $Zn(NO_3)_2.6H_2O$, sodiumcitratedihydrate ($Na_3C_6H_5O_7.2H_2O$), Na_2SO_4, andNaOHwerepurchasedfromVetec (Brazil); $CdCl_2.H_2O$, $CoCl_2.6H_2O$, HCl, and H_2SO_4wereobtainedfrom Merck (Germany).

1.3.2. Compositionandpreparationof ATPS

An aqueous solution of HCl, H_2SO_4, or NaOH (pH = 1.00, 3.00, 6.00, 9.00, or 12.0) was used as the solvent to prepare the macromolecule and electrolyte stock solutions.

The PEO1500 + $Na_3C_6H_5O_7$ + H_2O [30], PEO1500 + Na_2SO_4 + H_2O [31], L35 + $Na_3C_6H_5O_7$ + H_2O [32], L35 + Na_2SO_4 + H_2O [33], and L64 + $Na_3C_6H_5O_7$ + H_2O [34] ATPSs were prepared in centrifuge tubes by mixing adequate amounts stock solutions of PEO150060.0 % (m/m), L64 54.8 % (m/m), or L35 63.0 % (m/m) with $Na_3C_6H_5O_7$ 27.5 % (m/m) or sodium sulfate 20.0 % (m/m) as described in Table 1.1. The centrifuge tubes were then manually stirred for 3 min and centrifuged at 2,900 x *g* for 30 min. The tubes were kept in a thermostatic bath at (25.0 ± 0.1) °C for 24 h until two clear phases were obtained.

Table 1.1. Masses of macromolecule (m_m), electrolyte (m_e) stock solutions, and water (m_w) used for preparation of the ATPS.

ATPS	TLL / % (m/m)	m_m /g	m_e /g	m_w /g
PEO1500 + $Na_3C_6H_5O_7$ + H_2O	35.87	12.1	29.9	13.0
PEO1500 + $Na_3C_6H_5O_7$ + H_2O	43.35	13.5	32.9	8.60
PEO1500 + $Na_3C_6H_5O_7$ + H_2O	50.33	15.2	36.1	3.70
PEO1500 + $Na_3C_6H_5O_7$ + H_2O	56.04	16.3	38.7	0.00
PEO1500 + Na_2SO_4 + H_2O	35.96	12.7	33.3	9.00
L35 + $Na_3C_6H_5O_7$ + H_2O	34.78	12.4	21.6	21.0
L35 + $Na_3C_6H_5O_7$ + H_2O	48.18	16.2	26.6	12.1
L35 + $Na_3C_6H_5O_7$ + H_2O	54.84	17.9	30.1	7.00
L35 + Na_2SO_4 + H_2O	57.50	18.2	36.7	0.10
L64 + $Na_3C_6H_5O_7$ + H_2O	36.58	14.4	16.1	24.5
L64 + $Na_3C_6H_5O_7$ + H_2O	42.56	16.6	17.0	21.4
L64 + $Na_3C_6H_5O_7$ + H_2O	45.58	16.5	19.7	18.8
L64 + $Na_3C_6H_5O_7$ + H_2O	52.96	18.8	21.6	14.6

The TLL is determined from the differences in the concentrations of the components in each phase according to Eq. (1.1):

$$\boldsymbol{TLL} = \sqrt{(\boldsymbol{C}_P^{TP} - \boldsymbol{C}_P^{BP})^2 + (\boldsymbol{C}_E^{TP} - \boldsymbol{C}_E^{BP})^2} \tag{1.1}$$

where|. and |. are the macromolecule concentrations, and |. and |. are the electrolyte concentrations (in % (m/m)) in the top phase (TP) and bottom phase (BP), respectively.

1.3.3. Mercury extraction

The ATPS phases obtained in section 1.3.2, were separated and stocked. 2.00 g of the TP containing an appropriate amount of the KClextractant (0 to 0.449 mol kg^{-1}) and 2.00 g of the BP containing Hg(II) at a concentration of 1.50 mmol kg^{-1} were mixed in a centrifuge tube. After combining the two phases, the tube was manually stirred for

3 min, centrifuged at 9,503 x *g* for 10 min at 25 °C and placed in the thermostatic bath (25.0 ± 0.1) °C for 20 min. Aliquots from the TP were collected and diluted for the determination of mercury by FAAS (Varian AA-240 spectrometer, Australia) under the operating conditions summarized in Table S1. To calculate the extraction percentage (%E) was used in Eq. (1.2). Allexperimentswereperformed in triplicate.

$$\%E = \frac{(n_{M^{x+}})_{TP}}{(n_{M^{x+}})_{T}} \times 100 \tag{1.2}$$

where$+)_{TP}$ is the amount metallic ions in the TP, and $+)_{T}$ is the total amount of metallic ions in the system.

Table S1. Operating conditions FAAS for the determination of metals.

Element	Wavelength (nm)	Applied Current (mA)	Spectral Resolution (nm)	Flame Composition air/C_2H_2 (L min^{-1})
Cd	228.8	4.0	0.5	3.50 / 1.50
Cr	357.9	7.0	0.2	3.50 / 1.50
Co	240.7	7.0	0.2	3.50 / 1.50
Cu	324.7	4.0	0.5	3.50 / 1.50
Fe	248.3	5.0	0.2	3.50 / 1.50
Hg	253.7	4.0	0.5	3.50 / 1.50
Mn	279.5	5.0	0.2	3.50 / 1.50
Ni	232.0	4.0	0.2	3.50 / 1.50
Pb	217.0	5.0	1.0	3.50 / 1.50
Zn	213.9	5.0	1.0	3.50 / 1.50

1.3.4. Effect of the amount of extractant

To study the effect of the amount of extractant on the %E of the mercury, samples were prepared by mixing 2.00 g of the electrolyte solution containing 1.50 mmol kg^{-1} Hg(II) and 2.00 g of the macromolecule solution containing the extractant with concentrations ranging from 0 to 0.449 mol kg^{-1}.

1.3.5. Samples

The compositions of the synthetic samples of mercury waste are presented in Table 1.2. Sample A corresponds to the button-type battery (Zn-air) waste [35], sample B corresponds to the fluorescent lamp waste [36], and sample C corresponds to waste sludge from thechlor-alkali industry [37]. The button-type battery (Zn-air) sample was prepared by weighing appropriate amounts of Fe(III), Hg(II), and Zn(II) followed by dissolution in HNO_3 65 % (m/m) and making up to 100.0 mL with HNO_3 65 % (m/m). To prepare the fluorescent lamp sample, adequate amounts of Hg(II), Fe(III), Cd(II), Ni(II), Pb(II), Cr(III), Zn(II), Co(II), and Mn(II) were weighed and dissolved in 25.0 mL of HNO_3 65 % (m/m) and 5.00 mL of H_2O_2 30 % (m/m). The obtained solution was transferred to a 100.0 mL flask and the volume was made up with deionized water. Finally, the chlor-alkali sludge sample containing Hg(II), Fe(III), Cd(II), Ni(II), Pb(II), Cr(III), Zn(II), Cu(II), and Mn(II) was dissolved and the volume was made up to 100 mL with a mixture of $HCl:HNO_3$ in 1:1 volume ratio. The density of all sample solutions was measured.

Table 1.2. Mole ratio of metals in button-type battery (Zn-air) (sample A), fluorescent lamp (sample B), and chlor-alkali sludge (sample C) samples.

Metal	RatioM:Hg / mol:mol		
	Sample A	Sample B	Sample C
Zn	103	4.16	9.70×10^{-1}
Fe	14.0	1.32	35.3
Cd		6.20×10^{-1}	3.75×10^{-3}
Ni		59.6	7.00×10^{-2}
Pb		7.14	3.00×10^{-2}
Cr		7.48	1.10×10^{-1}
Co		2.64	-
Cu		-	3.90×10^{-1}
Mn		6.09	9.50×10^{-1}

Metal concentration: button-type battery (Zn-air), % (m/m): Zn = 30.2, Hg = 0.9, and Fe = 3.5. Fluorescent lamps 40 W, % (m/m): Fe = 0.19, Cd = 0.18, Mn = 0.86, and (μg g^{-1}): Zn = 7, Ni = 90, Pb = 38, Cr = 10, Co = 4, Hg = 5.153. Chlor-alkali sludge (mg kg^{-1}): Hg =

505, Zn = 159, Cd = 1.06, Ni = 10.4, Pb = 15.1, Cr = 15.0, Cu = 63,
Mn = 132, andFe = 4.97 g kg^{-1}.

1.3.6. Separationofmercuryfromsamples

In a 10 mL centrifuge tube was placed 2.93 g of the PEO1500 solution 50.0 % (m/m) and mixed with 0.449 mol kg^{-1}KCl, 2.47 g $Na_3C_6H_5O_7$ solution 38.0 % (m/m), and 0.600 g of the sample solution. The PEO1500 and $Na_3C_6H_5O_7$ solutions were prepared in pH 1.00 H_2SO_4solution. The solution was stirred for 3 min, centrifuged, and placed in a thermostatic bath for 20 min at 25.0 °C. Aliquots of each phase were collected and appropriately diluted for the FAAS metal analysis and %E was determined using Eq. (1.2). All assays were performed in triplicate.

1.4. RESULTS AND DISCUSSION

1.4.1. Influence of the ATPS component nature on the extraction of Hg(II)

Figure 1.1 shows the mercury %E in the PEO1500 + $Na_3C_6H_5O_7$ + H_2O, PEO1500 + Na_2SO_4 + H_2O, L35 + $Na_3C_6H_7O_5$ + H_2O, and L64 + $Na_3C_6H_7O_5$ + H_2O ATPSs at pH 6.00, 25.0 ºC, and TLL ≈ 36 % (m/m) in the absence of an extractant. The mercury %E increased from (16.4 ± 0.6) % to (30.1 ± 1.7) % with increasing hydrophobicity of the macromolecule (PEO1500 < L35 < L64) when the ATPS electrolyte was $Na_3C_6H_5O_7$. The lower %E observed for the ATPS containing the $Na_3C_6H_5O_7$ electrolyte is due to the interaction between the Hg(II) ions and $_5O_7^{3-}$ anions (log $K_{Hg(II)\text{-}Cit}$ = 10.9) [38]. At this pH, citrate anions are deprotonated, and are thus available for formation of complexes that interact more strongly with components from the ERP, resulting in remaining mercury ions at this stage. However, when the ATPS comprising PEO1500 + Na_2SO_4 was used, the %E increased to (83.7 ± 0.8) %. This can be explained by specific interactions between $^{-}$ ions from the ERP and the species of mercury to generate the anionic complex $(SO_4)_n]^{2n-2}$ (Eq. 1.3) that interacts electrostatically with the pseudopolycation in this TP. The pseudopolycation is formed due to interactions between the cations (Na^+) and the ethylene oxide groups (EO) of the macromolecule (for PEO or copolymer) forming the ATPS [20,22,39].The metal complex and EO segments interaction intensity is very dependent on the ligand nature, i.e, the sulfate complex interact more with PEO than citrate complex. As showed by da Silva et al. [40] the $[Fe(CN)_5(NO)]^{2-}$ anion interact strongly with PEO while the $[Fe(CN)_6]^{3-}$ anion interact weakly. The authors have showed that this PEO – metal complex interaction dependence on ligand nature should be understood, considering that not only electrostatic interaction contribute to PEO – metal complex binding, but charge transfer too. Charge transfer occurs between lower unoccupied molecular orbital from ligand and higher occupied molecular orbital from the oxygen atom in the PEO chain [39, 41].

