Jonske tečnosti-
Ionic liquids -

dizajnirani rastvarači za
designed solvents for
zelenu hemiju
green chemistry

- Selektivna ekstrakcija bakra,
- Ekstrakcija boja,
- Ekstrakcija pesticida,
- Ekstrakcija TKE

- Novi karbonski materijali na bazi JT za reakciju redukcije kiseonika

Tatjana Trtić-Petrović
Laboratorija za fiziku
Odeljenje za
separacionu hemiju
i obnovljive izvore energije

Jonske tečnosti- dizajnirani rastvarači za zelenu hemiju

Ionic liquids - designed solvents for green chemistry

Tatjana Trtić-Petrović
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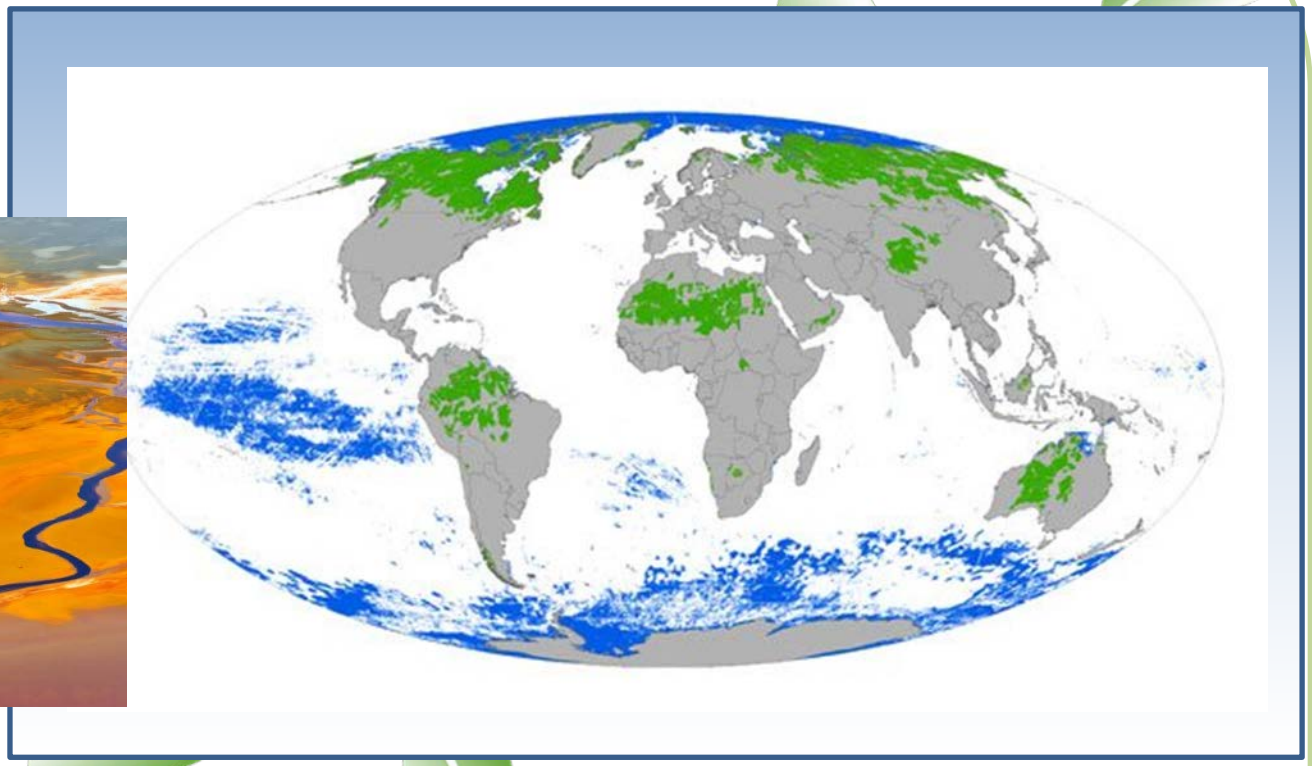
Odeljenje za
separacionu hemiju
i obnovljive izvore energije

Prirodno-matematički fakultet
Univerzitete u Novom Sadu
Departman za hemiju, biohemiju
i zaštitu životne sredine



Zelena (održiva) hemija je pojam koji se odnosi na kreiranje hemijskih proizvoda i procesa koji smanjuju ili eliminišu upotrebu i proizvodnju štetnih supstanci.

