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Cloud point or ionic liquid extraction of furfural from aqueous solution: a comparative study based upon experimental design

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ABSTRACT

The goal of the present work was to compare cloud point extraction and extraction using ionic liquid for the separation of furfural from a dilute aqueous solution. Aqueous solutions of the biodegradable non-ionic surfactant Dehydol LT 7 (equivalent to $C_{15}E_7$) and the pure ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate ([C4C1im]PF6) were investigated as extraction solvents. Phase diagrams of binary (water/surfactant) and pseudo-binary (water/surfactant/solute) systems were plotted. The extraction results were expressed by the following responses: percentage of solute extracted, E (%), residual concentrations of solute and surfactant in aqueous phase ($X_{s,w}$ and $X_{t,w}$, respectively), and volume fraction of coacervate at equilibrium (ϕ_C). For each parameter, the experimental results were fitted to empirical equations in three dimensions. The aim of this study was to find the best compromise between E and the other parameters ($X_{s,w}$, $X_{t,w}$, and ϕ_C, as low as possible). The comparison between experimental and calculated values allowed model validation. The highest extraction efficiency (98%) was reached with IL. Under optimal conditions, the solute concentration in the effluent was reduced to about 3 times using non-ionic surfactant against 31 times using ionic liquid. Finally, the possibility of recycling the ionic liquid has been proved.

Keywords: Furfural; Ionic liquid; Non-ionic surfactant; Cloud point; Extraction; Coacervate

1. Introduction

The release into the environment of complex chemicals from oil production, oil processing, petrochemical plants, and agro-based industries has been considered as a major source of air and water pollution [1,2]. Many of these materials are non-biodegradable or inhibitors for biological systems and often have a toxic effect on living organisms [3]. In natural environment they have a long life and are slow to decay and decompose. Some cyclic and aromatic organic compounds, such as phenols and furfural, are good examples. Phenol removal has been investigated extensively, e.g. by cloud point extraction (CPE) in our previous studies [4–8]. Furfural is produced from the

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digestion products of pentosan-containing non-food agricultural residues such as corn cobs, cotton seed, rice, or oat hulls, as well as from wood wastes and eucalyptus globules [9]. Furfural is the only organic compound derived from biomass that can replace the crude oil-based organics used in industry [10]. Moreover, it is an important compound in the fragrance industry, pharmacy, agriculture, and in leather manufacture, and it is widely used in the petrochemical and fine chemicals industries [11]. Owing to its unsaturated bonds and its aldehyde group, furfural has exceptional physical and chemical properties. This stable organic compound at room temperature decomposes into furan and carbon monoxide at high temperature. Its solubility in water at 20˚C is about 83 g/L [12,13] (or 8.3 wt.% [14]) and it becomes well soluble in hot water [9]. But the presence of furfural in wastewater emerges as the focus of environmental remediation efforts because of its toxicity and threat directly to aquatic and indirectly to non-aquatic life [14]. Several methods have been intensively investigated for the removal or recovery of furfural from dilute aqueous solutions, such as adsorption [12,13,15], supercritical carbon dioxide extraction [16], and membrane separation [17].

This work was devoted to study cloud point and ionic liquid (IL) extractions as methods of removal, recovery, and valorization of furfural from aqueous solutions. The aqueous solutions of most of the polyethoxylated non-ionic surfactants form two phases above their so-called cloud point (T_c): a surfactant-rich phase (coacervate) and a dilute phase in which the concentration of the surfactant is close to its critical micelle concentration (CMC). Then, solubilized solutes can be extracted into the coacervate after increasing temperature above the critical value, T_c. CPE has already been applied to the separation of various chemical species: metal ions, small organic and biological molecules [4–8,18–28], etc. This technique allows moving toward green chemistry. Many advantages were claimed for CPE compared with conventional liquid–liquid extraction. CPE is an efficient and selective process that avoids the use of volatile organic compounds, works continuously, saves energy, and can be easily scaled up [21]. On this basis, the CPE of furfural from its aqueous solution at 12.5 mg/L was investigated in the present work. The effects of temperature, surfactant concentration, and pH on extraction extent were studied and the experimental results were compared with those obtained using an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([C4C1im]PF6), which has been well described in the literature [29] and already checked in extraction procedures [27,30,31].

2. Materials and methods

2.1. Reagents

A commercial non-ionic surfactant was used in this work: “Dehydol LT 7”, supplied by the BASF Company (Ludwigshafen, Germany). It has the average chemical formula n-$C_{12–18}E_7$ and belongs to the family of ethoxylated fatty alcohols. The cloud point of this surfactant at 1 wt.% in water was 55.1˚C and its CMC at 20˚C was 0.012 g/L ($\approx 2.4 \times 10^{-5}$ M).

The ionic liquid, [C4C1im]PF6, purchased from SOLVIONIC (Toulouse, France), was available with the following characteristics: purity: 99%; FW = 284.18 g/mol; mp = 6–10˚C; $d = 1.37$. Furfural, methanol, acetonitrile, and sodium sulfate was provided by ACROS.

2.2. Cloud point measurements

The determination of the cloud point was carried out using a Mettler FP 900 apparatus. The temperature of the sample, placed inside a cell, was measured using a precise sensor placed in a small oven. At the bottom of the measuring cell, there is a luminous source and an optic driver which illuminate the sample. The transmitted light was converted by a photoelectric cell into an electric signal. The intensity of the transmitted light was measured continuously, while the cell temperature increased linearly according to the chosen heating rate. The cloud point is the temperature at which the unique limpid phase becomes cloudy, inducing a transmission decrease.