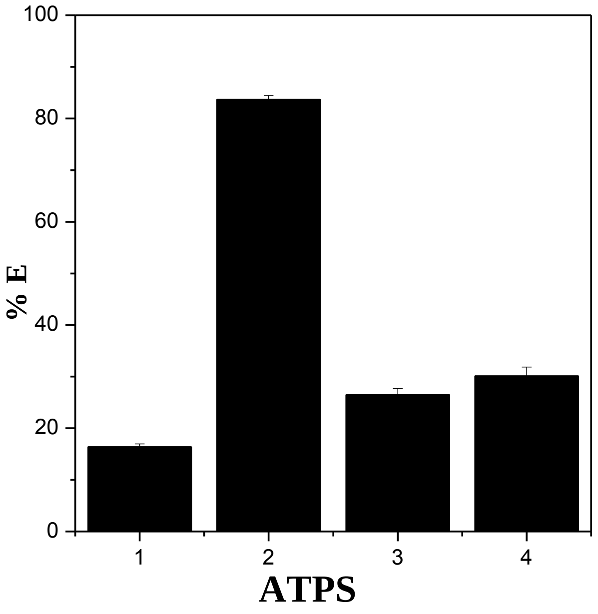


Fig. 1.1. %E oftheHg(II) in the ATPS: (1) PEO1500 + $Na_3C_6H_5O_7$ + H_2O, (2) PEO1500 + Na_2SO_4 + H_2O, (3) L35 + $Na_3C_6H_5O_7$ + H_2O e (4) L64 + $Na_3C_6H_5O_7$ + H_2O.

$$Hg^{2+}(aq) + nSO_4^{2-}(aq) \rightleftharpoons [Hg(SO_4)_n]^{2n-2}(aq) \tag{1.3}$$

This behavior demonstrates the influence of the anion formed in the ATPS on transfer of mercury to the macromolecule-rich phase (MRP).

The PEO1500 + Na_2SO_4 + H_2O ATPS at pH 6.00 and TLL 35.96 % (m/m), without extractant, was an excellent system for the extraction of Hg(II). However, this ATPS was inappropriate for application in synthetic samples due the precipitation of some metals such as lead and manganese. As ATPS BP is enriched in Na_2SO_4 and the solubility of $PbSO_4$ and $MnSO_4$ salts is low (for instance, the Kps of the Pb – sulfate is 6.3×10^{-7}) [42] occur the salt precipitation. In the case of the zinc, it addition on the BP induced phase separation process [43]. Thus, the subsequent studies were performed using the other ATPS.

1.4.2. Influence of chloride ions on %E of mercury

The ATPS composed of PEO1500 + $Na_3C_6H_5O_7$ + H_2O with TLL 35.87 and 56.04 % (m/m) was used to investigate the mercury extraction as a function of pH. H_2SO_4 (Fig. 1.2a) or HCl (Fig.1.2b) were used in both ATPS to adjust the pH to < 7 andNaOHwas used to adjust the pH to > 7.

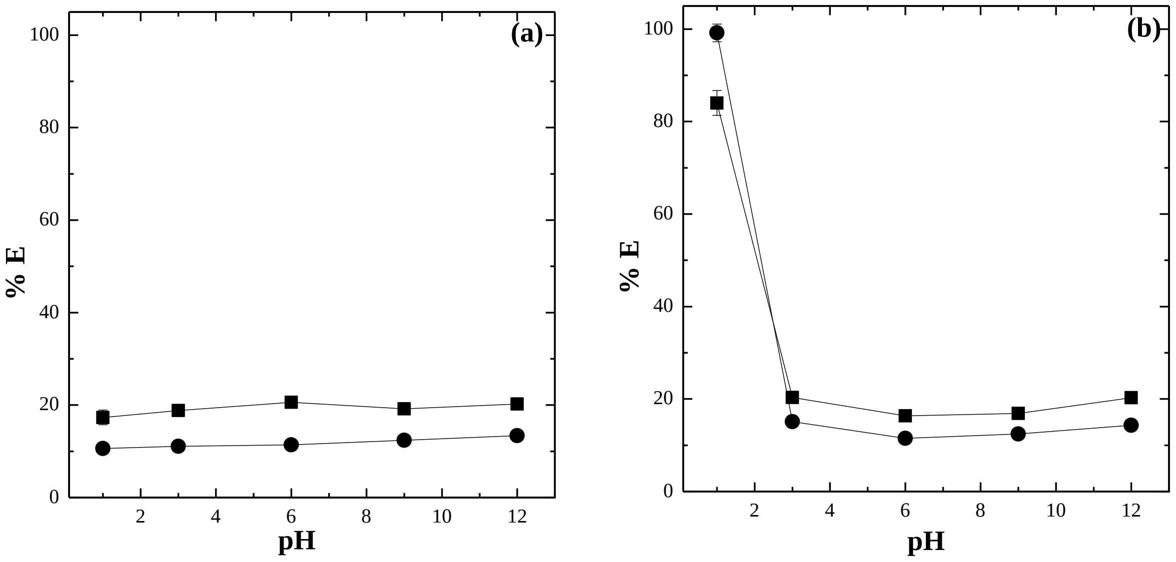


Fig. 1.2. Effect of acid used to adjust the pH of water used in ATPS on %E of mercury: (a) H_2SO_4 and (b) HCl using the PEO1500 + $Na_3C_6H_5O_7$ + H_2O ATPS with TLL (■) 35.87 % (m/m) and (●) 56.04 % (m/m).

Figure 1.2(a) shows that independent of pH, mercury is preferentially concentrated in the BP, with %E = (20.6 ± 0.5) % at pH = 6.00 and TLL = 35.87 % (m/m), and %E = (13.4 ± 0.2) % at pH = 12.0 and TLL = 56.04 % (m/m). In general way, without extracting agents in the ATPS, the metal ion prefer going to electrolyte-rich phase. Many authors observed that too [44]. This behavior is attributed to interactions of mercury with citrate-forming species that interact more strongly with components of the electrolyte-rich phase (ERP).

However, when HCl is used to adjust the pH of the medium (Fig. 1.2(b)), high mercury extraction (84.0 ± 2.7) % is achieved at pH 1.00 and TLL = 35.87 % (m/m), and %E = (99.2 ± 1.9) % at pH 1.00 and TLL = 56.04 % (m/m). The increase in %E when H_2SO_4 is replaced with HCl is associated with formation of a complex between Hg(II) and chloride to form charged species, which may generally be described by Eq. (1.4):

$$Hg^{2+}(aq) + nCl^{-}(aq) \rightleftharpoons [HgCl_n]^{2-n}(aq) \qquad (1.4)$$

These species are stable in aqueous solution since the stability constants of the Hg – chloride species are high: log $K_1 = 7.3$; log $K_2 = 14.0$; log $K_3 = 15.0$, and log $K_4 = 15.6$ [38]. The transfer of species $Cl_n]^{2-n}$ to the TP is mainly due to the electrostatic interaction of these species with the pseudopolycationpresent in theTP. The higher the TLL, the greater the amount of macromolecules in the TP, hence the greater the density of positive charges at this stage; these positive charges attract mercury-chloridespecies more strongly to the MRP, resulting in a higher %E at the highestTLL.

Since the presence of chloride strongly influenced the mercury extraction, mercury extraction was evaluated by adding different concentrations of KClto the ATPS.

Figure 1.3 shows the extraction of mercury in the PEO1500 + $Na_3C_6H_5O_7$ + H_2O ATPSfor TLL = 35.87 % (m/m) and 56.04 % (m/m) at pH 1.00 as a function of the KCl concentration of the extractant. When the ATPS withTLL 35.87 % (m/m) was used in the absence of KCl, only0.0825 mmol of mercury was transferred to the TP, %E = (11.0 ± 0.7) %.Addition of KClto the systemincreased the mercury extraction to a maximum value of %E = (93.5 ± 3.9) % when 0.225 mol kg^{-1}KCl was added. Low mercury extraction was also obtained using the ATPSwithTLL 56.04 % (m/m) in the absence of KCl. %E increased from (6.51 ± 0.4) % to (99.3 ± 1.0) % when 0.225 mol kg^{-1}KCl was added to the system. The increase in %E in the presence of higher amounts of chloride occurs because higher shifts the equilibrium (Eq. (1.4)), favoring formation of the anionic complex, which interacts with the pseudopolycation (macromolecule –Na^+), promoting the transfer of this complex to the MRP.

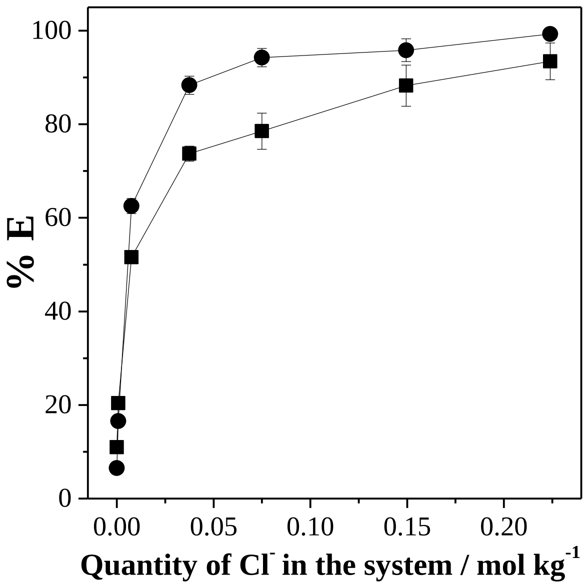


Fig. 1.3. Effect of the amount of extractant added to the TP of PEO1500 + $Na_3C_6H_5O_7$ + H_2O ATPS at pH 1.00 for TLL: (■) 35.87 % (m/m) and (●) 56.04 % (m/m).

1.4.3. Effect of the hydrophobicity of the macromolecule on %E of Hg(II)

To evaluate the contribution of hydrophobic interactions to transfer of mercury from the BP to the TP, the PEO macromolecule was replaced with L35 or L64 copolymers. L35 is a triblock copolymer with the $(EO)_{11}$–$(PO)_{16}$–$(EO)_{11}$ structure, having hydrophilic segments of ethylene oxide (EO) and a hydrophobic segment of propylene oxide (PO). The structure of L64 comprised $(EO)_{13}$–$(PO)_{30}$–$(EO)_{13}$. The top phases of the ATPSs consisting of L35 and L64 are more hydrophobic than those formed by PEO, mainly due to the presence of the PO segments. At the concentrations of L35 (or L64) used in forming the ATPS, the macromolecules are aggregated to form micelles with a hydrophobic core (PO segments) and a hydrophilic exterior (EO segments).

Figures 1.4(a) and 1.4(b) show the %E of mercury as a function of pH for different TLL using the PEO1500 + $Na_3C_6H_5O_7$ + H_2O and L64 + $Na_3C_6H_5O_7$ + H_2O ATPSs; the pH was adjusted to < 7 with HCl.

Regardless of the hydrophobicity of the macromolecule, %E was similar. At pH values ≥ 3.00, the %E of mercury was practically constant. When the PEO1500 (Fig. 1.4(a)) polymer was used, the maximum %E was (20.3 ± 0.6) % for TLL ≈ 36 % (m/m) at pH 3.00, whereas at pH 1.00, %E ranged from (76.7 ± 1.6) % for TLL ≈ 47 % (m/m) to (99.2 ± 1.9) % for TLL ≈ 54 % (m/m). For the copolymer L64 (Fig. 1.4(b)), the maximum %E was (97.2 ± 1.6) % for TLL ≈ 36 % (m/m).