https://www.nature.com/articles/d41586-018-07183-6

Principi zelene hemije*

1.Prevencija stvaranja otpada

2.„Atomska ekonomija“

Upotreba manje opasnih

3.Hemijskih sinteza

4.Reaktanata i proizvoda

5.Rastvarača

6.Energetska efikasnost

7.Upotreba obnovljivih izvora sirovina

8.Redukcija proizvodnje derivata

9.Upotreba katalizatora

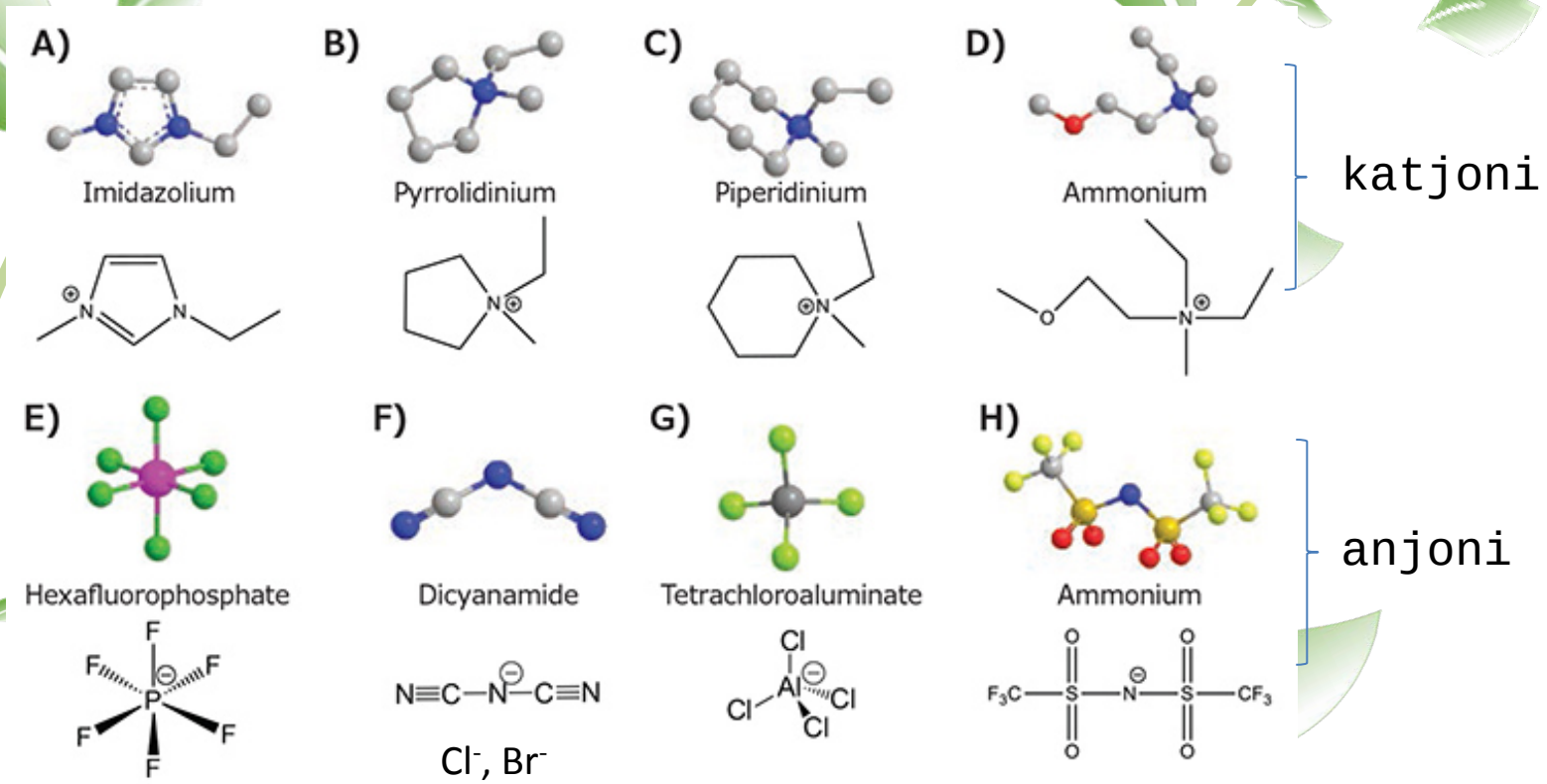
10.Postupci za razgradnju

11.Pravovremena analiza i prevencija zagađenja

12.Minimiziranje akcidenata

*Anastas, P. T.; Warner, J. C. Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998.

- Jonske tečnosti su organske soli koje su tečne na temperaturama <100 ^{o}C.
- Nova klasa rastvarača sa nemolekularnim karakterom.



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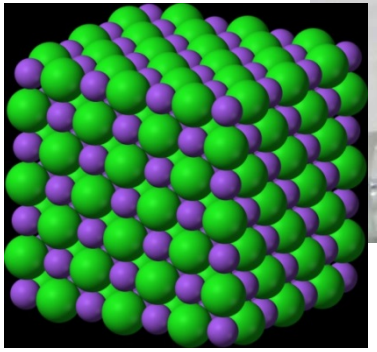
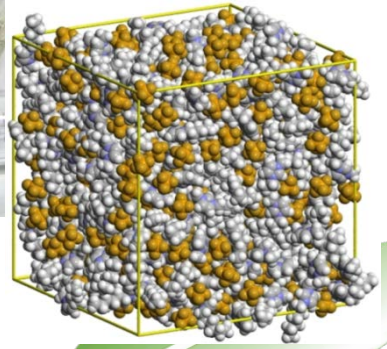
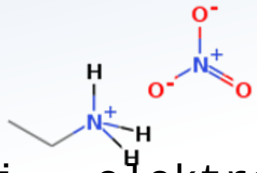


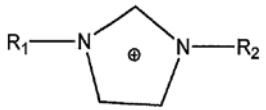


Istorija Jonskih Tečnosti

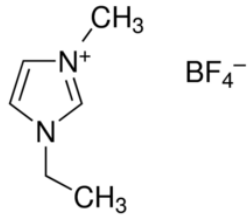
1. Generacija JT
- Prva IL (1914): etilamonijum nitrat.



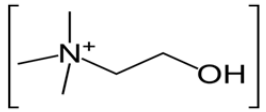
- ~ 1940 N-alkilpiridinium hloroaluminati - elektroliti za galvanizaciju aluminijuma.
- ~ 1980 JT sa dialkilimidazolijum hloroaluminata katalizatori / rastvarači za Friedel-Crafts reakciju.
- Glavni nedostaci: niska hemijska stabilnost, relativno visoka toksičnost i osetljivost na vlagu.



2. Generacija JT N- N'-dialkilimidazolium
- 1992. godine - etil metilimidazolijum tetrafluoroborat medijum za homogenu katalizu.
- Selektivna rastvorljivost, niska tačka topljenja, visoka hemijska stabilnost, relativno niža toksičnost.
- Primene: proces separacije, elektrohemija (elektroliti), kataliza, rastvarači.



3. Generacija JT - biokompatibilni, netoksične IL 2012.
- Katjon - holinijum, važan mikronutrijent, potpuno razgradljiv
- Anjon - prirodne kiseline (laktat i piruvat), aminokiseline (taurat)i vitamini (niacin - B3 vitamin),
- Primena u medicini, farmaciji, fitofarmaciji.



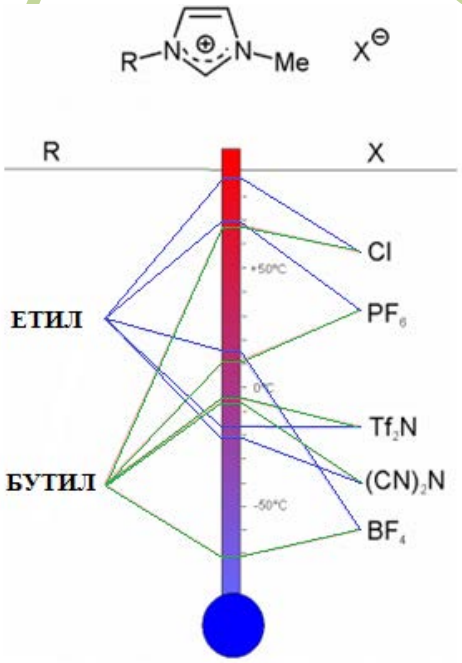
Osobine jonski tečnosti

Širok opseg tečnog stanja > 200°C

Zanemarljiv napon pare

Toplotni kapacitet

Rastvorljivost organskih i neorganskih jedinjenja



Termalna i elektrohemijska stabilnost

Visoka jonska konduktivnost

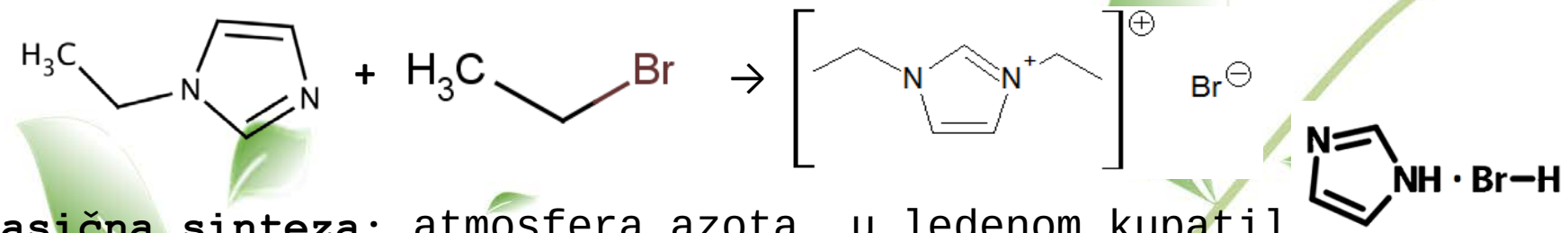
Електрохемијски прозор 2 - 4.5 V

Dizajn fizičko hemijskih osobina

Teorijski broj JT je 10^{18}

Sinteza jonskih tečnosti

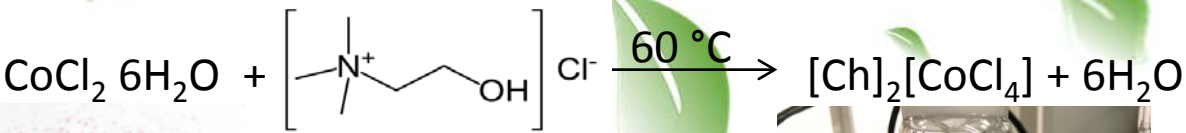
1-etil-3-alkil-imidazolijum bromid

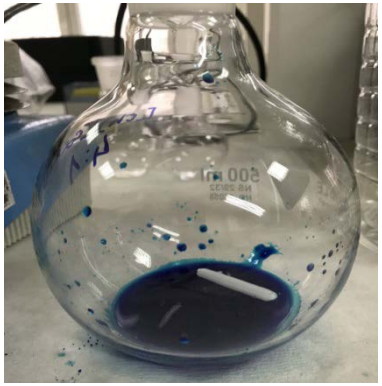


Klasična sinteza: atmosfera azota, u ledenom kupatil[illegible]

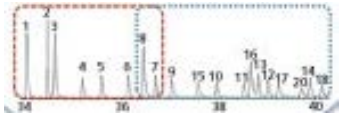
Mikrotalasno-stimulisana sinteza: mikrotalasno zračenje snage 240W, T = 80 °C, 7 min.
Prečišćavanje: ektrakcija etil-acetatom, uparavanje i sušenje na 70 °C pod sniženim pritiskom.