2.3. HPLC analyses

The surfactant, ionic liquid, and furfural concentrations in the dilute phase were determined using HPLC. The chromatographic conditions were as follows: column RP18 (ODS), 1 mL/min, pressure 160 bar; UV detector wavelength 275 nm (except for surfactant detection), injection volume 20 µL, mobile phase: $H_2O/CH_3CN/CH_3OH$, 7/60/33 (v/v). For ionic liquid analysis, the mobile phase was acidified to pH 3 with phosphoric acid (H_3PO_4).

An ELSD (DDL 31, EUROSEP Instruments) detector was used for surfactant analyses. The eluent from the HPLC column is introduced onto the top of a heated diffusion tube, followed by spraying with a stream of nitrogen gas. When passing through the diffusion tube, the sprayed beads evaporate, so that the mist formed in the nebulizer only contains non-volatile particles of the substance under examination. The intensity of the light scattered by the particles is proportional to the concentration of the substance. The sensitivity of the ELSD was optimized by the control of the air flow rate in the atomizer (relative pressure: 1 bar). The evaporator temperature was fixed at 55°C and the photomultiplier gain was 400.

2.4. Extraction procedure

For the extraction tests using a non-ionic surfactant, 10 mL of solution containing the surfactant (from 4 to 16 wt.%) and the effluent (at 12.5 mg/L) were poured into graduated cylinders and heated in a precise thermostated bath during 2 h, to reach phase separation (dilute phase and coacervate). The heating temperature range varied from the cloud point temperature to about 20°C above (50–70°C). The volumes of both phases were registered and a small amount of the dilute phase (aqueous phase) was pumped using a syringe and analyzed by HPLC for surfactant and furfural determination. Extraction using ionic liquid ([C4C1im]PF6) was conducted in the same way; however the ionic liquid phase was mixed with the effluent at a concentration between 10 and 30 wt.%.

3. Results and discussion

3.1. Binary and pseudo-binary phase diagrams

The cloud point of non-ionic surfactants is closely related to their chemical structure. In a homologous series of polyethoxylated non-ionic surfactants, the number of ethylene oxide groups and the length of the hydrophobic chain have a significant influence on the cloud point. The increase in the number of ethylene oxide (EO) units in polyethoxylated alcohols [32–34] raises T_c, because of the increased solubility of the surfactant in water due to the interaction of water molecules with EO groups through H-bonding. However, the lengthening of the hydrophobic chain is responsible for lowering T_c in the same family, as a direct consequence of the reduced solubility of non-ionic surfactants in water. Fig. 1 shows the effect of salt (Na_2SO_4) on the cloud point curve of Dehydol LT7. The addition of Na_2SO_4 lowers the cloud point by a phenomenon similar to salting-out, caused by the solvated electrolyte which weakens the hydrogen bond between the water molecule and the polar head of the surfactant.

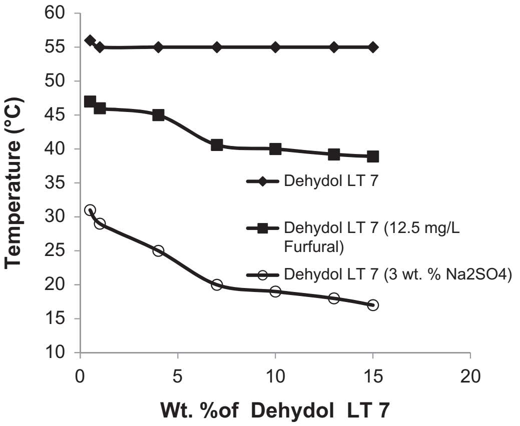

Fig. 1. Effect of furfural and Na_2SO_4 on the cloud point curve of Dehydol LT7.

3.2. Extraction using non-ionic surfactant

3.2.1. Modeling of results

The extraction results of furfural from its aqueous solutions at 12.5 mg/L by Dehydol LT7 according to two variables: wt.% surfactant (X_t), and temperature (T), were expressed by four responses (Y): percentage of extracted solute (E), residual concentrations of solute ($X_{s,w}$), and surfactant ($X_{t,w}$) in the dilute phase and coacervate volume fraction at equilibrium (ϕ_C). For each parameter determined and by considering central composite designs [35], the results were analyzed by an empirical fitting. In this method, the experimental values are used to determine the polynomial model constants to be adjusted. The models were checked by plotting computed data against experimental results. A quadratic correlation was chosen to give the slope and the regression coefficient (R^2) closest to unity.

$$Y = a_0 + a_1 X_t + a_2 T + a_{12} X_t T + a_{11} X_t^2 + a_{22} T^2 \tag{1}$$

Such a correlation allows building the response surface. The quadratic equations for the properties (E, $X_{s,w}$, $X_{t,w}$, and ϕ_C), whose reliability was checked, are as follows:

$$E = 145.005 - 37.733 X_t - 0.930 T + 0.741 X_t T - 0.302 X_t^2 \tag{2}$$

$$X_{(s,w)}\ (\mathrm{mg/l}) = 0.031 + 0.231 \times 10^{-2} X_t - 0.106 \times 10^{-2} T - 0.044 \times 10^{-3} X_t T + 0.108 \times 10^{-4} X_t^2 + 0.0118 \times 10^{-4} T^2 \tag{3}$$

$$X_{t,w} = 1.4031 + 9.9 \times 10^{-3} X_t - 4.7 \times 10^{-2} T - 0.1 \times 10^{-3} X_t T + 1.8 \times 10^{-5} X_t^2 + 0.4 \times 10^{-1} T^2 \tag{4}$$

$$\phi_{\mathrm{C}} = -1.004 - 5.394 \times 10^{-1} X_{\mathrm{t}} + 0.733 \times 10^{-1} T + 0.104 \times 10^{-1} X_{\mathrm{t}} T - 0.004 X_{\mathrm{t}}^2 - 0.009 \times 10^{-1} T^2 \quad (5)$$