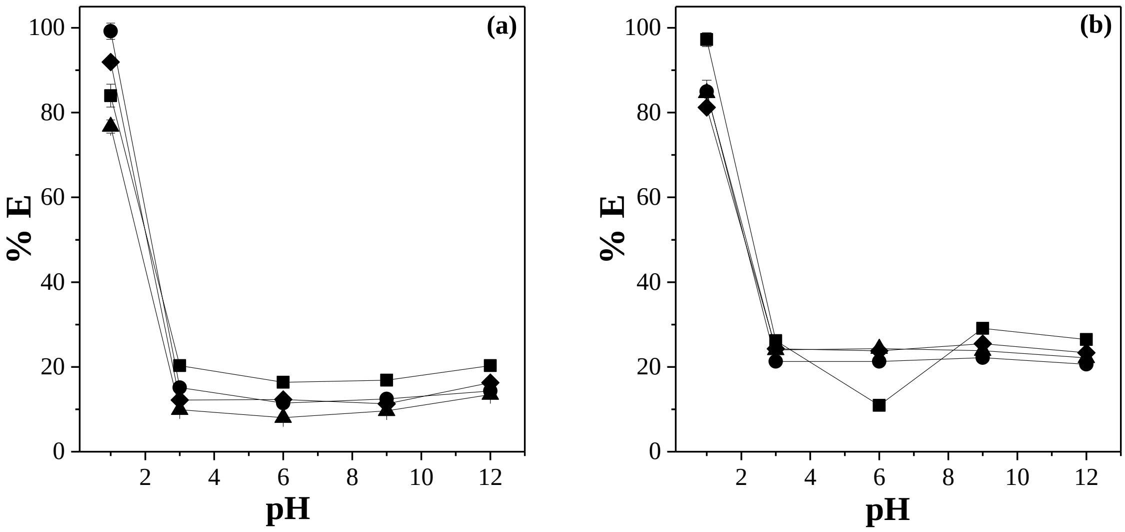


Fig. 1.4. Effectofmacromoleculeon %E ofmercuryusing ATPS: (a) PEO1500 + $Na_3C_6H_5O_7$ + H_2O and (b) L64 + $Na_3C_6H_5O_7$ + H_2O for TLL (■) ≈ 36 % (m/m), (◆) ≈ 43% (m/m), (▲) ≈ 47% (m/m), and (●) ≈ 54% (m/m).

The effects of replacing the L64 macromolecule with L35 on %E are shown in Fig.1.5(a) and 1.5(b). These figures show %E of Hg(II) based on the amount of chloride (KCl) added to the L35 + $Na_3C_6H_5O_7$ + H_2O and PEO1500 + $Na_3C_6H_5O_7$ + H_2O ATPS at different pH for TLL ≈ 55 % (m/m).

For the ATPS containing L35, the maximum %E was (99.6 ± 0.5) % at pH = 9.00, while for the system containing PEO1500, the highest %E was (99.3 ± 1.0) % at pH

1.00. At pH 12.0, %E declined for both ATPS. However, the ATPS employing L35 produced the highest %E of (27.7 ± 0.5) % compared to (17.3 ± 2.4) % for the PEO1500 + $Na_3C_6H_5O_7$ + H_2O ATPS. The highest %E for the ATPS consisting of L35 may be explained by the ability of L35 to form micellar aggregates, favoring the extraction of hydrophobic species. At pH 12.0, formation of the hydroxo – complex is favored (log $K_1 = 10.6$; log $K_2 = 21.8$, and log $K_3 = 20.9$) [38]. ATPS employing L35 can extract $Hg(OH)_2$ species into the interior of the hydrophobic micelles because this a higher percentage of mercury is extracted into the MRP [45].

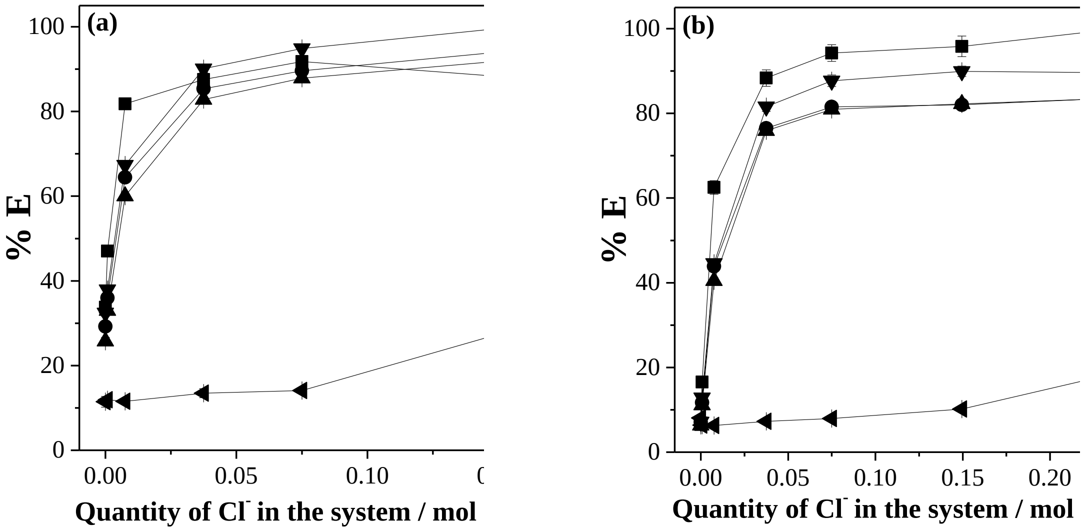


Fig. 1.5. Effect of the macromolecule on %E of the mercury using ATPS: (a) L35 + $Na_3C_6H_5O_7$ + H_2O and (b) PEO1500 + $Na_3C_6H_5O_7$ + H_2O for TLL ≈ 55 % (m/m) at pH: (■) 1.00; (●) 3.00; (▲) 6.00; (▼) 9.00, and (◀) 12.0.

In general, it was observed that regardless of the hydrophobicity of the ATPS, the mercury extraction was similar, conforming to the model that suggests a specific interaction between EO segments and anions formed by the interaction of Hg(II) and Cl^- [20,22,39]. Thus, the species are transferred to the MRP due to the strong interaction of the macromolecule with anionic species.

1.4.4. Effect of the electrolyte on %E of Hg(II)

The effect of the ATPS-forming electrolyte is an important factor affecting the %E of the metal ions. Figure 1.6 shows the %E of Hg(II) based on the amount of KCl added to the PEO1500 + $Na_3C_6H_5O_7$ + H_2O and PEO1500 + Na_2SO_4 + H_2O ATPS for TLL ≈ 36 % (m/m) and pH = 1.00. Mercury is observed to be better extracted by the ATPS containing Na_2SO_4 as the electrolyte with %E remaining practically constant at ≈ 98 %. In contrast, for the system consisting of $Na_3C_6H_5O_7$, the %E maximum was (93.5 ± 3.9) % when 0.225 mol kg^{-1}KCl was added to the ATPS.

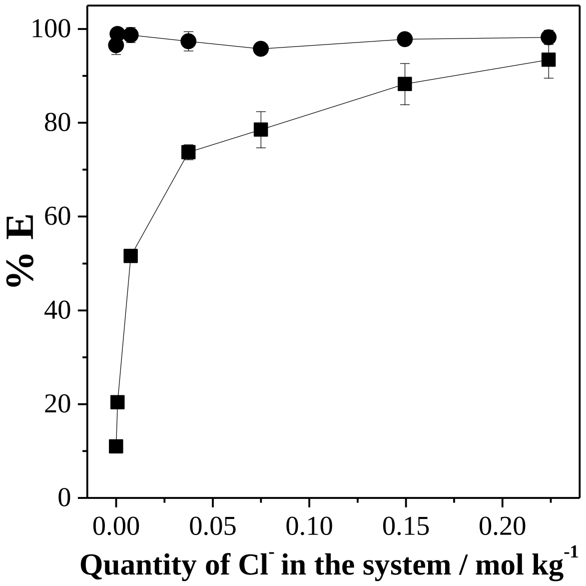


Fig. 1.6. Effect of the electrolyte on %E of mercury using ATPS: (■) PEO1500 + $Na_3C_6H_5O_7$ + H_2O and (●) PEO1500 + Na_2SO_4 + H_2O.

Replacing PEO1500 by L35 produced slightly different extraction behavior. Figure 1.7 shows the %E as a function of the amount of KCl added to the medium for the ATPSs consisting of L35 + $Na_3C_6H_5O_7$ + H_2O and L35 + Na_2SO_4 + H_2O. When the ATPS consisting of Na_2SO_4 was used for extraction, it was not possible to use the maximum concentration of chloride (0.225 mol kg^{-1}) because the thermodynamic properties of the ATPS were modified. The change of $Na_3C_6H_5O_7$ by Na_2SO_4 alter the

ATPS binodal curve making necessary more electrolyte to induce phase separation behind to make less soluble the KCl added.

The use of ATPS containing $Na_3C_6H_5O_7$ produced mercury extraction of (91.7 ± 0.8) %; however, when $Na_3C_6H_5O_7$ was substituted for Na_2SO_4, the %E increased to (99.8 ± 1.5) %.

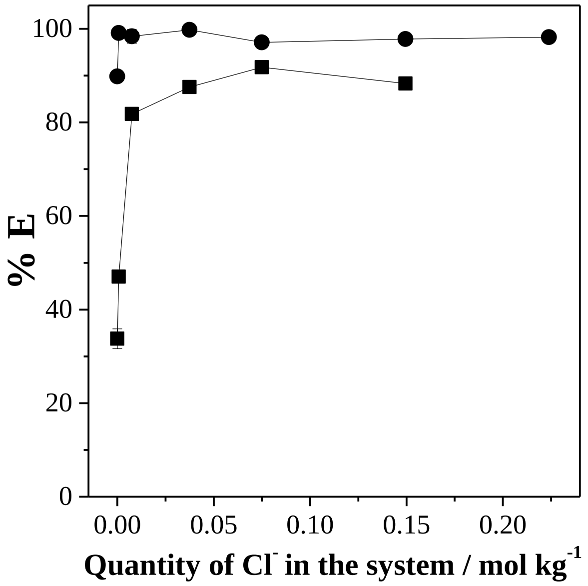


Fig. 1.7. Effect of electrolyte on %E of mercury using ATPS: (■) L35 + $Na_3C_6H_5O_7$ + H_2O and (●) L35 + Na_2SO_4 + H_2O.

The ATPS containing Na_2SO_4 was more efficient for extraction of Hg(II) than that containing $Na_3C_6H_5O_7$ as the electrolyte because the high concentration of sulfate ions in the system contributes to the formation of anionic complexes (as described in Eq. 1.3) that have affinity for the MRP.

1.4.5. Effect of pH on mercury extraction

The PEO1500 + $Na_3C_6H_5O_7$ + H_2O ATPS with TLL = 56.04 % (m/m) was used to investigate the influence of pH on the %E of mercury. The dependence of the %E of mercury on the amount of extractantKCl at different pH values is shown in Fig. 1.5(b). Regardless of the pH, little mercury was extracted in the absence of KCl (%E less than ((8.1 ± 0.6) %).

Quantitative extraction of mercury, %E = (99.3 ± 1.0 %), was obtained at pH 1.00 using 0.225 mol kg^{-1} of KCl. At pH 12.0, extraction was less efficient, (17.3 ± 2.4) %, with the mercury species being concentrated in the ERP. This occurs because the ATPS comprises PEO1500 that has more hydrophilic character and is not able to extract hydroxo complexes that are usually formed at this pH.

1.4.6. Effect of ATPS composition on mercury extraction

The TLL is a thermodynamic parameter that expresses the difference in the intensive thermodynamicproprieties between ATPS phases in equilibrium. Thus, the TP and BP become more distinct with increasing TLL. Figure1.3 illustrates the effect of theTLL on the %E of mercury. As theTLLincreased from 35.87 to 56.04 % (m/m), partitioning ofHg(II) into the TP of the ATPS increased from (93.5 ± 3.9) % to (99.3 ± 1.0) % when the maximum concentration of KCl was used. Extraction of mercury into theTP with increasingTLL occurs due to the enhanced interaction between the complexes formed, i.e., $Cl_n]^{2-n}$ and the hydrophilic segments of ethylene oxide (EO).

1.4.7. Separation of mercury from co-existing metals

Figure 1.8 shows the extraction behavior of Hg(II), Co(II), Fe(III), Cr(II), Zn(II), Cd(II), Cu(II), Ni(II), and Pb(II) using the PEO1500 + $Na_3C_6H_5O_7$ + H_2O ATPS for TLL = 56.04 % (m/m), at pH 1.00, in the presence of 0.225 mol kg^{-1}KCl and co-existing metal ions at Hg(II)/metal molar ratios of 1.00, 5.00, 10.0, and 15.0.