Holinijum tetrahloro kobaltat



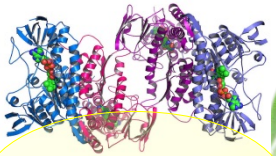


Primena jonskih tečnosti



Stacionarna faza u GC

Priprema uzorака



Sinteza proteina

Biohemija

Analitička hemija

Elektrohemija

Baterije

Gorivne ćelije

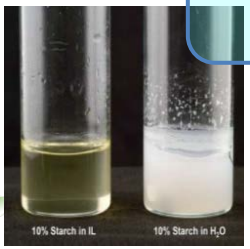
Hemijska sinteza i kataliza

Jonske tečnosti

Sinteza novih materijala

Ugljenični

Alternativni, podesivi rastvarači



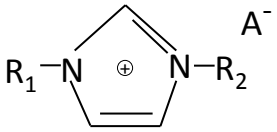
Separacioni procesi

Apsorpcija CO_2

Ekstrakcija

Jonske tečnosti kao rastvarači i ekstragensi

- Dizajn JT



1,3-dialkil imidazolijum

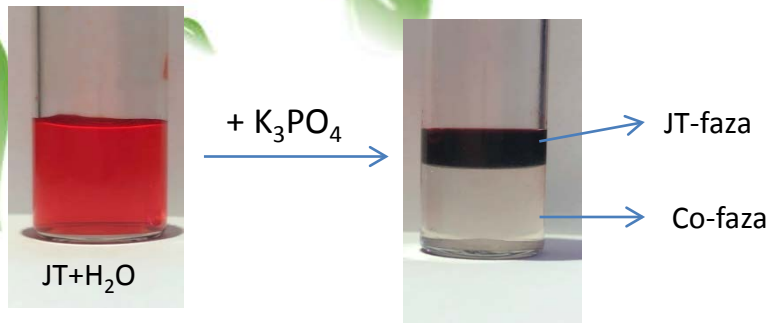
hidrofobni → hidrofilni

$[PF_6^-]$ $[BF_4^-]$ $[CH_3CO_2^-]$
$[N(SO_2CF_3)_2^-]$ $[CF_3SO_3^-]$ $[CF_3SO_2^-]$
$[BR_1R_2R_3R_4^-]$ $[NO_3^-]$, $[Cl^-]$

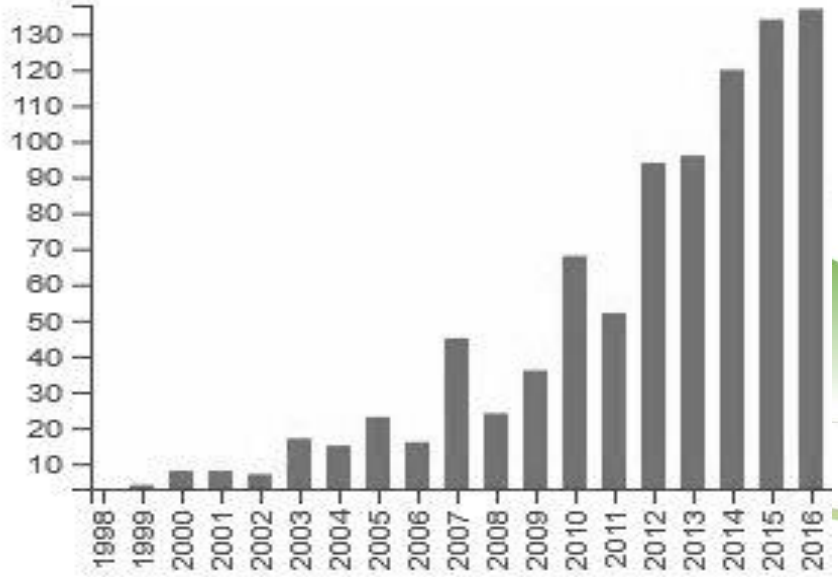
Ekstrakcija → Tečno-tečna

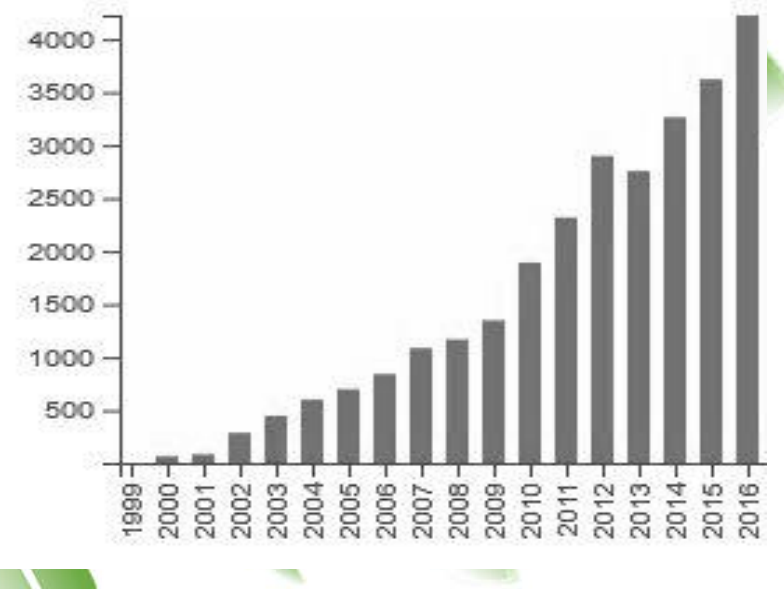
Vodeni bifazni sistemi

- oba konstituenta (polimer-so, polimer-polimer, JT-so, JT-polimer) su pojedinačno rastvorna u vodi
- mešanjem njihovih vodenih rastvora, iznad određene koncentracije dolazi do razdvajanja dve faze