Fig. 2(a) represents the three-dimensional isoresponse curves of the studied properties smoothed with the quadratic model (Eq. (2)). Fig. 2(a) shows that the extent of furfural extraction (E) increases with X_{t}. However, a temperature increase has a slight effect on extraction yield. This trend was also observed in other extraction systems [5,19,24,25]. Indeed, the temperature rise induces simultaneous and opposite effects: it increases the concentration of solute in the micellar aggregates as a result of the decrease of ϕ_{C} [6,8]. In this work, the right temperature for a good extraction yield is 60°C for Dehydol LT7. The most favorable area is the region of high surfactant concentration and temperature slightly above the cloud point.

Fig. 2(b) represents the three-dimensional isoresponse curves for $X_{\mathrm{s,w}}$, smoothed by the quadratic model (Eq. (3)). The residual concentration of furfural in the dilute phase increases at low surfactant concentration and high temperature. Therefore, an excessive rise in temperature has a negative effect on solute removal and causes an increase in $X_{\mathrm{s,w}}$. This negative

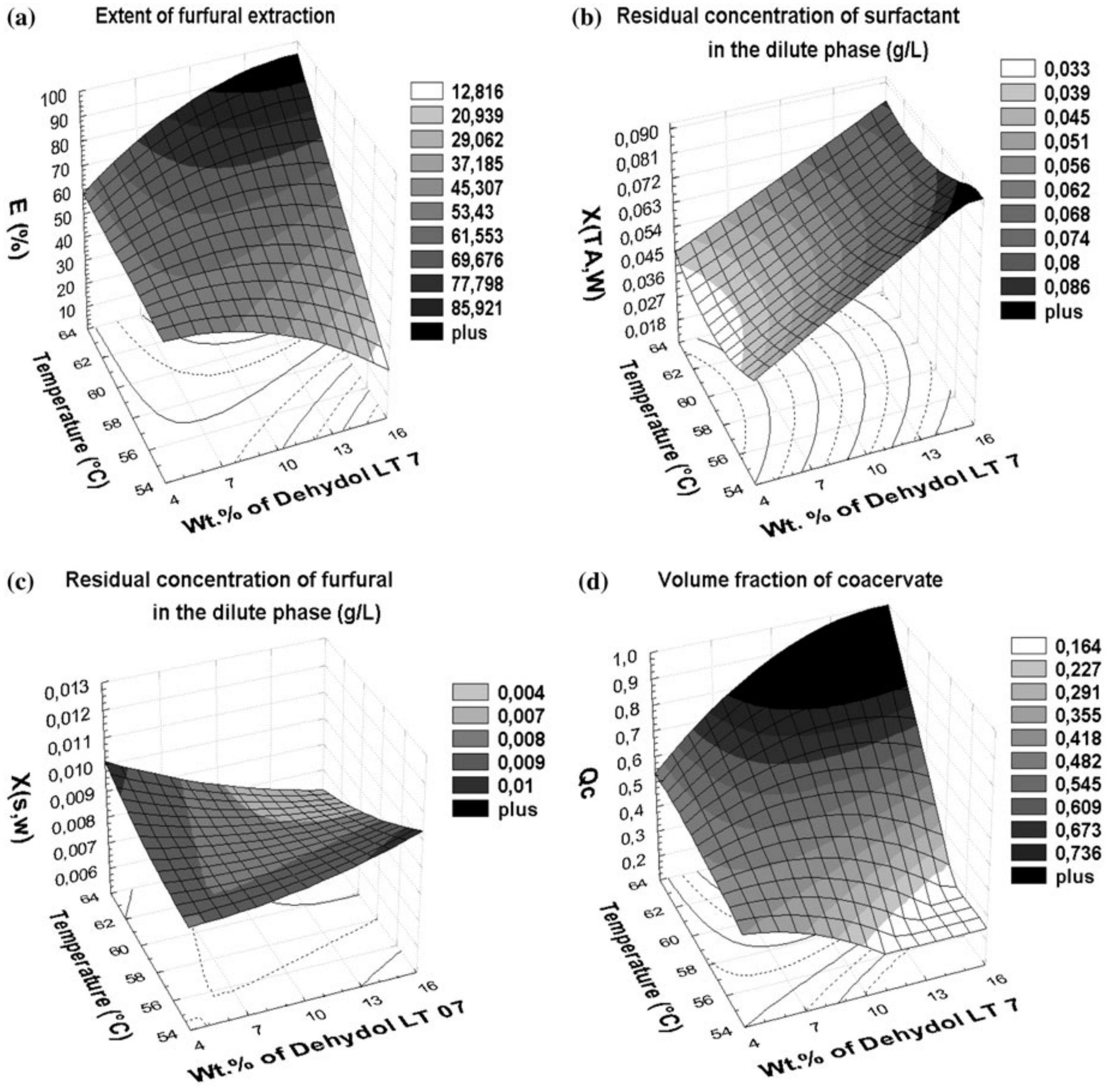

Fig. 2. Three-dimensional isoresponse curves smoothed by a quadratic model (Eqs. (2)–(5)).

effect of temperature is more pronounced at low surfactant concentration, X_t, probably due to an increase in the solubility of furfural in water, unfavourable to extraction.