Selective extraction of Hg(II) exceeding (96.7 ± 0.8) % in the presence of co-existing metal ions was achieved, regardless of the molar ratio. Thus, Hg(II) may be separated from the aforementioned metal ions at all molar ratios analyzed.

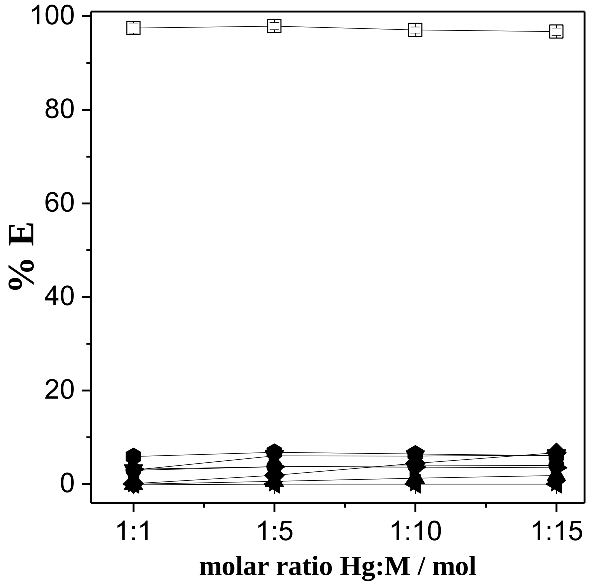


Fig. 1.8. Influence of the metal ions (●) Cr(III), (▲) Fe(III), (▼) Co(II), (◀) Cd(II), (▶) Cu(II), (◆) Ni(II), (▯) Pb(II), and (⬢) Zn(II) on the %E of (☐) Hg(II) using the PEO1500 + $Na_3C_6H_5O_7$ + H_2O ATPS.

The efficiency of separation of Hg(II) and other metal ions was evaluated by determining the separation factor ($S_{Hg,M}$) which is expressed by Eq. (1.5):

$$S_{Hg,M} = \frac{D_{Hg}}{D_M} \tag{1.5}$$

D_{Hg} is the distribution coefficient of all mercury species and D_M is the distribution coefficient of all metal species M (Co, Cu, Fe, Cr, Zn, Cd, Ni, or Pb). The distribution coefficient can be determined from Eq. (1.6):

$$D_M = \frac{\% E}{100 - \% E} \tag{1.6}$$

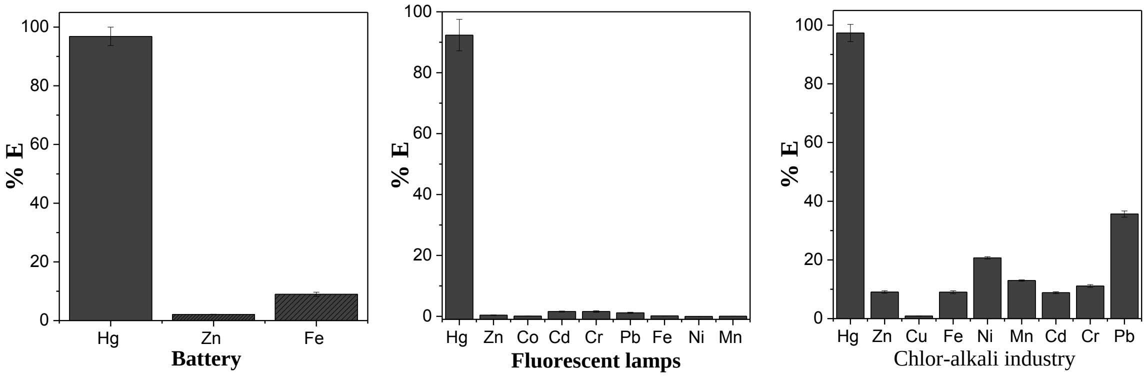
$S_{Hg,M}$ values greater than 10^3 imply effective separation of mercury from other metals. The $S_{Hg,M}$ values ranged from $S_{Hg(II),Zn(II)} = 1.54 \times 10^2$ to $S_{Hg(II),Cd(II)} = 3.21 \times 10^{10}$ (Table 1.3). The results indicate that Hg(II) can be efficiently separated from most metal ions.

Table 1.3. Separation factors ($S_{Hg,M}$) for Hg and other metals studied (M).

	Molar ratioHg:M			
	1 : 1	1 : 5	1 : 10	1 : 15
$S_{Hg(II),Co(II)}$	7.96×10^3	2.49×10^3	1.05×10^3	7.22×10^3
$S_{Hg(II),Fe(III)}$	6.91×10^5	7.82×10^3	3.82×10^3	4.25×10^3
$S_{Hg(II),Cr(III)}$	1.98×10^3	1.96×10^3	1.11×10^3	6.00×10^2
$S_{Hg(II),Zn(II)}$	6.44×10^2	7.44×10^2	2.73×10^2	1.54×10^2
$S_{Hg(II),Cd(II)}$	3.21×10^{10}	2.09×10^{10}	4.47×10^9	5.01×10^9
$S_{Hg(II),Cu(II)}$	6.75×10^2	5.12×10^2	6.02×10^2	1.57×10^3
$S_{Hg(II),Ni(II)}$	2.64×10^4	1.48×10^3	7.15×10^2	1.01×10^3
$S_{Hg(II),Pb(II)}$	2.39×10^5	6.76×10^5	2.30×10^5	2.60×10^5

1.4.8. Mercury separationfromthesamples

Figure 1.9 shows the %E obtained for each metal present in synthetic fluorescent lamp, button-type battery (Zn-air), and chlor-alkali leachate samples using the PEO1500 + $Na_3C_6H_5O_7$ + H_2O ATPS containing 0.225 mol kg^{-1} of KCl at pH = 1.00 for TLL 56.04 % (m/m).



Battery **Fluorescent lamps** Chlor-alkali industry

Fig. 1.9. Extraction of metals present in button-type battery (Zn-air),fluorescent lamp, and chlor-alkali waste using PEO1500 + $Na_3C_6H_5O_7$ + H_2O.

Even high concentrations of metals did not affect the extraction efficiency of mercury %E ≥ (92.3 ± 5.2) %, indicating that Hg(II) is extracted to the TP, while other metals remain in the BP with %E ≤ (35.6 ± 1.1) %. Extraction of mercury into the MRP occurs due to the formation of complexes between anionic Hg(II) and Cl$^-$, which interact with the pseudopolycation present at this stage. Other metals do not form complexes with chloride, with the exception of cadmium; thus, they interact more strongly with the components present in the ERP.

The PEO1500 + $Na_3C_6H_5O_7$ + H_2O ATPS proved to be very effective for mercury extraction from these samples.

1.5. CONCLUSIONS

An efficient new method based on the principles of Green Chemistry was developed for separation of Hg(II) present in batteries, chlor-alkali waste, and fluorescent lamps. The proposed method is an excellent alternative to extraction methods using organic solvents, given that extraction using the ATPS is environmentally safe because the system is composed predominantly of water and the components can be recycled. The obtained %E of Hg(II) was ≥ (92.3 ± 5.2) %, achieved with the ATPS comprising PEO1500 + $Na_3C_6H_5O_7$ + H_2O for a TLL of 56.04 % (m/m) with 0.225 mol kg^{-1} of the KClextractant at pH 1.00, demonstrating the efficiency of the extraction method even in highly complex matrices.

1.6. REFERENCES

[1] S.S. de Souza, A.D. Campiglia, F. Barbosa, A simple method for methylmercury, inorganic mercury and ethylmercury determination in plasma samples by high performance liquid chromatography–cold-vapor-inductively coupled plasma mass spectrometry, Anal. Chim.Acta 761 (2013) 11-17.

[2] Y. Date, A. Aota, S. Terakado, K. Sasaki, N. Matsumoto, Y. Watanabe, T. Matsue, N. Ohmura, Trace-level mercury ion (Hg^{2+}) analysis in aqueous sample based on solid-phase extraction followed by microfluidic immunoassay, Anal. Chem. 85 (2013) 434-440.

[3] N. Vasimalai, G. Sheeba, S.A. John, Ultrasensitive fluorescence-quenched chemosensor for Hg(II) in aqueous solution based on mercaptothiadiazole capped silver nanoparticles, J. Hazard. Mater. 213 (2012) 193-199.

[4] E. Fernandez, L. Vidal, D. Martin-Yerga, M.D. Blanco, A. Canals, A. Costa-Garcia, Screen-printed electrode based electrochemical detector coupled with ionic liquid dispersive liquid–liquid microextraction and microvolume back-extraction for determination of mercury in water samples, Talanta 135 (2015) 34-40.

[5] S.X. Zhang, Y.Y. Zhang, J.S. Liu, Q. Xu, H.Q. Xiao, X.Y. Wang, H. Xu, J. Zhou, Thiol modified Fe_3O_4@SiO_2 as a robust, high effective, and recycling magnetic sorbent for mercury removal, Chem. Eng. J. 226 (2013) 30-38.

[6] K. Leopold, M. Foulkes, P. Worsfold, Methods for the determination and speciation of mercury in natural waters - A review, Anal. Chim.Acta 663 (2010) 127-138.

[7] F. Raji, M. Pakizeh, Study of Hg(II) species removal from aqueous solution using hybrid $ZnCl_2$-MCM-41 adsorbent, Appl. Surf. Sci. 282 (2013) 415-424.

[8] P.J. Lloyd-Jones, J.R. Rangel-Mendez, M. Streat, Mercury sorption from aqueous solution by chelating ion exchange resins, activated carbon and a biosorbent, Process Saf. Environ. 82 (2004) 301-311.

[9] L.Y. Blue, P. Jana, D.A. Atwood, Aqueous mercury precipitation with the synthetic dithiolate, $BDTH_2$, Fuel 89 (2010) 1326-1330.

[10] X.J. Jiang, W.E. Gan, L.Z. Wan, H.C. Zhang, Y.Z. He, Determination of mercury by electrochemical cold vapor generation atomic fluorescence spectrometry using polyaniline modified graphite electrode as cathode, Spectrochim. Acta B 65 (2010) 171-175.

[11] A. Ismaiel, M.K. Aroua, R. Yusoff, Palm shell activated carbon impregnated with task-specific ionic-liquids as a novel adsorbent for the removal of mercury from contaminated water, Chem. Eng. J. 225 (2013) 306-314.

[12] T. Wajima, K. Sugawara, Adsorption behaviors of mercury from aqueous solution using sulfur-impregnated adsorbent developed from coal, Fuel Process. Technol. 92 (2011) 1322-1327.

[13] M.K. Rofouei, A. Sabouri, A. Ahmadalinezhad, H. Ferdowsi, Solid phase extraction of ultra-traces mercury (II) using octadecyl silica membrane disks modified by 1,3-bis(2-ethoxyphenyl)triazene (EPT) ligand and determination by cold vapor atomic absorption spectrometry, J. Hazard. Mater. 192 (2011) 1358-1363.

[14] F.D.M. Fábrega, M.B. Mansur, Liquid–liquid extraction of mercury (II) from hydrochloric acid solutions by Aliquat 336, Hydrometallurgy 87 (2007) 83-90.

[15] X.X. Song, M.D. Ye, X.J. Tang, C.J. Wang, Ionic liquids dispersive liquid–liquid microextraction and HPLC-atomic fluorescence spectrometric determination of mercury species in environmental waters, J. Sep. Sci. 36 (2013) 414-420.

[16] A. Niazi, T. Momeni-Isfahani, Z. Ahmari, Spectrophotometric determination of mercury in water samples after cloud point extraction using nonionic surfactant Triton X-114, J. Hazard. Mater. 165 (2009) 1200-1203.

[17] M. Huebra, M.P. Elizalde, A. Almela, Hg(II) extraction by LIX 34. Mercury removal from sludge, Hydrometallurgy 68 (2003) 33-42.