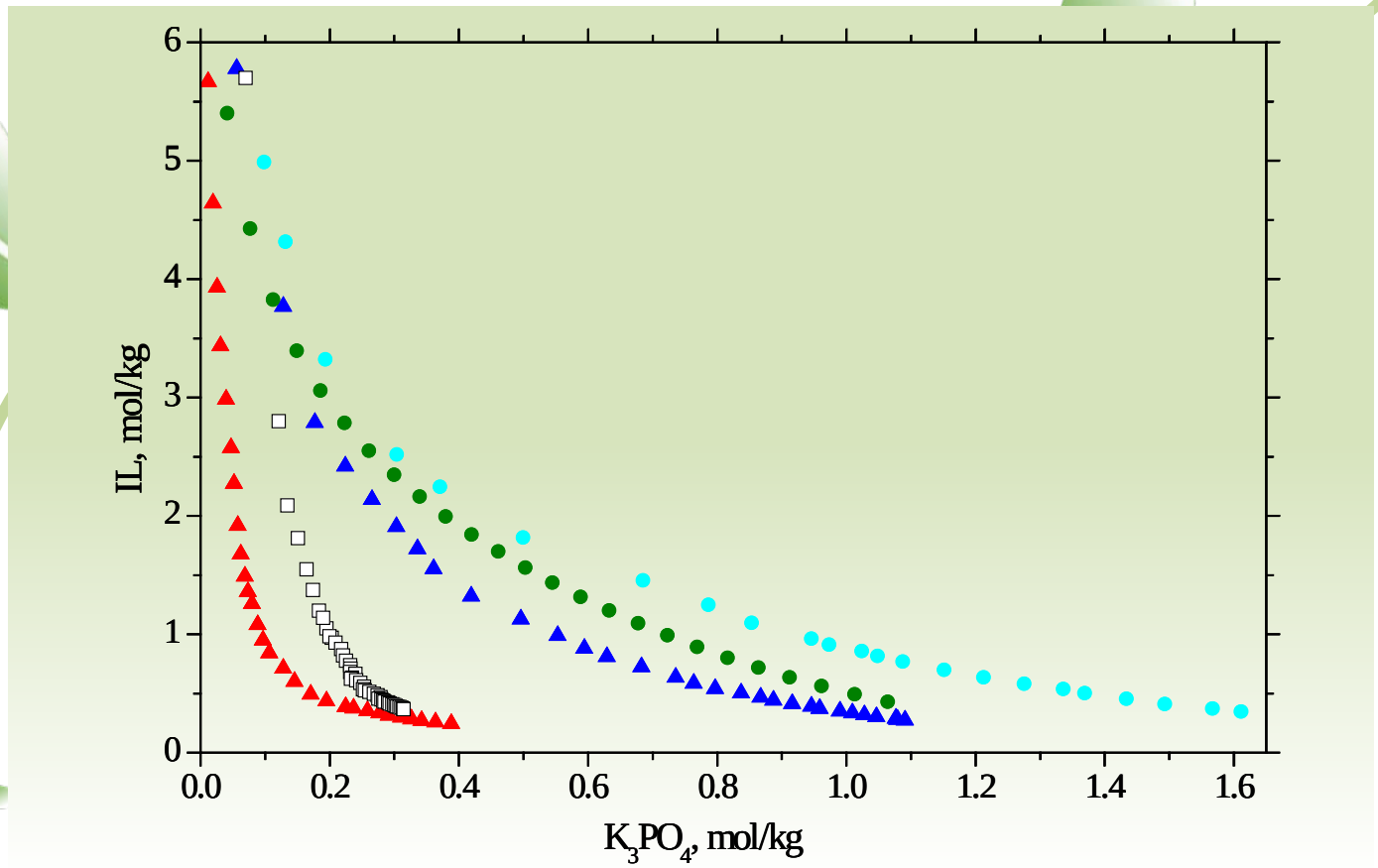


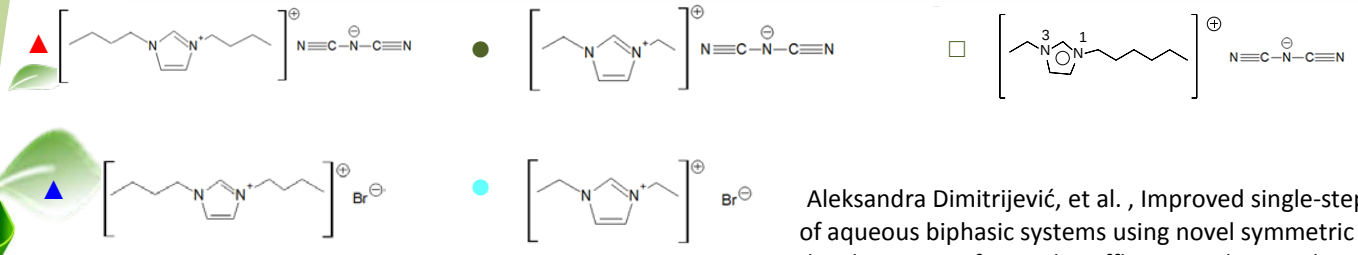
Broj radova i citata o vodenim bifaznim sistemima na bazi jonskih tečnosti



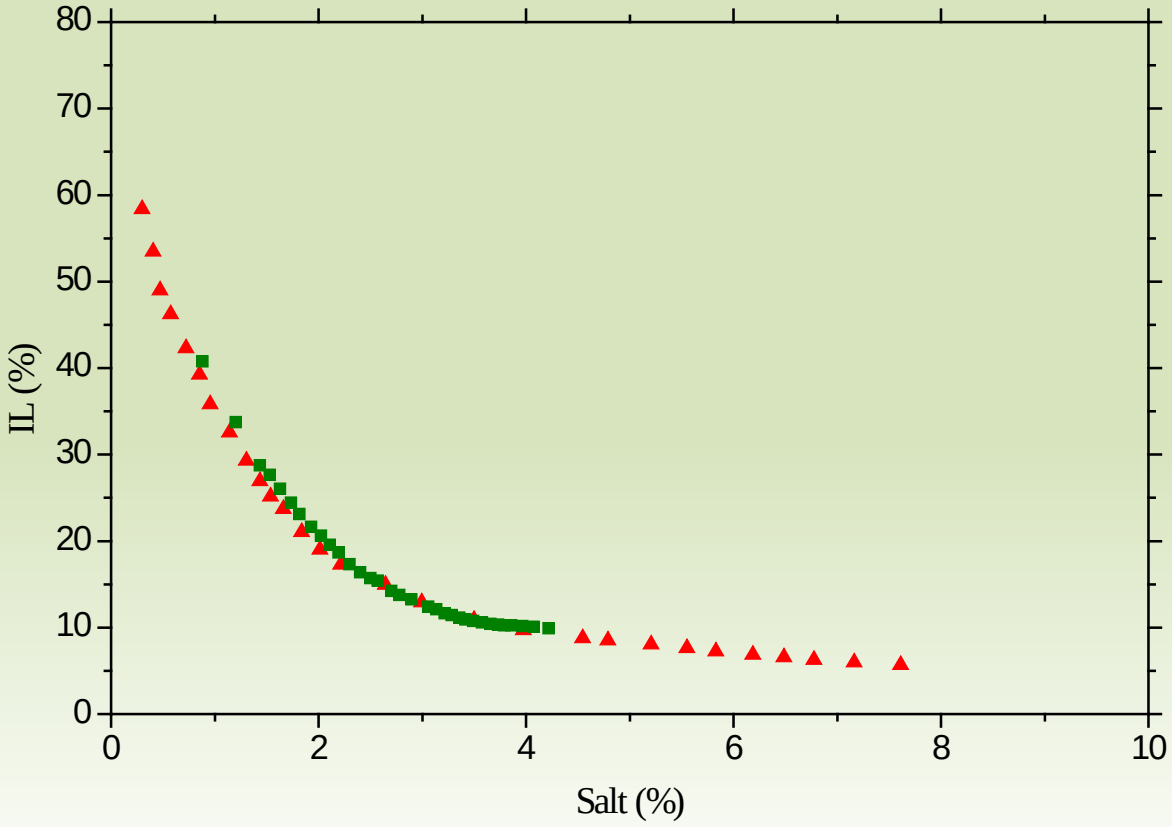


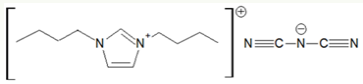
Uticaj strukture JT na fazne dijagrame





Aleksandra Dimitrijević, et al. , Improved single-step extraction performance of aqueous biphasic systems using novel symmetric ionic liquids for the decolorisation of toxic dye effluents. Submetted in J. Ind. Eng. Chem