Treating the data of a CPE process is quite complicated; most workers have utilized the phase separation model of micellization [36], i.e. they have treated the micelles as a separate phase and considered the distribution of solubilizate between this phase and the non-micellar fluid. However, in this model, the volumes of aqueous and micellar phases were not included and the values of the distribution coefficient cannot, therefore, be compared with classical oil–water partition coefficient [37]. Moreover, the volume of micellar phase is somewhat arbitrary: it could be the volume of either the hydrocarbon core, the entire micelle or the entire micelle including water. On the other hand, in the micelle, organic solubilizates can interact with the surfactant polar head group or with its hydrophobic chain. Hence, the site of incorporation of the solubilizate is closely related to its chemical nature. In aqueous systems, it is generally accepted that non-polar solubilizates are dissolved in the hydrocarbon core of the micelle. Semi-polar and polar solubilizates may be oriented radially in the micelle with the polar group either buried (deep penetration) or near the micellar surface (short penetration) [38]. Furfural may be incorporated near the micellar surface, because it is a weakly polar solubilizate. Furthermore, temperature has an effect on the extent of micellar solubilization, due to the change in the aqueous solubility of the solubilizate or a modification of micelle properties. The thermodynamic parameters of the CPE, determined with different solutes [39], show that the process is spontaneous, but endothermic, therefore entropy-driven. The absolute value of the negative Gibbs free energy change increases with temperature and decreases with both surfactant and solute concentrations. The changes in enthalpy and entropy of extraction decrease with solute concentration but increase with surfactant concentration.

The residual surfactant concentration ($X_{t,w}$) is a very important parameter. High loss of surfactant in the dilute phase can compromise the process reliability. Indeed, the presence of another contaminant in the dilute phase is sufficient to make the process useless. Although these surfactants are known for their good biodegradability, it would be detrimental to squander them in the dilute phase. The behavior of $X_{t,w}$ vs. X_t and T is shown in Fig. 2(c) (smoothed by the quadratic model, Eq. (4)). This figure shows that the residual concentration of surfactant is low at low surfactant concentration and goes through a minimum according to temperature. These results are in good agreement with previous studies using polyethoxylated alkylphenols [4], as well as polyethoxylated alcohols [5,6,8,19,23,24,26]. Indeed, heating desolvates the surfactant hydrophilic groups gradually and thus reduces surfactant hydrophilicity. In general, the desolvation energy of the surfactant molecule can be associated with its energy of transfer from the hydrophilic (aqueous solution) to the hydrophobic medium (micellar system) [24].

In order to increase the concentration factor of solute, a minimal volume fraction of coacervate (ϕ_C) should be obtained when temperature increases. In effect, according to Fig. 2(d), the smoothed value of ϕ_C using Eq. (5) is low at high temperature and low surfactant concentration. However, high surfactant concentrations induce more surfactant loss in the dilute phase (Fig. 2(c)). Although the surfactant is biodegradable, this loss is not economical. So, as previously noticed [5,8,19,24,26], the optimization of the process needs to compromise between the four studied parameters E, $X_{s,w}$,$X_{t,w}$ and ϕ_C. Indeed, a lower surfactant concentration should be used to give a smaller volume fraction of coacervate. On the basis of these findings, an optimal value of ϕ_C (i.e. 0.35) was obtained using 10 wt.% Dehydol LT7 at 60˚C.

3.2.2. *Effect of sodium sulfate*

One can see clearly in Fig. 3 that the electrolyte increases the extraction extent (E %) of furfural. The presence of the electrolyte induces a decrease in the solubility of furfural in water by a salting-out phenomenon. According to Saito and Shinoda [40], the addition of electrolyte to non-ionic surfactant solutions

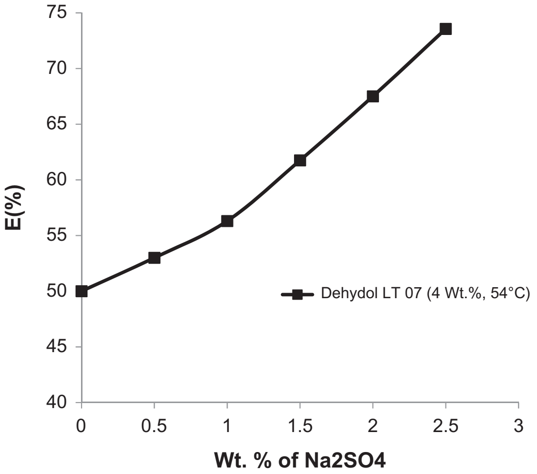

Fig. 3. Three-dimensional isoresponse curves smoothed by a quadratic model (Eqs. (6)–(8)).

increases their hydrocarbon solubilization capacity, by lowering their CMC. This behavior may be the result of an increase in micellar number in the presence of electrolyte. So, the addition of electrolyte to non-ionic surfactant solutions increases their solubilization capacity towards an organic solute and, consequently, improves the efficiency of its coacervate extraction (Fig. 3). These results agree with several previous ones [5,8,19,24,26] on the effect of ionic strength on extraction power.