[18] G.D. Rodrigues, M.D.H. da Silva, L.H.M. da Silva, L.D. Teixeira, V.M. de Andrade, Liquid-liquid phase equilibrium of triblock copolymer L64, poly(ethylene oxide-b-propylene oxide-b-ethylene oxide), with sulfate salts from (278.15 to 298.15) K, J. Chem. Eng. Data 54 (2009) 1894-1898.

[19] L.R. de Lemos, R.A. Campos, G.D. Rodrigues, L.H.M. da Silva, M.C.H. da Silva, Green separation of copper and zinc using triblock copolymer aqueous two-phase systems, Sep. Purif. Technol. 115 (2013) 107-113.

[20] G.D. Rodrigues, L.R. de Lemos, L.H.M. da Silva, M.C.H. da Silva, Application of hydrophobic extractant in aqueous two-phase systems for selective extraction of cobalt, nickel and cadmium, J. Chromatog. A 1279 (2013) 13-19.

[21] L.R. de Lemos, I.J.B. Santos, G.D. Rodrigues, L.H.M. da Silva, M.C.H. da Silva, Copper recovery from ore by liquid-liquid extraction using aqueous two-phase system, J. Hazard. Mater. 237 (2012) 209-214.

[22] P.D. Patricio, M.C. Mesquita, L.H.M. da Silva, M.C.H. da Silva, Application of aqueous two-phase systems for the development of a new method of cobalt(II), iron(III)

and nickel(II) extraction: A green chemistry approach, J. Hazard. Mater. 193 (2011) 311-318.

[23] V.G. Lacerda, A.B. Mageste, I.J.B. Santos, L.H.M. da Silva, M.D.H. da Silva, Separation of Cd and Ni from Ni–Cd batteries by an environmentally safe methodology employing aqueous two-phase systems, J. Power Sources 193 (2009) 908-913.

[24] R.D. Rogers, J.H. Zhang, Effects of increasing polymer hydrophobicity on distribution ratios of TcO_4^- in polyethylene/poly(propylene glycol)-based aqueous biphasic systems, J. Chromatog. B 680 (1996) 231-236.

[25] R.D. Rogers, A.H. Bond, C.B. Bauer, Metal ion separations in polyethylene glycol-based aqueous biphasic systems, Separ. Sci. Technol. 28 (1993) 1091-1126.

[26] B. Dutta, S. Lahiri, B.S. Tomar, Application of PEG based aqueous biphasic systems in extraction and separation of no-carrier-added Re-183 from bulk tantalum, Radiochim. Acta 101 (2013) 19-26.

[27] R.D. Rogers, S.T. Griffin, Partitioning of mercury in aqueous biphasic systems and on ABEC(TM) resins, J. Chromatog. B 711 (1998) 277-283.

[28] K. Roy, S. Lahiri, Extraction of Hg(I), Hg(II) and methylmercury using polyethyleneglycol based aqueous biphasic system, Appl. Radiat. Isotopes 67 (2009) 1781-1784.

[29] S. Lahiri, K. Roy, A green approach for sequential extraction of heavy metals from Li irradiated Au target, J. Radioanal. Nucl. Ch. 281 (2009) 531-534.

[30] J.G.L.F. Alves, J. Brenneisen, L. Ninni, A.J.A. Meirelles, G. Maurer, Aqueous two-phase systems of poly(ethylene glycol) and sodium citrate: Experimental results and modeling, J. Chem. Eng. Data 53 (2008) 1587-1594.

[31] J.P. Martins, C.D. Carvalho, L.H.M. da Silva, J.S.D. Coimbra, M.D.H. da Silva, G.D. Rodrigues, L.A. Minim, Liquid–Liquid equilibria of an aqueous two-phase system containing poly(ethylene) glycol 1500 and sulfate salts at different temperatures, J. Chem. Eng. Data 53 (2008) 238-241.

[32] J.P. Martins, A.B. Mageste, M.D.H. da Silva, L.H.M. da Silva, P.D. Patricio, J.S.D. Coimbra, L.A. Minim, Liquid-Liquid Equilibria of an Aqueous Two-Phase System

Formed by a Triblock Copolymer and Sodium Salts at Different Temperatures, J. Chem. Eng. Data 54 (2009) 2891-2894.

[33] M.D.H. da Silva, L.H.M. da Silva, J. Amim, R.O. Guimaraes, J.P. Martins, Liquid-liquid equilibrium of aqueous mixture of triblock copolymers L35 andF68 with Na_2SO_4, Li_2SO_4, or $MgSO_4$, J. Chem. Eng. Data 51 (2006) 2260-2264.

[34] V.M. de Andrade, G.D. Rodrigues, R.M.M. de Carvalho L.H.M. da Silva, M.C.H. da Silva, Aqueous two–phase systems of copolymer plus organic salt plus water: Enthalpic L64–salt interaction and Othmer–Tobias, NRTL and UNIFAC thermodynamic modeling, Chem. Eng. J. 171 (2011) 9-15.

[35] C.N. da Silva, J.C. Afonso, Processing of spent button cells, Quim. Nova 31 (2008) 1567-1572.

[36] C. Raposo, C.C. Windmöller, W.A.D. Júnior, Mercury speciation in fluorescent lamps by thermal release analysis, Waste Manage. 23 (2003) 879-886.

[37] Y. Busto, X. Cabrera, F.M.G. Tack, M.G. Verloo, Potential of thermal treatment for decontamination of mercury containing wastes from chlor-alkali industry, J. Hazard. Mater. 186 (2011) 114-118.

[38] A.E. Martell, R.M. Smith, Critical Stability Constants of Metal Complexes Database, National Institute of Standards and Technology, 2001.

[39] L.H.M. da Silva, M.C.H. da Silva, R.A.N. de Aquino, K.R. Francisco, M.V.C. Cardoso, L.A. Minim, J.S.R. Coimbra, Nitroprusside–PEO enthalpic interaction as a driving force for partitioning of the $[Fe(CN)_5NO]^{2-}$ anion in aqueous two-phase systems formed by poly(ethylene oxide) and sulfate salts, J. Phys. Chem. 110 (2006) 23540-23546.

[40] L.H.M da Silva, M.D.H. da Silva, J. Amin, J.P. Martins, J.S.D. Coimbra, L.A. Minim, Hydrophobic effect on the partitioning of $[Fe(CN)_5(NO)]^{2-}$ and $[Fe(CN)_6]^{3-}$ anions in aqueous two-phase systems formed by triblock copolymers and phosphate salts, Sep. Purif. Technol. 60 (2008) 103-112.

[41] L.H.M. da Silva, M.C.H. da Silva, K.R. Francisco, M.V.C. Cardoso, L.A. Minim, J.S.R. Coimbra, PEO−$[M(CN)_5NO]^{x-}$ (M = Fe, Mn, or Cr) interaction as a driving force in the partitioning of the pentacyanonitrosylmetallate anion in ATPS: Strong effect of

the central atom, J. Phys. Chem. B 112 (2008) 11669-11678.

[42] D. Harris, Quantitative Chemical Analysis, eighth ed., W. H. Freeman and Company,New York, 2010.

[43] L.R. de Lemos, P.D. Patrício, G.D.Rodrigues, R.M.M. de Carvalho, M.C.H. daSilva, L.H.M. da Silva, Liquid–liquid equilibrium of aqueous two-phase systems composed of poly(ethylene oxide) 1500 and different electrolytes ($(NH_4)_2SO_4$, $ZnSO_4$ and K_2HPO_4): Experimental and correlation, Fluid Phase Equilibr. 305 (2011) 19-24.

[44] R.D. Rogers, C.B. Bauer, Partitioning behavior of Group 1 and 2 cations in poly(ethylene glycol)-based aqueous biphasic systems, J. Chromatogr. B Biomed. Sci. Appl. 680 (1996) 237-241.

[45] G.D. Rodrigues, M.D.H. da Silva, L.H.M. da Silva, F.J. Paggioli, L.A. Minim, J.S.D. Coimbra, Liquid–liquid extraction of metal ions without use of organic solvent, Sep. Purif. Technol. 62 (2008) 687-693.

CAPÍTULO 2

Separation of cobalt, nickel, and iron using a green extraction system without extractant

2.1. Abstract

The extraction Co(II), Fe(III), and Ni(II) was studied in new aqueous two-phase systems consisting of poly(ethylene oxide) (i.e., PEO1500) or triblock copolymers (L64 and F68), electrolytes (sodium thiocyanate, potassium, and ammonium), and water without the use of any extractant. The extraction of metal ions was affected by the pH and the type of macromolecule used to form the ATPS. Using aqueous two-phase systems consisting of L64 + NH_4SCN + H_2O at 25.0 ºC and a tie line length (TLL) equal to 28.93 % (w/w), a separation factor ($S_{M,N}$) equal to 1.20×10^2 was obtained for the separation of Co(II) and Ni(II) at pH 3.00, and $S_{Ni(II),Fe(III)} = 3.03 \times 10^2$ for separation of Ni(II) and Fe(III) at pH = 6.00.Fe(III) can be successfully separated from both Co(II) and Ni(II) at pH = 12.0 due to the formation $Fe(OH)_3$ which is not soluble at medium pH.

Keywords:aqueous two-phase system; green chemistry; without extractant; thermodynamic properties; partition.

2.2. INTRODUCTION

Solvent extraction is conventionally used to extract/separate metals. Different solvents and extractants have been utilized in this process, with successful separation of many metals. However, the use of organic solvents is undesirable due to the potentially deleterious effects on human health and the environment. Therefore, it is necessary to develop extraction methods that can extract a wide range of metals and at the same time fit within the principles of Green Chemistry.

The aqueous two-phase system (ATPS) is an environmental and economic sustainable alternative for extraction of metals because this system consists mainly of water, and the additional components can be recycled and are biodegradable.

ATPS can be prepared by mixing an aqueous solution of two components, i.e., polymer and electrolyte (organic or inorganic) [1,2], two polymers [3,4], or two electrolytes [5]. After mixing, the system segregates into two aqueous phases, the water content of which is of the order of up to 80 % (w/w); one phase is rich in one component and the other is rich in the other component [6].

Historically, the ATPS has been successfully employed for extraction of various biomolecules [7-10], but is still little investigated for metal ion extraction. The first investigation of metal ion partition was performed in the mid-80s by Zvarova and co-workers [11]. Typically, the ATPS used in the extraction comprised poly(ethylene oxide), PEO1500, and an inorganic salt [12,13]. In these studies, a hydrophilic extractant was found to be necessary for extraction of the metal ion into the polymer-rich phase.

Recently, it was shown that these metal ions can be extracted in the presence of hydrophobic extractants using ATPS formed by a triblock copolymer [14-16]. This

ATPS is more hydrophobic than the typical ATPS formed by PEO given that under certain conditions of temperature and composition, the copolymers form aggregates with a hydrophobic core; thus, the less soluble compounds can be solubilized in water [15-18]. In these studies, the authors attributed the extraction of metal ions into the polymer-rich phase due to the formation of anionic or neutral complexes (hydrophobic) that interact most strongly with the pseudopolycation formed between the macromolecule and ATPS-forming cation [14,19].

With the objective of further investigate the driving forces governing the preferential partition of the metal ion into the polymer-rich phase, herein, we investigate the partition behavior of cobalt, nickel, and iron in a new ATPS formed by a copolymer (L64 or F68) or polymer (PEO1500), sodium, potassium or ammoniumthiocyanate, and water. The extraction behavior of the metals was investigated without the use of any extractant and with variation of the pH, tie-line length (TLL), macromolecule, and electrolyte.