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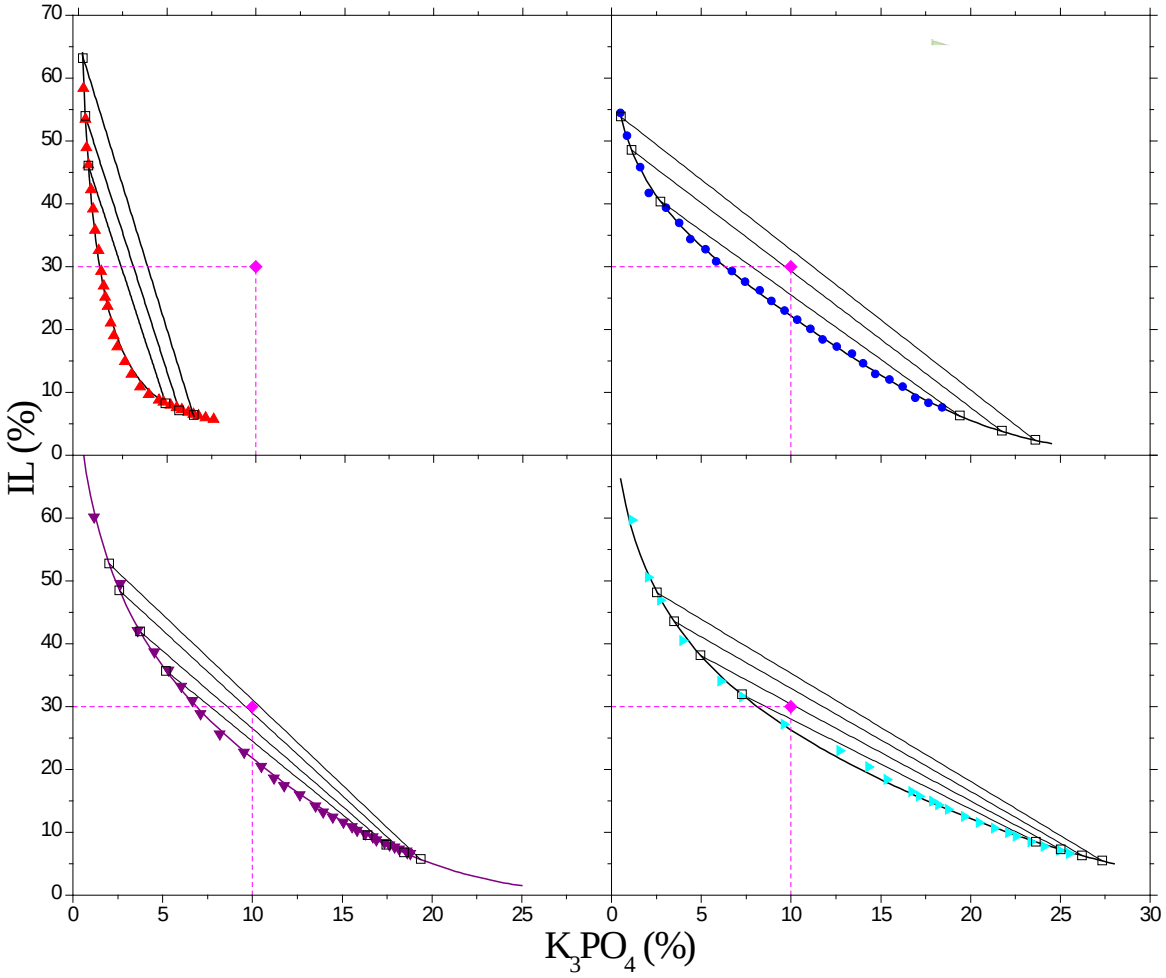
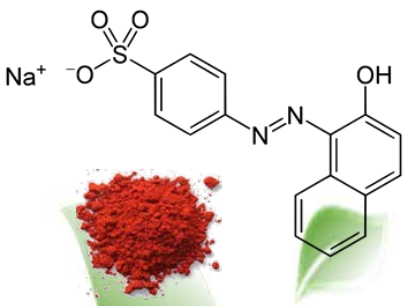


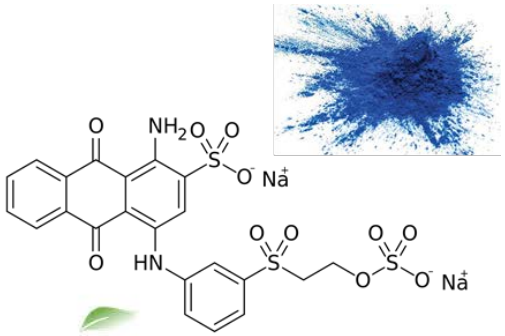
Ternary phase diagrams of the studied{JT + K_3PO_4+ H_2O}with experimentally determined TLLs. Legend:▲ [bbim][DCA], ▼ [bbim][Br], ● [eeim][DCA],► [eeim][Br] and ♦ -extraction point.

Aleksandra Dimitrijević, et al. , Improved single-step extraction performance of aqueous biphasic systems using novel symmetric ionic liquids for the decolorisation of toxic dye effluents. Submetted in J. Ind. Eng. Chem