3.3. Modeling of extraction results using ionic liquid

The extraction results of furfural from its aqueous solutions at 12.5 mg/L with [C4C1im]PF6, according to two variables: wt.% ionic liquid (X_{IL}), and temperature (T), were expressed by three responses (Y): percentage of extracted solute (E), residual concentration of solute ($X_{s,w}$), and residual concentration of ionic liquid ($X_{IL,w}$) in the dilute phase The quadratic correlation was chosen to give the slope and the regression coefficient (R^2) closest to unity. The

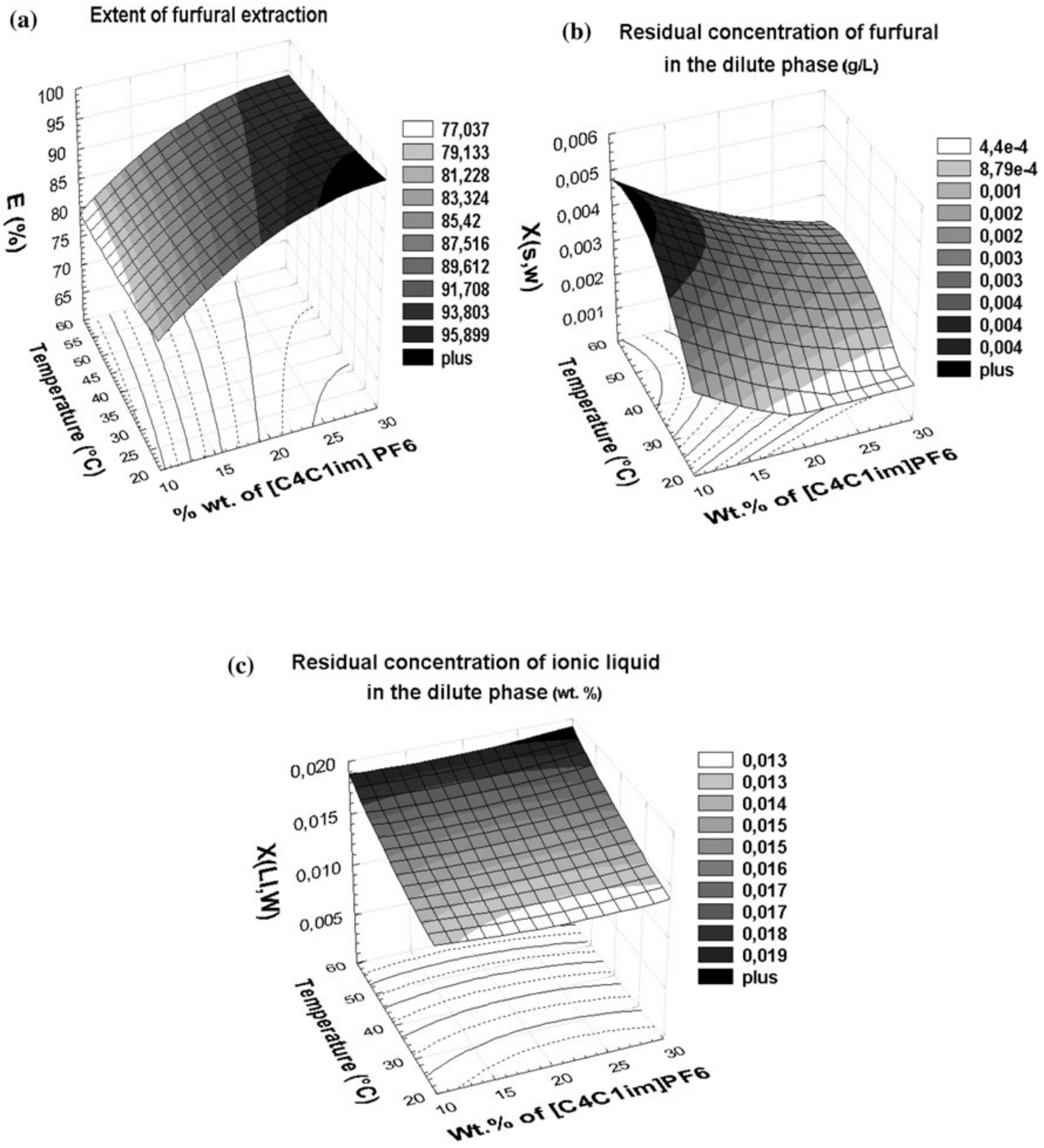

Fig. 4. Effect of Na_2SO_4 on the extraction extent of furfural (E %).

quadratic equations for the properties (E, $X_{\mathrm{s,w}}$, $X_{\mathrm{IL,w}}$), whose reliability was checked, are as follows:

$$E = 48.080 + 2.871X_{\mathrm{IL}} - 0.206T + 0.022 \times 10^{-1}X_{\mathrm{IL}}T - 0.461 \times 10^{-1}X_{\mathrm{IL}}^2 + 0.018 \times 10^{-1}T^2 \quad (6)$$

$$X_{\mathrm{s,w}} = -0.134 \times 10^{-2} - 0.303 \times 10^{-3}X_{\mathrm{IL}} + 0.354 \times 10^{-3}T - 0.321 \times 10^{-6}X_{\mathrm{IL}}T - + 0.422 \times 10^{-5}X_{\mathrm{IL}}^2 - 0.035 \times 10^{-4}T^2 \quad (7)$$

$$X_{\mathrm{IL,w}} = 0.014 \times 10^{-1} - 2.526 \times 10^{-4}X_{\mathrm{IL}} + 0.121 \times 10^{-5}T + 0.151 \times 10^{-5}X_{\mathrm{IL}}T + 0.477 \times 10^{-5}X_{\mathrm{IL}}^2 + 0.151 \times 10^{-5}T^2 \quad (8)$$