2.3. MATERIALS ANDMETHODS

2.3.1. Equipments

Deionized water was used in the preparation of all solutions (Milli-Q II, Millipore, USA). Solutions of 1 mol L^{-1}NaOH or H_2SO_4 were prepared using a pH meter (HI221, Hanna Instruments, Brazil). The solutions were prepared by weighing appropriate amounts of the polymer or copolymer, salt, and water with the aid of a Shimadzu AY220analytical balance (Japan; with uncertainty ± 0.0001 g). A Thermo Scientific–HerauesMegafuge 11R (Germany) centrifuge was used to accelerate the phase separation ATPS and a Microquimica - MQBTC 99-20 thermostatic bath (Brazil) was used to maintain the temperature of the ATPS. The concentrations of iron, cobalt, and nickel were determined by flame atomic absorption spectrometry, FAAS, (Varian AA-240, Australia) with the following operating conditions (Table 2.1):

Table 2.1. Instrumental conditions for FAAS measurement

Element	Wavelength (nm)	Applied Current (mA)	Spectral Resolution (nm)	Flame Composition air/C_2H_2 (L min^{-1})
Fe	248.3	5	0.2	3.50 / 1.50
Co	240.7	7	0.2	3.50 / 1.50
Ni	232.0	4	0.2	3.50 / 1.50

2.3.2. Chemicals

All reagents were of analytical grade. Poly(ethylene oxide) (termed PEO1500; average molar mass 1,500 g mol^{-1}) was purchased from Synth (Brazil). Triblock copolymers (poly(ethylene oxide)$_x$–poly(propylene oxide)$_y$–poly(oxide ethylene)$_x$: $(EO)_{13}$–$(PO)_{30}$–$(EO)_{13}$, called L64, with an average molar mass of 2,900 g $mol^{-1}$and 40 % EO), and $(EO)_{80}$–$(PO)_{30}$–$(EO)_{80}$, termed F68, with average molar mass 8,400 g $mol^{-1}$and 80% EO were purchased from Sigma Aldrich (USA). The reagents $FeCl_3.6H_2O$, $Ni(C_2H_3O_2)_2.4H_2O$, $CoCl_2.6H_2O$, KSCN, NaSCN,NH_4SCN, and NaOH were purchased from Vetec (Brazil), and H_2SO_4 was purchased from Merck (Germany).

2.3.3. Composition and preparation of the ATPS

Macromolecule stock solutions (L64, F68, or PEO1500) and salt (NaSCN, KSCN, or NH_4SCN) were prepared by using a solution of NaOH or H_2SO_4 at pH 3.00, 6.00, or 12.0. The concentrations of the stock solutions were chosen such that upon mixing each of theATPS listed in Table 2.2 would be obtained. The ATPS were prepared by mixing 29.0 g of macromolecule stock solution with 26.0 g of electrolyte stock solution in a 50 mL centrifuge tube. The centrifuge tube was manually agitated for 3 min and centrifuged at 2,900 x *g* for 30 min at 25.0 °C. The tube containing the ATPS was kept in the thermostatic bath (25.0 ± 0.1) °C for 24 h until the thermodynamic equilibrium was reached. The top phase (TP) and bottom phase (BF) were collected and reserved.

Table 2.2. Concentrations, in % (w/w), of polymer/copolymer (w_m) and electrolyte (w_s) in the top phase (TP) and bottom phase (BP), and overall composition for the ATPS studied; evaluation was performed at 25.0 °C for the tie-line length (TLL)

ATPS	TLL	Composition / % (w/w)					
		Overall*		TP*		BP*	
		w_m	w_s	w_m	w_s	w_m	w_s
L64 + NaSCN + H_2O	28.74	16.34	25.60	29.66	22.90	1.49	28.61
L64 + NaSCN + H_2O	31.47	16.56	26.19	31.06	22.89	0.38	29.88
L64 + NaSCN + H_2O	33.36	17.13	26.61	32.44	22.83	0.05	30.83
L64 + NaSCN + H_2O	34.93	17.85	27.02	33.80	22.76	0.05	31.78
L64 + NaSCN + H_2O	37.57	19.08	27.48	36.15	22.56	0.05	32.96
L64 + NaSCN + H_2O	38.02	19.56	26.69	37.02	22.43	0.08	31.44
L64 + KSCN + H_2O	28.33	16.56	24.40	29.74	21.95	1.86	27.13
L64 + KSCN + H_2O	34.17	17.61	25.58	33.35	21.97	0.05	29.61
L64 + KSCN + H_2O	43.64	22.18	29.25	42.03	23.62	0.05	35.54
L64 + NH_4SCN + H_2O	28.93	16.89	27.44	1.88	30.17	30.34	25.00
L64 + NH_4SCN + H_2O	32.51	18.14	28.48	1.27	31.54	33.26	25.73
F68 + KSCN + H_2O	41.46	22.42	34.11	40.99	27.84	1.71	41.11
PEO1500 + KSCN + H_2O	44.39	13.68	43.84	43.38	36.17	0.40	44.39

***Uncertaintyof ± 0.01**

2.3.4. Extractionofmetals

A 10 mL centrifuge tube was charged with 2.00 g of TP, 2.00 g of BP (obtained as described in Section 3.3.3), and 0.100 g of stock solution of nickel, iron, and cobalt (3.48, 13.9, or 27.8 mmol kg^{-1}). The tube was then manually stirred for 3 min, centrifuged at 9,503 x*g* for 10 min, and kept for 20 min at 25.0 °C in a thermostatic bath. All experiments were performed in triplicate.

For determination of the metal ions by FAAS, aliquots of the TP and BP were collected and properly diluted and the percentage extraction (%E) of the metal ions was calculated using Eq. (2.1):

$$\%E = \frac{(n_{M^{x+}})_{TP}}{(n_{M^{x+}})_{T}} \times 100 \qquad (2.1)$$

Here, $^{+})_{TP}$ is the amount of metal ions in the TP (mol) and $^{+})_{T}$ is the total amount of metal ions in the system (mol).

2.4. RESULTS AND DISCUSSION

2.4.1. Influence of the composition of ATPS on extraction of the metal ions

Figure 2.1 shows the %E of the metal ions Ni(II), Fe(III), and Co(II) according to the tie-line length (TLL) using the ATPS comprising L64 + NaSCN + H_2O; data were acquired at pH 6.00 and 25.0 ºC without the addition of an extractant.

The %E of the ions is essentially independent of the TLL. The %E of Ni(II) ranged from (62.6 ± 0.8) % to (66.2 ± 0.4) % compared to (94.3 ± 0.3) % to (103 ± 0) % for Co(II) and (93.9 ± 5.5) % to (104 ± 2) % for Fe(III).

It has been reported that when various ATPS were used for the extraction of metal ions without the presence of an extractant, the abovementioned ions generally concentrated preferably in the electrolyte-rich phase; thus, the %E did not exceed 10 to 15 % [14-17]. The ATPS systems investigated in this work are the first with which %E values of 60 and 104 % could be achieved without the use of an extractant.

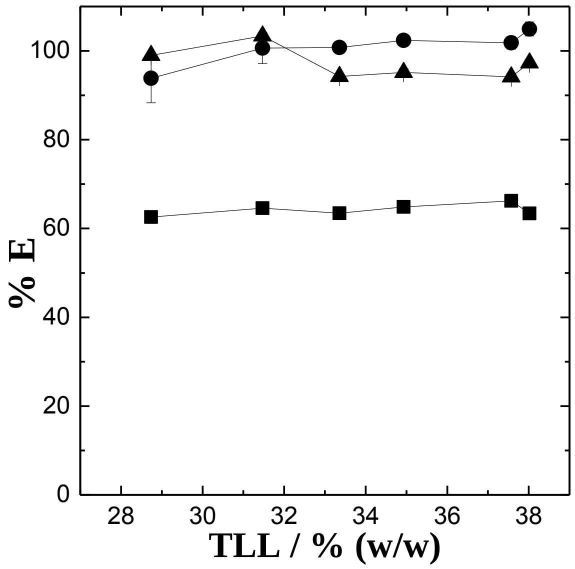


Fig. 2.1. Effect of the TLL on the %E of the metal ions (■) Ni(II), (●) Fe(III), and (▲) Co(II) employing the L64 + NaSCN + H_2O ATPS; pH 6.00, 25.0 °C, [metal] in the system = 0.339 mmol kg^{-1}, n = 3.

This extraction behavior is caused by the different intermolecular interactions between the ATPS-forming components and different chemical species formed between the metal and these different components. SCN^- anions form various anionic complexes with iron, nickel, and cobalt $(SCN)_x]^{(x-m)-})$ having different chemical structures (Eq. 2.2).

$$M^{m+}(aq) + xSCN^-(aq) \rightleftharpoons [M(SCN)_x]^{(x-m)-}(aq) \tag{2.2}$$

The standard thermodynamic constant of formation of the metal–thiocyanate complex $M(SCN)_x^{(x-m)-})$ can be represented by (Eq. 2.3):

$$K^{\theta}{}_{M(SCN)_x^{(x-m)-}} = \frac{\gamma_{M(SCN)_x^{(x-m)-}} \cdot \left[M(SCN)_x^{(x-m)-}\right]}{\gamma_M^{m+} \cdot [M^{m+}] \cdot \gamma_{SCN^-} \cdot [SCN^-]^x} \tag{2.3}$$

where, γ_X is the activity coefficientof the ionic species X and [X] is the concentration of this species (where X is M^{m+}, SCN^-,or $SCN)_x]^{(x-m)-}$). The thermodynamic constant$_{[M(SCN)_x]^{(x-m)-}}$) defines the relationship between the concentrations of the complex ion, the free ligand, and metal ions in solution. Thus, the higher the value of the thermodynamic constant of complex formation, the more favorable the formation of the metal complex.

The chemical equilibrium described in Eq. (2.2) shows that the higher the concentration of the thiocyanate anion, the higher the concentration of the complex$SCN)_x]^{(x-m)-}$ formed. The experimental results show a higher metal concentration in the macromolecule-rich phase. This suggests a favorable intermolecular interaction between $SCN)_x]^{(x-m)-}$ and segments of the macromolecule, resulting in favorable transfer of the species to the macromolecule-rich phase.

The extraction behavior of the studied metal ions can be explained as described above and also by the standard formation constant of the complex $SCN)_x]^{(x-m)-}$ having the following values: Fe (log K_1 = 3.2, log K_2 = 4.6, log K_3 = 3.9, log K_4 = 64) [20], Co (log K_1 = 1.72, log K_2 = 2.02) [20], and Ni (log K_1 = 1.18, log K_2 = 0.46, log K_3 = 0.17) [21]. Thus, the Fe(III) ion complex is more stable than the Co(II) complex; however, both had a similar percentage extraction of around 100%. The Ni(II) ion that forms the least stable complex presented the lowest %E.

The difference in the extraction behavior of the various metals is due to the fact that the different central atom of the $SCN)_x]^{(x-m)-}$ complex undergo distinct intermolecular interactions with the macromolecule. It was demonstrated by da Silva et al. [22] that the complex coordination interaction of the macromolecules with the EO segments occurs via charge transfer processes and electrostatic interactions.In the charge transfer interaction, oxygen electrons of the EO group are transferred to the antibonding orbital of the SCN^- complex. The energy and the electron density of these antibonding orbitals are modulated by the electronic structure of the central metal. Thus, the higher the donor capacity of the central atom, the higher the electron density of the antibonding orbital and the lower the tendency of the complex to bind to the EO segment of the macromolecule.The electronic retrodonationby the cations studied in this work follows the following order: Ni > Co ≈ Fe; therefore expect a lower interaction of the $\boldsymbol{SCN)_x]^{(x-m)-}}$ complex of than the $\boldsymbol{SCN)_x]^{(x-m)-}}$, and $\boldsymbol{SCN)_x]^{(x-m)-}}$ complexes with the EO segments of the macromolecule.This model is corroborated by the study by Patricio et al. [16] of separation of Fe(III), Co(II), and Ni(II) using systems formed by the PEO1500 polymer or copolymer L35 and the electrolyte $(NH_4)_2SO_4$ with the aid of KSCN as an extractant. In this study, in the absence of thiocyanate ions, all of the metal ions remained in the macromolecule-poor phasedue to complexation with the sulfate anion mainly in the macromolecule-poor phase. However, with increasing concentrationof the thiocyanate anion, greater extraction of the metallic ions was obtained. The maximum %E was 99.8, 12.7, and 3.17 % for Co(II), Fe(III), and Ni(II), respectively, when the ATPS formed by the PEO1500polymer and the $(NH_4)_2SO_4$electrolyte was employed at pH 4.00 and 25.0 ºC and with the addition of 1.40 mmol KSCN.