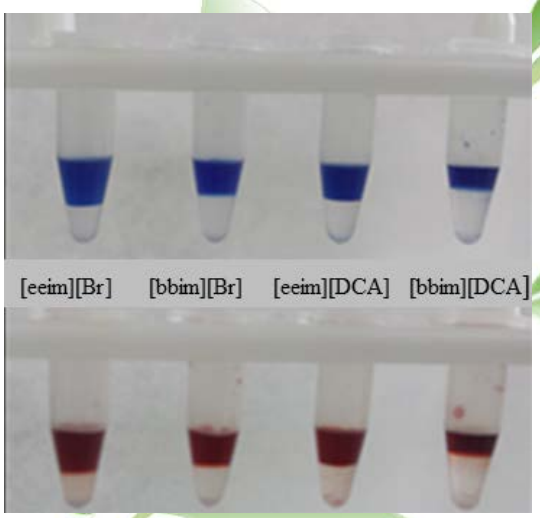
Ekstrakcija boja

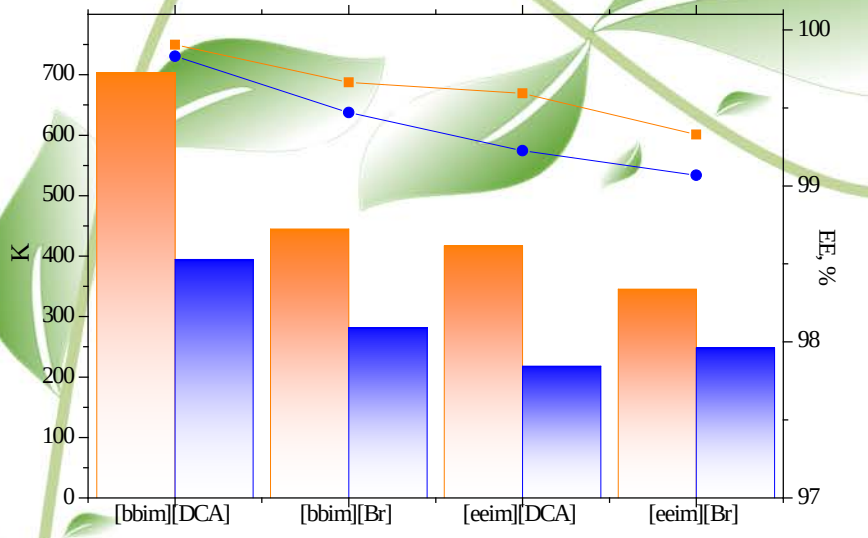


Oranž II
$logP_{ow}$=-1.48



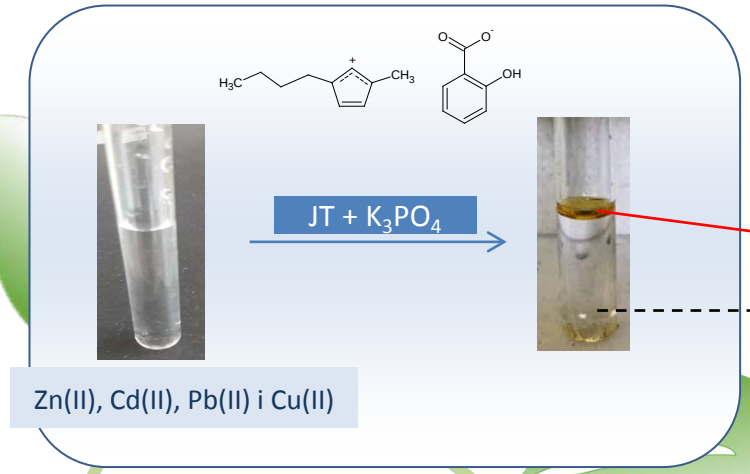
Ramazol briliant plava R
$logP_{ow}$=-3

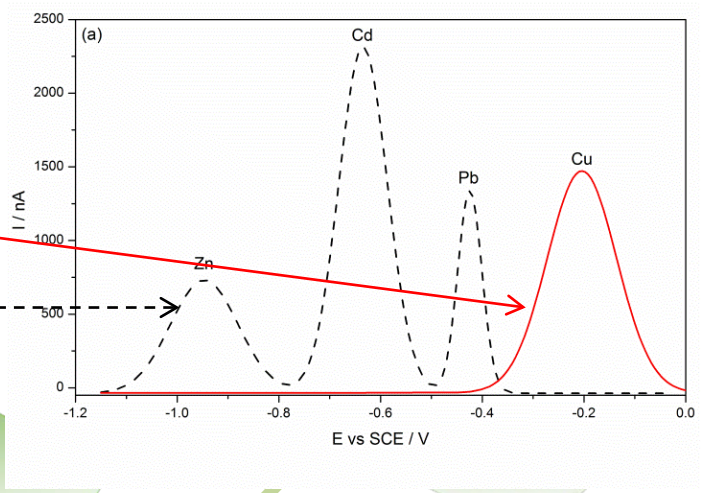


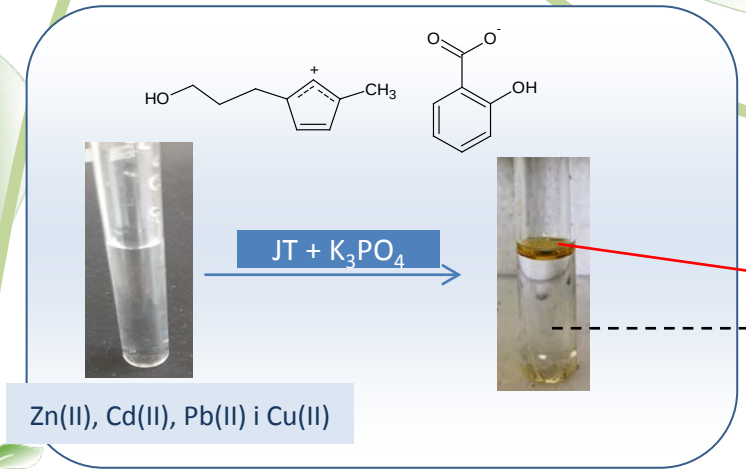


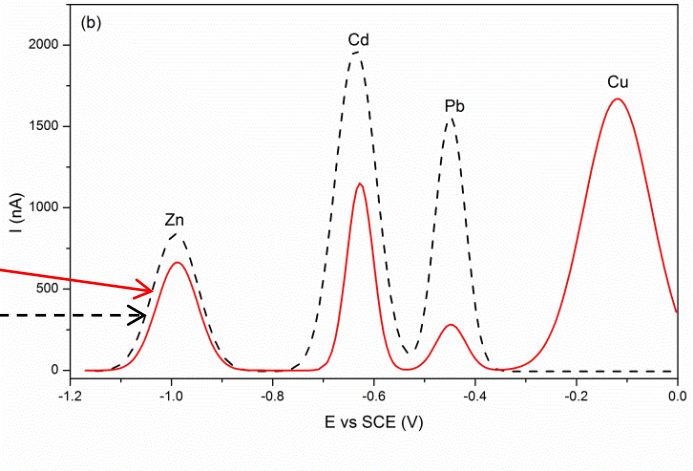
Aleksandra Dimitrijević, et al. , Improved single-step extraction performance of aqueous biphasic systems using novel symmetric ionic liquids for the decolorisation of toxic dye effluents. Submetted in J. Ind. Eng. Chem

Ekstrakcija metala



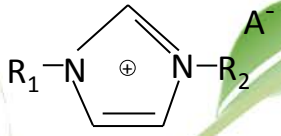


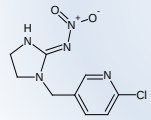
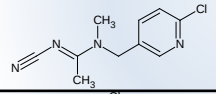
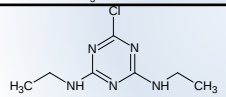
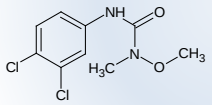
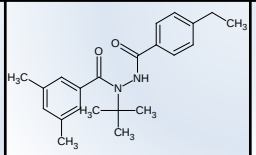


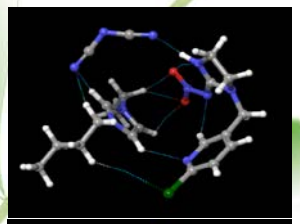


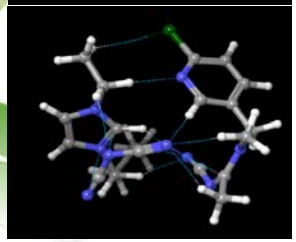
Tatjana Trtić-Petrović, et al. New sample preparation method based on task-specific ionic liquids for extraction and determination of copper in urine and wastewater, Anal. Bioanal. Chem. 410 (2018) 155-166.