Fig. 4(a) (variations in E smoothed by Eq. (6)) shows that a temperature increase has a slight effect on furfural extraction using [C4C1im]PF6. However, the extent of furfural extraction (E) increases significantly with X_{IL}. Indeed, E reaches 98% under optimal conditions ($X_{\mathrm{IL}} = 30\%$, $T = 25$°C) against 88% using non-ionic surfactant (Fig. 2(a)).

One can notice in Fig. 4(b) (variations in $X_{\mathrm{s,w}}$ smoothed by Eq. (7)) that the residual concentration of furfural ($X_{\mathrm{s,w}}$) in the aqueous phase after extraction decreases as X_{IL} increases; the figure also shows that a temperature rise increases $X_{\mathrm{s,w}}$. Hence, heating has an opposite effect on extraction process using [C4C1im] PF6, probably because of furfural aqueous solubility increase with temperature. Thereby, furfural concentration was reduced about 31 times using ionic liquid [C4C1im]PF6 and 6 times using non-ionic surfactant (Dehydol LT7).

The behavior of the residual concentration of ionic liquid in the aqueous phase after extraction ($X_{\mathrm{IL,w}}$) is shown in Fig. 4(c) (variations of $X_{\mathrm{IL,w}}$ smoothed by Eq. (8)). $X_{\mathrm{IL,w}}$ is independent of X_{IL} but increases with temperature, certainly because of the increase in the ionic liquid aqueous solubility [27].

This result is in agreement with the literature: Pei et al. [31] determined the partition coefficients of furfural between IL and aqueous phases and, thereby, the thermodynamic parameters of transfer of furfural from the aqueous to the IL phase. The obtained $\Delta H_{\mathrm{T}}^{\circ}$ and $\Delta G_{\mathrm{T}}^{\circ}$ values were negative, whereas those of $\Delta S_{\mathrm{T}}^{\circ}$ were positive. The entropy term, $T\Delta S_{\mathrm{T}}^{\circ}$, being about twice as high as $\Delta H_{\mathrm{T}}^{\circ}$, this exothermic extraction process is therefore more entropy than enthalpy driven. This could reveal hydrophobic interaction as the main driving force for IL-based removal of furfural from aqueous solutions [30]. However, with a $\log P$ value of 0.41 [41], furfural is rather hydrophilic. Therefore, the high extraction efficiency of [C4C1im]PF6 should be due to stronger Coulombic interactions between furfural and ionic liquid compared with hydrogen bonding of the carbonyl group in water. On the other hand, the efficiency of the endothermic CPE process is likely to be limited by the solubilization capacity of the micelles. Many factors can affect the amount of a given substance which can be solubilized in micelles. Polarity and polarizability, chain length and chain branching, molecular size, shape, and structure have all been shown to have various effects. Furthermore, the coacervate contains water, so it is less hydrophobic than the ionic liquid. Hence, IL extraction shows better performances than CPE.

4. Recycling of ionic liquid

The effect of pH on the extraction extent, E, of furfural is shown in Fig. 5; extraction tests were made under the conditions mentioned in the figure. Furfural extraction either with non-ionic surfactant or with ionic liquid is insensitive to pH. Indeed, furfural is a neutral solute; thus, contrary to the cases of humic acid [25], phenol [7] and aniline [6], the back-extraction of such a species is not possible with a pH change. A more thorough analysis of the back-extraction of solute for solvent recycling is essential to ensure the effectiveness of the proposed process and its feasibility for an application on an industrial scale. Given the negative results of the back-extraction of solute with pH change, a stripping technique was attempted. The ionic liquid phase containing furfural was heated at a temperature close to the boiling point of furfural ($T = 161.7$°C) [9]. The results are shown in

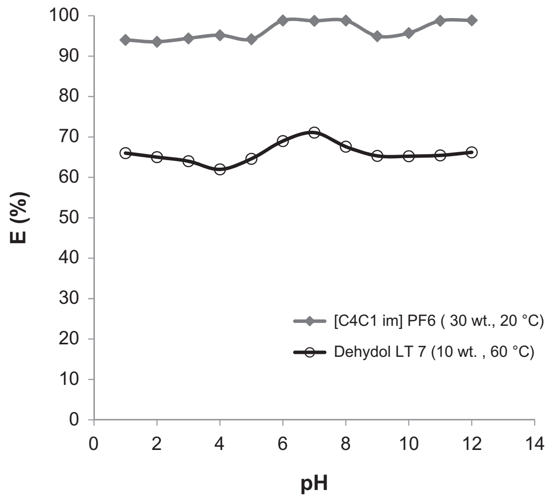

Fig. 5. Effect of pH on the extraction extent of furfural (E %).