2.4.2. Influence of pH on the extraction of metal ions

Given that the formation constants of the $\boldsymbol{SCN)_x]^{(x-m)-}}$ complexes and the interaction of these complexes with the EO segments of the macromolecule are dependent on the hydrogen ion concentration, we studied the influence of pH on the %E of Co(II), Ni(II), and Fe(III).

Figure 2.2 shows the %E of Fe(III), Co(II), and Ni(II) as a function of the pH of the L64 + NaSCN + H_2O ATPS for TLL 28.74 % (w/w). For the Co(II) ion, as the pH increased, the %E increased from (89.5 ± 2.6) % at pH = 3.00 to (93.9 ± 1.4) % at pH 12.0.

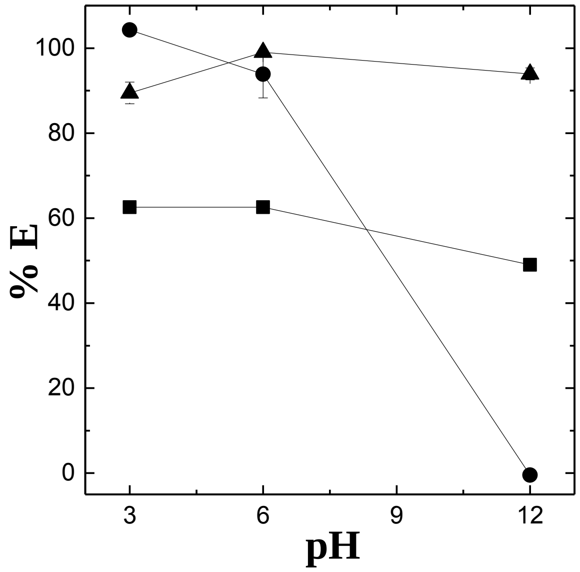


Fig. 2.2. Influence of pH on the %E of metal ions: (■) Ni(II), (●) Fe(III), and (▲) Co(II) using the L64 + NaSCN + H_2O ATPS for TLL 28.74 % (w/w), [metal] in the system = 0.339 mmol kg^{-1} at 25.0 °C, n = 3.

In the case of the Ni(II) extraction, a decrease in the hydrogen ion concentration caused a decrease in %E from (62.6 ± 0.4) % at pH 3.00 to(49.0 ± 0.5) % at pH = 12.0. For the Co(II) ion, the $SCN)_x]^{(x-m)-}$ compound is formed in acidic or neutral media, and at basic pH, $Co(OH)_2$ is generated; under neutral conditions, the hydrophobic characteristic results in partitioning into the triblock copolymer-rich phase having a hydrophobic region formed by PO segments. For the Ni(II) ion,higher pH is unfavorable for formation of the $SCN)_x]^{(x-m)-}$ complex, but favors formation of the aquacomplex$H_2O)_6]^{2+}$, which is positive and tends to interact more strongly with components of the electrolyte-rich phase. For the Fe(III) ion, between pH 3.00 and 6.00, there was a slight decrease in the %E, but at pH 12.0 there was a marked decrease in the %E due to formation of $Fe(OH)_3$which is not soluble in ATPS.

2.4.3. Effect of the electrolyte nature on the extraction of metal ions

Figures2.3a and2.3b show the values of %E forCo(II), Fe(III), and Ni(II) using the L64 + NaSCN + H_2O, L64 + KSCN + H_2O,and L64 + NH_4SCN + H_2O ATPS at pH 6.00 and 25.0 ºC for two TLL..

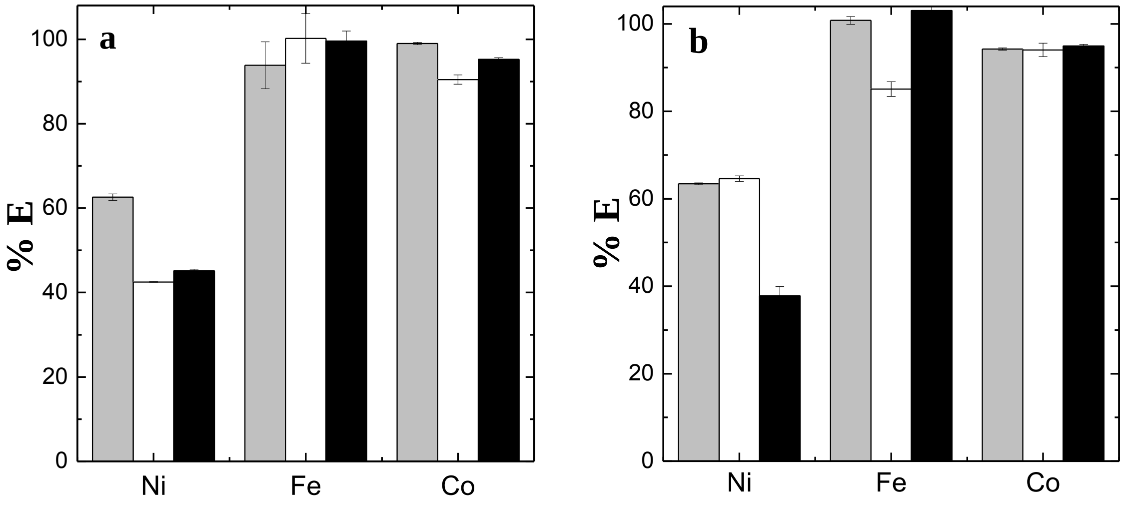


Fig. 2.3. Effect of electrolyte comprising the ATPS on the %E of the metal ions Ni(II), Co(II), and Fe(III) using ATPS consisting of: (a) L64 + thiocyanate (■) Na, (☐) K, and (■) NH_4 for TLL ≈ 28% (w/w), (b) L64 + thiocyanate (■) Na, (☐) K, and (■) NH_4 for TLL ≈ 33% (w/w) at pH 6.00; metal concentration = 0.339 mmol kg^{-1}, temperature = 25.0 °C.

In Figure 2.3a, for TLL ≈ 28 % (w/w), it is observed that the best system for extraction of both Ni(II) and Co(II) is that employing the NaSCN electrolyte, where the maximum %E values for nickel and cobalt were (62.6 ± 0.8) % and (99.0 ± 0.3) %, respectively. In the case ofFe(III), a high %E was obtained with both the ATPSemploying the KSCN electrolyte %E = (100 ± 6) % and that employing NH_4SCN, %E = (99.6 ± 2.3) %.

When TLL ≈ 33 % (w/w) was applied, the %E valuesdiffered from those obtainedat TLL ≈ 28%. At most TLL values, there was greater segregation between the

ATPS-forming components thereby decreasing the concentration of cations in the macromolecule-rich phase. If the electrostatic interaction between the $SCN)_x]^{(x-m)-}$ complex and the pseudopolycation formed by the cation and the macromolecule was the determinant interaction for extraction, a reduction in the %E would be expected. The Ni(II) ions were extracted into the macromolecule-richphase when the ATPS employing KSCN as the electrolyte was used, with %E = (64.6 ± 0.6) %. For Fe(III), the most efficient system was that consisting of NH_4SCN, with a %E value of (103 ± 1) %. However, for the Co(II) ion, the electrolyte did not influence the extraction of the ion, where %E was largely invariable ranging from (94.0 ± 1.5) % to (94.9 ± 0.4) %. The results for %E at both TLLs show that the $SCN)_x]^{(x-m)-}$ - macromolecule interaction is not dominated by the electrostatic component, but by the charge transfer interaction.

2.4.4. Effect of metal concentration on the extraction of the metal ions

Figure 2.4 shows the %E of Ni(II), Fe(III), and Co(II) according to the metal concentration using the L64 + NaSCN + H_2O ATPS at pH 6.00. The maximum metal concentration in the ATPS was determined by the solubility of the metal in the ATPS.

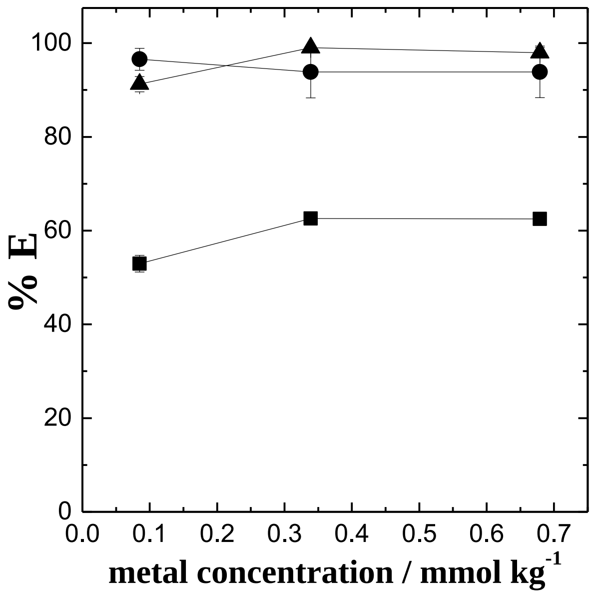


Fig. 2.4. Effect of the metal concentration on the %E of the metal ions (■) Ni(II), (●) Fe(III), and (▲) Co(II) using the ATPS consisting of L64 + NaSCN + H_2O for TLL = 28.74 % (w/w) at pH 6.00 and 25.0 °C.

Regardless of the metal concentration used herein, the %E remained practically constant, showing that under these thermodynamic conditions the extraction behavior is not affected by the metal:ligand ratio. This is because the amount of thiocyanate is more than 6,500 times the amount of metal, so the predominant species present in the medium is$\boldsymbol{SCN)_x}]^{(x-m)-}$, causing the %E to remain practically constant irrespective of the metal concentration.

2.4.5. Influence of hydrophobic/hydrophilic balance and size of the macromolecule on the extraction of the metal ions

Figure 2.5 shows the %E of Ni(II), Fe(III), and Co(II) ions in the MACRO + KSCN + H_2O (MACRO = L64, F68, or PEO1500) ATPS, at pH 6.00, 25.0 ºC, and TLL close to 43% (w/w).

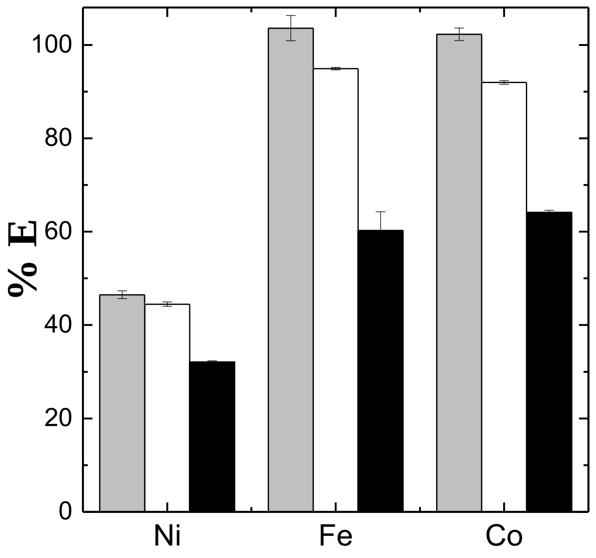


Fig. 2.5. Influence of the hydrophobicity of the polymer present in the ATPS on the %E of Ni(II), Co(II), and Fe(III) metal ions using ATPS consisting of KSCN + (▨) L64 (43.64 % (w/w)) or (☐) PEO1500 (44.39 % (w/w)) or (■) F68 (41.46 % (w/w)), [metal] in the system = 0.339 mmol kg^{-1} at pH 6.00 and 25.0ºC.