Ekstrakcija pesticida



Pesticidi	Struktura	$logP_{ow}$	$LogP_{IL}$		
			[beim][Br]	[bmim][DCA]	[beim][DCA]
Imidacloprid		0.46	1.65	2.36	3.2
Acetamiprid		1.55	1.79	2.54	3.7
SImazin		2.28	1.81	2.85	4.1
Linuron		3.12	1.88	3.07	4.5
Tebufenozid		4.38	2.63	∞	4.38



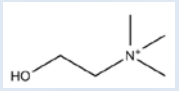
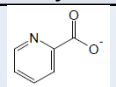
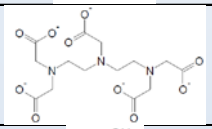


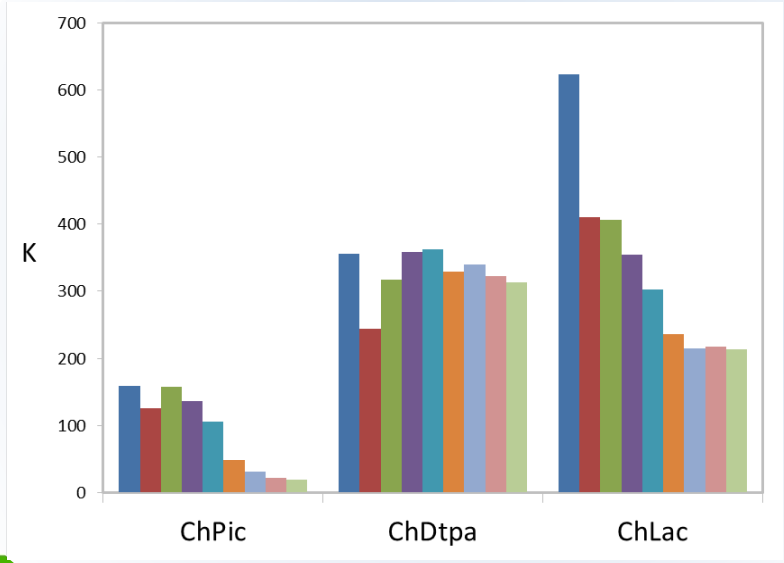
Izračunati % hidrofilnih površina imidakloprida i acetamiprida bez i u prisustvu JT

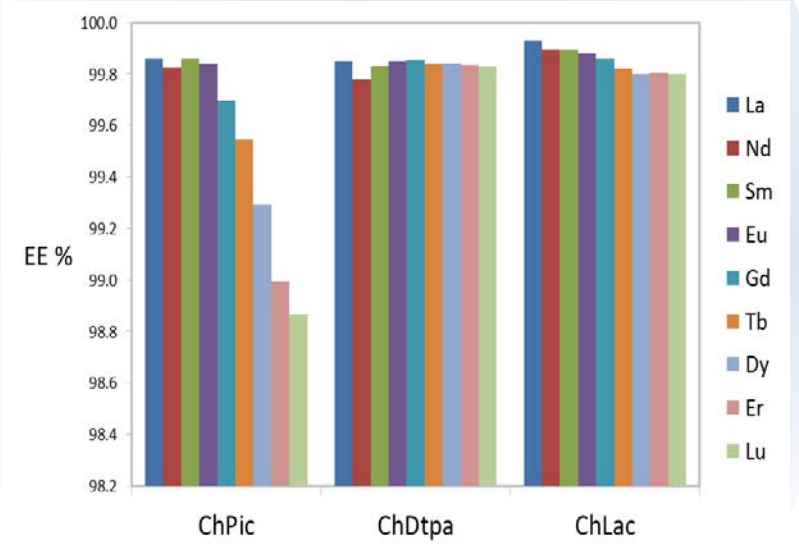
Pesticid	bez JT	[bmim][DCA]	[beim][DCA]	[beim][Br]
Imidakloprid	6.20	1.71	0	8.95
Acetamiprid	7.55	1.28	0	7.48

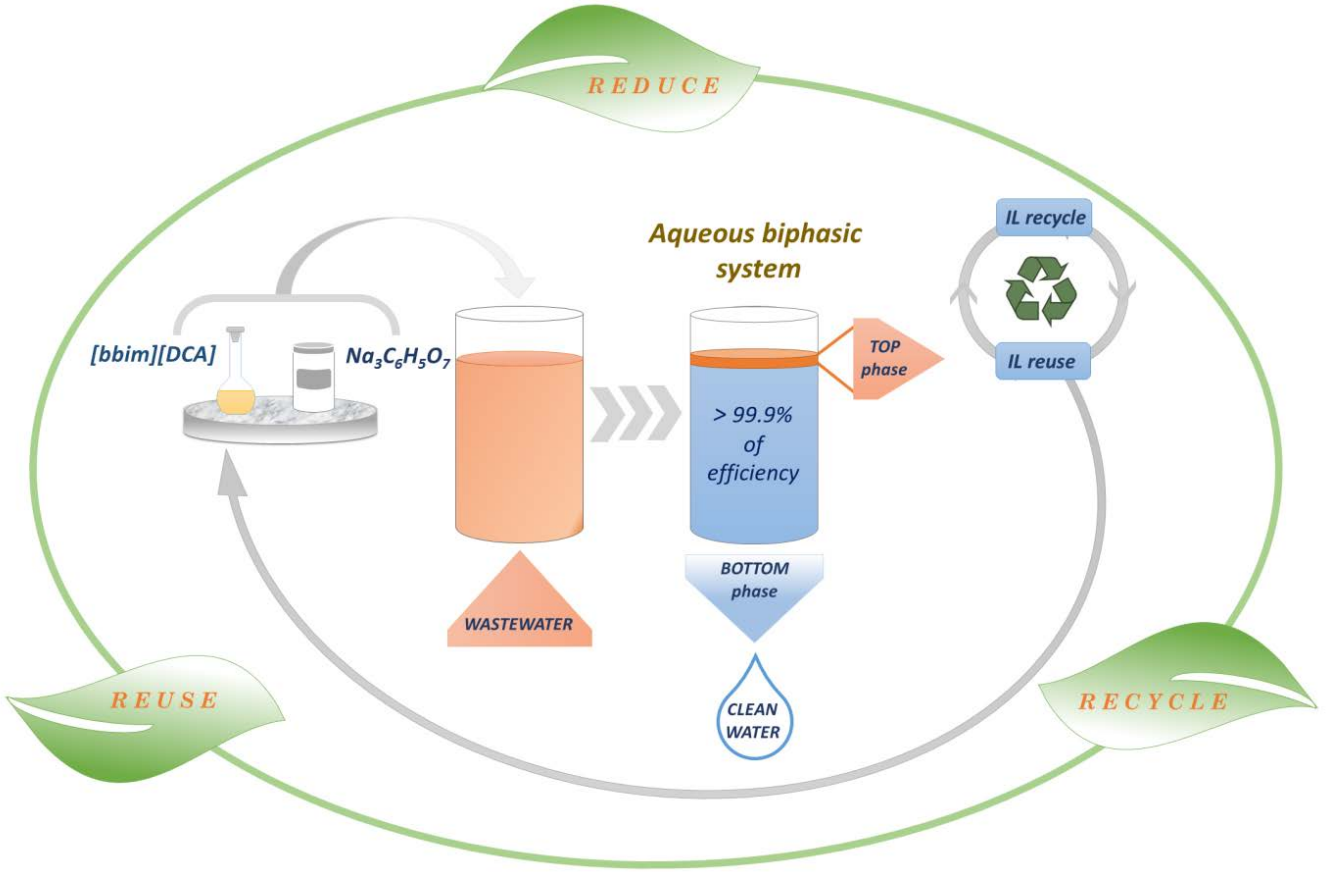
Aleksandra Dimitrijević, et al., Simultaneous extraction of pesticides of different polarity applying aqueous biphasic systems based on ionic liquids, Journal of Molecular Liquids, 243 (2017) 646-653.

Ekstrakcija tehnološki kritičnih elemenata

JT	Katjon	Anjon
Holijijum pikolinat ChPic		
Holinijum pentat ChDTPA		
Holinijum laktat ChLac		

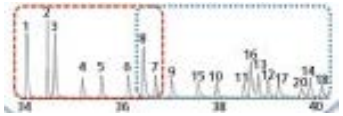






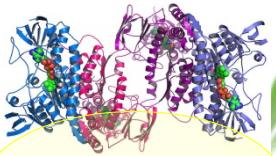
Aleksandra Dimitrijević, et al., Simultaneous extraction of pesticides of different polarity applying aqueous biphasic systems based on ionic liquids, Journal of Molecular Liquids, 243 (2017) 646-653.