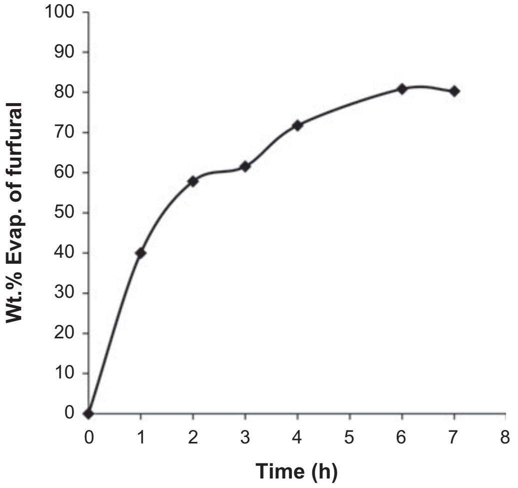

Fig. 6. Effect of heating time on the rate of evaporation of the solute.

Fig. 6. An evaporation percentage close to 80% after 6 h of heating was obtained. From these results, it can be said that furfural extraction and recovery through back extraction, as well as ionic liquid recycling can be achieved.

5. Conclusion

The application of coacervate extraction (CPE) to aqueous solutions of furfural proved successful. In order to optimize its operation, the parameters that control the effectiveness of this technique: (% E), ($X_{s,w}$), (ϕ_C), and ($X_{t,w}$) were analyzed. Thus, the choice of the optimal conditions requires a compromise between all four parameters. Under favorable conditions of surfactant concentration (10 wt.% Dehydol LT7) and temperature (60–62˚C), a first contact between the surfactant and furfural solutions gives extraction percentages around 80%. Na_2SO_4 increases the extraction extent of furfural. On the other hand, pH change does not affect extraction yield.

The ionic liquid ([C4C1im]PF6) gives better extraction yields even at a low temperature ($E = 98\%$ at 30˚C with 30 wt.% IL). Furthermore, extraction using IL can be achieved at ambient temperature. Finally, ionic liquid recycling was proved using a stripping method.

References

[1] Control of pollution in the petroleum industry, in: B. Nath, G. St. Cholakov, Pollution Control Technologies, vol. III, EOLSS Publishers Co., Oxford, 2009.

[2] B.K. Sharma, Environmental Chemistry, eleventh ed., GOEL Publishing House, Meerut, 2007.

[3] K. Verschueren, Handbook of Environmental Data on Organic Chemicals, four, fifth ed., Volume Set, Wiley, New York, NY, 2008.

[4] E.L. De Barros Neto, J.P. Canselier, C. Gourdon, Organic Solvent-free extraction of phenol through liquid-coacervate systems, Solvent Extraction for the 21st Century, in: M. Cox, M. Hidalgo, M. Valiente (Eds.), Proceedings of the International Solvent Extraction Conference, Barcelone, July 1999 (ISEC'99), Society of Chemical Industry, London, vol. 1, 2001, pp. 171–176.

[5] B. Haddou, J.P. Canselier, C. Gourdon, Purification of effluents by two-aqueous phase extraction, Chem. Eng. Res. Des. (Trans. IChem E, England) 81 (2003) 1185–1192.

[6] L.J.N. Duarte, J.P. Canselier, Extração no ponto nuvem de compostos orgânicos homólogos e isômeros, Química Nova (Extraction of homologous and isomeric organic compounds by two-phaseaqueous extraction) 28 (2005) 426–432.

[7] B. Haddou, J.P. Canselier, C. Gourdon, Cloud point extraction of phenol and benzyl alcohol from aqueous stream, Sep. Purif. Technol. 50 (2006) 114–121.

[8] B. Haddou, J.P. Canselier, C. Gourdon, Use of cloud point extraction with ethoxylated surfactants for organic pollution removal, in: M. Fanun (Ed.), The Role of Colloidal Systems in Environmental Protection, Elsevier, Amsterdam, 2014, pp. 97–142.

[9] K.J. Zeitsch, The Chemistry and Technology of Furfural and its Many By-Products, Elsevier, Amsterdam, 2000.

[10] X.M. Huang, Q. Zhang, T.J. Wang, Q.Y. Liu, L.L. Ma, Q. Zhang, Production of jet fuel intermediates from furfural and acetone by aldol condensation over MgO/NaY, J. Fuel Chem. Technol. 40 (2012) 973–978.

[11] H.E. Hoydonckx, W.M. Van Rhijn, W. Van Rhijn, D.E. De Vos, P.A. Jacobs, Furfural and derivatives, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007.

[12] M. Anbia, N. Mohammadi, A nanoporous adsorbent for removal of furfural from aqueous solutions, Desalination 249 (2009) 150–153.

[13] M. Anbia, N. Mohammadi, K. Mohammadi, Fast and efficient mesoporous adsorbents for the separation of toxic compounds from aqueous media, J. Hazard. Mater. 176 (2010) 965–972.

[14] I. Richard, Toxicology and Carcinogenesis Studies of Furfural, National Toxicology Program, Technical Report Series, No. 382, U.S. Department of Health and Human Services, Public Health Service, National Institutes of Health, Bethesda, MD, 1990.

[15] K. Zhang, M. Agrawal, J. Harper, R. Chen, W.J. Koros, Removal of the fermentation inhibitor, furfural, using activated carbon in cellulosic-ethanol production, Ind. Eng. Chem. Res. 50 (2011) 14055–14060.

[16] T. Games, R. Marr, F. Fröschl, M. Siebenhofer, Extraction of furfural with carbon dioxide, Sep. Sci. Technol. 32 (1997) 355–371.