All macromolecules used in this study are composed of ethylene oxide (EO) unit segments. For copolymers L64 and F68, blocks of propylene oxide (PO) unit segments are connected to these EO units. The chemical structures of the macromolecules studied are PEO1500: $HO–(CH_2–CH_2–O)_{34}–H$, L64: $HO–(CH_2–CH_2–O)_{13}–(CH_3–CH–CH_2–O)_{30}–(CH_2–CH_2–O)_{13}–H$, and F68: $HO–(CH_2–CH_2–O)_{80}–(CH_3–CH–CH_2–O)_{30}–(CH_2–CH_2–O)_{80}–H$. These macromolecules have different hydrophobic/hydrophilic balance. The hydrophobic/hydrophilic balance is expressed by the *m/n* ratio (*m* = number of PO units and *n* = number EO units) and the higher this ratio, the more hydrophobic is the macromolecule. This is because the PO segments interact weakly with the water molecules and interact more favorably with hydrophobic compounds. However, these macromolecules differ not only in terms of the hydrophobic/hydrophilic balance, but also in terms of size, that is, molar mass. The PEO1500 and L64 copolymer have comparable molar masses (PEO1500: 1,500 g mol^{-1} and L64: 2,900 g mol^{-1}). However, the F68 copolymer is a larger macromolecule (8,400 g mol^{-1}).

The experimentally determined %E forCo(II), Fe(III), and Ni(II) show that the hydrophobic/hydrophilic balance of these ions does not affect the extraction behavior, but the size of the macromolecule has a profound effect on the %E. It is observed that the larger the macromolecule, the lower the%E for the three metal ions. This is because the larger the macromolecule, the smaller the variation of the configurational entropy of the system caused by transferring the metal ion.

The predominance of the Fe(III) and Co(II) ions in the macromolecule-rich phaseand the consequently higher %E is influenced by the strong interaction of the Fe–SCN or Co–SCN complex with the macromolecule segments, while the Ni–SCN complex shows a weak interaction.

2.4.6. Efficiency of the ATPS for separation of Co(II), Ni(II), and Fe(III)

The separation factor ($S_{M,N}$) is a parameter that expresses the effective separation between two species M and N in a liquid-liquid extraction, as expressed by Eq.(2.4):

$$S_{M,N} = \frac{D_M}{D_N} \tag{2.4}$$

whereD_M is the distribution coefficient of all species of the M component and D_N is the distribution coefficient of all species of the Ncomponent. The first distribution coefficient mentioned above is obtained from Eq. (2.5):

$$D_M = \frac{\%E}{100 - \%E} \tag{2.5}$$

The $S_{M,N}$ obtained for separation of cobalt, nickel, and iron in different ATPS are summarized in Table 2.3. Using the L64 + NH_4SCN + H_2O ATPS with TLL = 28.93 % (w/w) at pH 3.00, Co(II) and Ni(II)could be separated with $S_{Co(II),Ni(II)}$equal to 1.20 × 10^2. Ni(II) could be separated from Fe(III) using the same system, but at pH 6.00 ($S_{Ni(II),Fe(III)}$ = 3.03 × 10^2). Fe(III) can be successfully separated from both Co(II) and Ni(II) using the L64 + NH_4SCN + H_2O ATPS withTLL = 28.93 % (w/w), albeit at pH = 12.0 due to the formation $Fe(OH)_3$ which is not soluble at medium pH. Thus, we propose sequential separation of the three metals using a single ATPS.

Table2.3. Separation factors $S_{Co(II),Ni(II)}$, $S_{Ni(II),Fe(III)}$,and $S_{Co(II),Fe(III)}$ obtained for different ATPS

ATPS	*Separationfactors ($S_{M,N}$)*								
	$S_{Co(II),Ni(II)}$			$S_{Ni(II),Fe(III)}$			$S_{Co(II),Fe(III)}$		
	pH 3.00	pH 6.00	pH 12.0	pH 3.00	pH 6.00	pH 12.0	pH 3.00	pH 6.00	pH 12.0
L64 + NaSCN + H_2O (28.74 % (m/m))	5.09	5.91×10^{1}	1.60×10^{1}	1.55×10^{1}	9.20	-	3.28×10^{-1}	1.55×10^{-1}	-
L64 + NaSCN + H_2O (33.36 % (m/m))	1.12×10^{1}	9.55	6.71×10^{1}	5.71×10^{1}	5.83×10^{1}	-	1.96×10^{-1}	6.10	-
L64 + KSCN + H_2O (28.33 % (m/m))	4.66×10^{1}	1.29×10^{1}	1.61×10^{1}	2.46×10^{1}	1.35×10^{3}	-	1.90	1.05×10^{2}	-
L64 + KSCN + H_2O (34.17 % (m/m))	1.60×10^{1}	1.95×10^{1}	2.56×10^{1}	4.32×10^{1}	7.09	-	3.70×10^{-1}	3.65×10^{-1}	-
L64 + KSCN + H_2O (43.64 % (m/m))	5.99×10^{1}	5.87×10^{1}	6.21×10^{1}	2.47×10^{1}	2.99×10^{1}	-	2.43	1.96	-
L64 + NH_4SCN + H_2O (28.93 % (m/m))	1.20×10^{2}	2.41×10^{1}	3.58×10^{1}	6.04×10^{1}	3.03×10^{2}	-	1.98	1.26×10^{1}	-
L64 + NH_4SCN + H_2O (32.51 % (m/m))	2.12×10^{1}	3.06×10^{1}	3.22×10^{1}	7.93×10^{1}	5.65×10^{2}	-	2.67×10^{-1}	1.85	-
PEO1500 + KSCN + H_2O (44.39 % (m/m))	1.91×10^{1}	1.42×10^{1}	2.31×10^{1}	1.78×10^{1}	2.32×10^{1}	-	1.07	1.64	-
F68 + KSCN + H_2O (41.46 % (m/m))	1.06×10^{2}	3.63×10^{1}	5.90×10^{1}	8.20	3.20	-	1.29×10^{1}	1.14×10^{1}	-

2.5. CONCLUSION

This work demonstrated the preferential partition of the Fe(III), Ni(II), and Co(II) ions to macromolecule-rich phase without using any extractant. The new ATPSs have high thyocianate concentration in both phases, but the ions concentrated in macromolecule-rich phase. The driving force governing the extraction of Fe(III), Ni(II), and Co(II) into the macromolecule-rich phase is the strong interaction of the complex formed $\boldsymbol{SCN})_{\boldsymbol{x}}]^{(x-m)-}$ at the EO segments of the macromolecule and electronic retrodonation of the metal center of the complex. The interaction of the complex with the macromolecule is independent of the concentration of the metal ion and ATPS-forming cation. However, this interaction is dependent on the pH of the medium and the size of the macromolecule, where a higher molar mass of the macromolecule leads to a lower %E.

2.6. REFERENCES

[1] S. Hamzehzadeh, M.T. Zafarani-Moattar, FluidPhaseEquilibr. 385 (2015) 37-47.

[2] L.R. de Lemos, P.R. Patrício, G.D. Rodrigues, R.M.M. de Carvalho, M.C.H. da Silva, L.H.M. da Silva, FluidPhaseEquilibr. 305 (2011) 19-24.

[3] Y. Liu, Z.Y. Wu, Y.J. Zhao, Thermochim. Acta602 (2015) 78-86.

[4] D.F.C. Silva, A.M. Azevedo, P. Fernandes, V. Chu, J.P.Conde, M.R. Aires-Barros, J. Chromatogr.A (2014) 115-120.

[5] N. J. Bridges, K. E. Gutowski, R. D. Rogers, Green Chem. 9 (2007) 177-183.

[6] Albertsson, P.A. Partition of Cell Particles and Macromolecules, 3rd ed., John Wiley & Sons, New York, 1986.

[7] Y.H. Chow, Y.J. Yap, M.S. Anuar, B.A. Tejo, A. Ariff, P.L. Show, E.P. Ng, T.C. Lin, J. Chromatogr. B 934 (2013) 71-78.

[8] M.C.B. Pimentel, A.I. Araujo, Z.M.B. Figueiredo, R.A. Silva, M.T.H. Cavalcanti, K.A. Moreira, J.L.L. Filho, A.L.F. Porto, Sep. Purif. Technol. 110 (2013) 158-163.

[9] F. Luechau, T.C. Ling, A. Lyddiatt, Process Biochem. 45 (2010) 1432-1436.

[10] A. Chavez-Santoscoy, J. Benavides, W. Vermaas, M. Rito-Palomares, Chem. Eng. Technol. 33 (2010) 177-182.

[11] T.I. Zvarova, V.M. Shkinev, G.A. Vorobeva, B.Y. Spivakov, Y.A. Zolotov, Microchimica Acta 3 (1984) 449-458.

[12] R.D. Rogers, J.H. Zhang, A.H. Bond, C.B. Bauer, M.L. Jezl, D.M. Roden, Solvent Extr. Ion Exch. 13 (1995) 665-688.

[13] R.D. Rogers, A.H. Bond, C.B. Bauer, Separ. Sci. Technol. 28 (1993) 1091-1126.

[14] G.D. Rodrigues, L.R. de Lemos, L.H.M. da Silva, M.C.H. da Silva, J. Chromatogr. A 1279 (2013) 13-19.

[15] L.R. de Lemos, I.J.B. Santos, G.D. Rodrigues, L.H.M. da Silva, M.C.H. da Silva, J. Hazard. Mater. 237 (2012) 209-214.

[16] P.D. Patricio, M.C. Mesquita, L.H.M. da Silva, M.C.H. da Silva, J. Hazard. Mater. 193 (2011) 311-318.

[17] V.G. Lacerda, A.B. Mageste, I.J.B. Santos, L.H.M. da Silva, M.D.H. da Silva, J. Power Sources193 (2009) 908-913.

[18] G.D. Rodrigues, M.D.H. da Silva, L.H.M. da Silva, F.J. Paggioli, L.A. Minim, J.S.D. Coimbra, Sep. Purif. Technol. 62 (2008) 687-693.

[19] L.H.M. da Silva, W. Loh, J. Phys. Chem. B 104 (2000) 10069-10073.

[20] A.E. Martell, R.M. Smith, 2001. Critical Stability Constants of Metal Complexes Database, National Institute of Standards and Technology.

[21] W.B. Guenther, Quantitative Chemistry: Measurements and Equilibrium. Edgard BlücherLtda, São Paulo, 1972, pp. 397.

[22] L.H.M. da Silva, M.D.H. da Silva, K.R. Francisco, M.V.C. Cardoso, L.A. Minim, J.S.R. Coimbra, J. Phys. Chem. B 112 (2008) 11669-11678.

Conclusões Gerais

Novas metodologias foram desenvolvidas neste trabalho para extração eseparação de metais de maneira ambientalmente segura e em conformidade com os princípios da Química Verde. O SAB formado por PEO1500 + citrato de sódio + água foi um eficiente sistema para separação do íon Hg(II) na presença de íons concomitantes como Cr(III), Fe(III), Co(II), Cd(II), Ni(II), Pb(II) e Zn(II) com fatores de separação variando de $1{,}54 \times 10^{2}$ a $3{,}21 \times 10^{10}$ possibilitando a sua aplicação em matrizes contendo elevadas quantidades destes metais como lâmpadas fluorescentes, bateria do tipo botão (Zn-ar) e resíduos de indústria cloro-soda.Os SABs utilizados paraextração de Co(II), Ni(II) e Fe(III) foram os primeiros sistemas em que, sem utilização de extratantes, os metais concentraram-se preferencialmente na fase rica em polímero. Empregando o SAB L64 + tiocianato de amônio + água é possível a separação sequencial dos três metais por meio da modulação dos valores de pH.

Os resultados obtidos neste trabalho ratificam o emprego dos SABsna extração e separação de diversos metais,sendo uma alternativaeconomicamente viávele ambientalmentesustentável, quando comparado à extração líquido-líquido convencional. Esses sistemas possuem ainda outras vantagens como a não utilização de solventes orgânicos,além de serem constituídos majoritariamente por água.

De forma conclusiva, este estudocontribui para elucidação dos parâmetros que regem a partição das espécies de interesse nos SABs, permitindo a potencializaçãoextratora e aplicabilidade deste sistema.