Primena jonskih tečnosti



Stacionarna faza u GC

Priprema uzorака



Sinteza proteina

Analitička hemija

Biohemija

Elektrohemija

Baterije

Gorivne ćelije

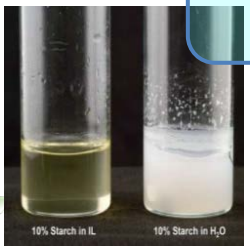
Jonske tečnosti

Hemijska sinteza i kataliza

Sinteza novih materijala

Ugljenični

Alternativni, podesivi rastvarači



Separacioni procesi

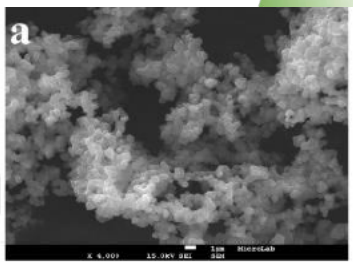
Apsorpcija CO_2

Ekstrakcija

Sinteza poroznih ugljeničnih materijala

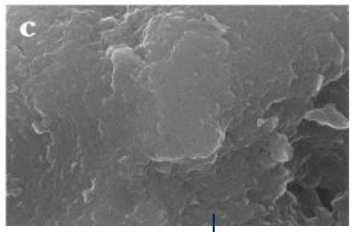
Hidrotermalna sinteza

+ H_2O → T=200°C, t=24h → HTC → 800°C

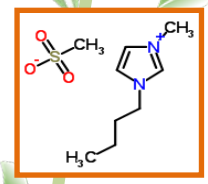


Jonotermalna sinteza, JT = butilmetilimidazolijum metansulfonat

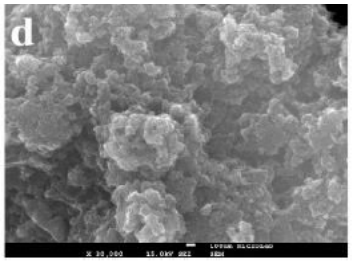
+ JT → T=200°C, t=24h → ITC → 800°C



Direktna karbonizacija JT, Carb-IL



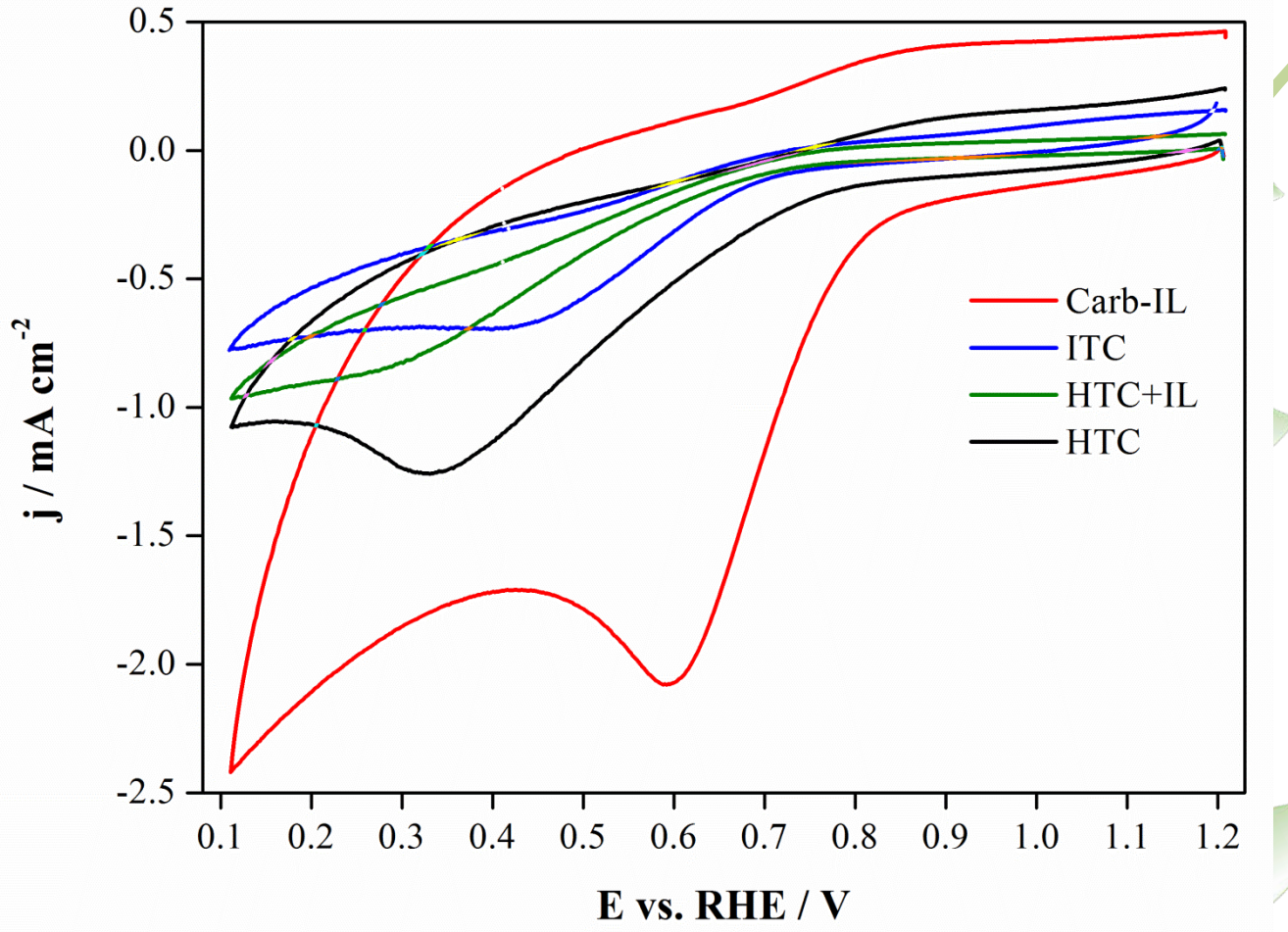
→ 800°C →



Material	Surface composition / wt.%			
	C	O	N	S
Carb-IL	81.4	14.9	3.2	0.5
ITC	90.1	9.9	-	-
HTC+IL	90.4	9.6	-	-
HTC	82.8	17.2	-	-

Nikola Zdolsek et al., Electrocatalytical activity of ionic liquid-derived porous carbon materials for oxygen reduction reaction, ChemElectroChem, 5 (2018) 1037-1046.

Ispitivanje materijala za reakciju redukcije O_2
Ciklična voltametrija u 0.1 M NaOH, rastvor zasićen O_2



Cena 1 m^2 katode: pripremljene od Carb-IL 100 $, a od Pt/C 2700 $.

Nikola Zdolsek et al., Electrocatalytical activity of ionic liquid-derived porous carbon materials for oxygen reduction reaction, ChemElectroChem, 5 (2018) 1037-1046.

Sinteza karbonskih materijala dopiranih Co i N

Materijal	Elektrohemija	
	$E_{onset,RHE}$ / V	$J_{k,@0,2V}$ / mA cm^{-2}
Co/N-C_{bm}	0.85	5.4
Co/N-C_{ch}	0.91	13.4
Fe/N-C_{bm}	0.76	3
Fe/N-C_{ch}	0.77	4.3

„Zelena hemija predstavlja stubove koji drže našu održivu budućnost. Najvažniji zadatak je preneti i usaditi vrednosti i načela zelene hemije hemičarima budućnosti.“