[17] M. Sagehashi, T. Nomura, H. Shishido, A. Sakoda, Separation of phenols and furfural by pervaporation and reverse osmosis membranes from biomass-superheated steam pyrolysis-derived aqueous solution, Bioresour. Technol. 98 (2007) 2018–2026.

[18] W.L. Hinze, Cloud point Extraction and preconcentration procedures for organic and related pollutants of states concern, Water Resour. Res. Inst. Univ. N.C. 30 (1992) 269–275.
[19] S. Akita, H. Takeuchi, Cloud-point extraction of organic compounds from aqueous solutions with nonionic surfactant, Sep. Sci. Technol. 30 (1995) 833–846.
[20] F.H. Quina, W.L. Hinze, Surfactant-mediated cloud point extraction: An environmentally benign alternative separation approach, Ind. Eng. Chem. Res. 38 (1999) 150–168.
[21] W. Kimchuwanit, S. Osuwan, J.F. Scamehorn, J.H. Harwell, K. Haller, Use of a micellar-rich coacervate phase to extract trichloroethylene from water, Sep. Sci. Technol. 35 (2000) 1991–2002.
[22] J.P. Canselier, C. Gourdon, L.J. Nogueira Duarte, E.L. De Barros Neto, B. Haddou, C. Gumila, Procédé d'extraction sans solvant des polluants organiques et métalliques, French Patent no. 06/03632, 21 April 21, 2006 (PCT/EP2007/053777, WO-2007-122158).
[23] B. Haddou, Z. Bouberka, Z. Derriche, A. Taibi, H. Bouabdesselam, Separation of neutral red and methylene blue from wastewater using two aqueous phase extraction methods, Sep. Sci. Technol. 42 (2007) 2677–2691.
[24] Z. Talbi, B. Haddou, Z. Bouberka, Z. Derriche, Simultaneous elimination of dissolved and dispersed pollutants from cutting oil wastes using two aqueous phase extraction methods, J. Hazard. Mater. 163 (2009) 748–755.
[25] H. Ghouas, B. Haddou, M. Kameche, Z. Derriche, C. Gourdon, Extraction of humic acid by coacervate: Investigation of direct and back processes, J. Hazard. Mater. 205–206 (2011) 171–178.
[26] H. Ghouas, B. Haddou, M. Kameche, L. Louhibi, Z. Derriche, J.P. Canselier, C. Gourdon, Cloud point extraction of α-amino acids, Sep. Sci. Technol. 49 (2014) 2142–2150.
[27] Z. Talbi, B. Haddou, H. Ghouas, M. Kameche, Z. Derriche, C. Gourdon, Cationic dye removal from aqueous solutions using ionic liquid and nonionic surfactant-ionic liquid systems: A comparative study based upon experimental design, Chem. Eng. Commun. 201 (2014) 41–52.
[28] T. Suoranta, O. Zugazua, M. Niemelä, P. Perämäki, Recovery of palladium, platinum, rhodium and ruthenium from catalyst materials using microwave-assisted leaching and cloud point extraction, Hydrometallurgy 154 (2015) 56–62.
[29] S. Carda-Broch, A. Berthod, D.W. Armstrong, Solvent properties of the 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid, Anal. Bioanal. Chem. 375 (2003) 191–199.
[30] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, Room temperature ionic liquids as novel media for 'clean' liquid–liquid extraction, Chem. Comm. 1765–1766 (1998).
[31] Y. Pei, K. Wu, J. Wang, J. Fan, Recovery of furfural from aqueous solution by ionic liquid based liquidliquid extraction, Sep. Sci. Technol. 43 (2008) 2090–2102.
[32] V. Degiorgio, in: V. Degiorgio, M. Corti M, Physics of Amphiphiles: Micelles, Vesicles and Microemulsions, North-Holland, Amsterdam 1985.
[33] L.A.M. Rupert, A thermodynamic model of clouding in ethoxylate mixtures, J. Colloid Interface Sci. 153 (1992) 92–105.
[34] L.J.N. Duarte, J.P. Canselier, Cloud point, critical micelle concentration and HLB relationships for alcohol ethoxylates, PharmaChem 4 (2005) 36–39.
[35] G. Box, N. Draper, Empirical Model-Building and Response Surfaces, Wiley, Ser. Prob. Math. Stat. 44 (1987) 660–669.
[36] M.E.L. McBain, E. Hutchinson, Solubilization and Related Phenomena, Academic Press, New York, NY, 1955.
[37] T. Ingram, T. Mehling, I. Smirnova, Partition coefficients of ionizable solutes in aqueous micellar two-phase systems, Chem. Eng. J. 218 (2013) 204–213.
[38] D. Attwood, A.T. Florence, Surfactant Systems: Their Chemistry, Pharmacy and Biology, Chapman and Hall, London, 1983.
[39] M.K. Purkait, S. DasGupta, S. De, Determination of thermodynamic parameters for the cloud point extraction of different dyes using TX-100 and TX-114, Desalination 244 (2009) 130–138.
[40] H. Saito, K. Shinoda, The solubilization of hydrocarbons in aqueous solutions of nonionic surfactants, J. Colloid Interface Sci. 24 (1967) 10–15.
[41] C. Hansch, A. Leo, D. Hoekman, Exploring QSAR—Hydrophobic, Electronic, and Steric Constants, American Chemical Society, Washington, DC, 1995, p. 11.