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# **Ionic Liquids for Desulphurization: A Review**

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#### Abstract

The literature survey has shown that not much work has been reported on the interaction mechanism of ionic liquids (ILs) with sulfur in model oil system. In recently published work, the interaction was predicted using COSMO-RS where the strength of hydrogen bond of anion should be reduced in order to increase thiophene extraction capacity. On the other hand, the same researchers also found that the smaller sized cations would lead to higher selectivity, which could lower the capacity and vice versa. While others have reported that the absorption capacity of sulfur compounds in ILs are strongly dependent on the chemical structures, physical properties and compactness between the cation and the anion of the ILs. However, these conclusions lead to a broad selection of ILs for extractive desulphurization process.

**Keywords:** ionic liquids, sulfur compounds, extractive desulphurization, absorption capacity

# 1. How do ILs interact with sulfur compounds?

Within recent years, ILs has gained increasing interest for application to different kinds of processes, amongst those is as separation media for LLE processes. Basically the optimization in LLE process or technique is mostly influenced by the interaction mechanism between the solute and solvent. Therefore, for desulphurization process it is vital to identify the interaction mechanism between sulfur compounds (solute) and ILs (solvent) since the interaction mechanism will determine the extraction efficiency and recycling capability of the ILs. Since the number of conceivable combinations between cations and anions are almost unlimited, and sole experimental screening is impossible, the use of simulation tools becomes important. Since ILs are a relatively new class of compounds, the use of common activity coefficient model for

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example group contribution method like UNIFAC is complicated, because it requires the input of interaction parameters, which for ILs have not been fully determined thus far. In order to describe the interaction mechanism and behavior of ILs, the dielectric continuum model COSMO-RS has been introduced, and it is gaining more interest for ILs prediction for various applications [1, 2].

#### 1.1. Interaction mechanism in COSMO-RS

COSMO-RS is independent of specific interaction parameters; therefore it is a promising approach for ILs. The name of COSMO-RS is derived from "**Co**nductor-like-**S**creening-**Mo**del" (COSMO) and its extension RS stands for "real solvents". This approach belongs to the class of quantum chemistry of continuum solvation models (CSMs). CSMs are an extension of the basic quantum chemistry where a molecule in solution is described through a quantum chemical calculation of the solute molecule with an approximate representation of the surrounding solvent as a continuum. The solute is treated as if embedded in a dielectric medium via a molecular surface or cavity that is constructed around the molecule [3].

COSMO-RS uses only structural information of the molecules for the priori prediction of activity coefficients and other thermophysical data; thus the program is independent of specific interaction parameters. In COSMO-RS, a number of quantum chemical calculations are combined with statistical thermodynamics in order to enable the prediction of thermodynamic properties without any experimental data [4].

COSMO-RS is a combination of electrostatic theory of locally interacting molecular surface descriptors, which are computed by quantum chemical method (QM) with exact statistical thermodynamics methodology. In other words, it integrates concepts from quantum chemistry, dielectric continuum models, electrostatic forces interactions and statistical thermodynamics. It is based upon information evaluated by QM-COSMO calculations, which describe discrete surface around a molecule embedded in a virtual conductor. It treats a liquid as an ensemble of closely packed ideally screened molecules, where the molecular surface is in close contact with one another. Assuming that each molecule is still enclosed by virtual conductor, the interaction energies of the surface pairs are defined in terms of screening charge densities (SCDs), where  $\sigma$  and  $\sigma'$  of the respective surface segments. The SCDs measure electrostatic screening of the solute molecule by its surrounding and the back-polarization of the solute molecule [2–5].

Meanwhile, the statistical thermodynamic provides a link between the microscopic surface interaction energy and the macroscopic thermodynamic properties of a liquid. Since in COSMO-RS all molecular interactions are viewed as consisting of local pair-wise interactions of surface segments, the statistical averaging can be done in the ensemble of interacting surface pieces. In order to describe the composition of the surface segment ensemble which depends on  $\sigma$ , it is sufficient to consider histograms of the SCDs, the so-called  $\sigma$ -profiles. Such probability distribution gives the relative amount of surface with polarity  $\sigma$  for a molecule [5].

The COSMO-RS prediction that starts with QM-COSMO calculation is performed on the density functional theory (DFT) level, utilizing the BP functional with RI (resolution of identity) approximation and a triple-ζ valence polarized (TZVP) basis set. These QM-COSMO

calculations are done in a Turbomole program package. The geometries of all molecules involved in these calculations are first fully optimized and the calculations are only performed once for each compound. The result of the COSMO calculation which is the charge distribution on the molecular surface is stored in the so-called COSMO-files, which are collected in the database. COSMO-RS calculations are then performed using COSMOtherm program, which provides an efficient and flexible implementation of the COSMO-RS method. Thus in combination with a large database of solvents including ILs, COSMO-RS allows fast and efficient large scale solvent screening [4–6].

In COSMO-RS, the bulk of a liquid phase is considered to be built of closely packed molecular cavities, and each molecule is divided into discrete segments, where each segment is assigned with a screening charge density,  $\sigma_i$ . Then, the interactions between the molecules are reduced to the interactions of the molecular segments, or rather the interactions of the screening charge densities. In order to describe the entire molecule and molecular properties the screening charge density distribution of a molecule, the so called  $\sigma$ -profile as shown in **Figure 1** is used [6].

Initially, the assumption has been made that a liquid consists of close packed molecules, as a logical consequence, the properties of this liquid can also be described by means of the  $\sigma$ -profiles. Next, based on the  $\sigma$ -profiles, the  $\sigma$ -potential,  $\mu$  ( $\sigma$ ) of a molecule is calculated. The  $\sigma$ -potential is the central equation in COSMO-RS where all other equations for the calculation of thermodynamic data are based on. Additionally, electrostatic interactions ( $E_{misfit}$ ) and hydrogen bond interactions ( $E_{HB}$ ) between the molecular surfaces pieces are described in dependence of  $\sigma$ . Therewith, the screening charge distribution profile holds all the information which is necessary for COSMO-RS [5–7].



**Figure 1.** Screening charge distribution and  $\sigma$ -profile of BT.

Activity coefficient at infinite dilution,  $\ln (\gamma_i^{inf})$  is an important parameter in order to study the deviation from ideal behavior in a mixture of ILs + sulfur compound in hydrocarbon. Basically, it provides information regarding non-ideality of the chosen species in a mixture. The value describes the extreme case in which only solute-solvent interaction contributes to non-ideality that has practical implications in chemical and industrial processes. In the case of desulphurization, it provides information about interaction between solvent, where in this case is ILs (solvent) and solute i.e. sulfur compounds. This is a useful tool for solvent selection for extractive desulphurization process. The separation factor of species to be separated at infinite dilution is sufficient for determining the suitability of an IL as solvent for selective extraction. Experimentally, the activity coefficient at infinite dilution of some ILs in hydrocarbons, polar and non-polar solvents is measured using either gas–liquid chromatography or the dilutor technique [5–8].

Several thermodynamic models are available such as NRTL and UNIFAC for predicting activity coefficient at infinite dilution, but the accuracy of the measurement needs to be improved in order to enhance the prediction. Besides that, new experimental data are required to generate quantitative interaction parameter, which hinders the use of these models [8]. On the other hand, COSMO-RS is a novel and efficient model for priori prediction of activity coefficient at infinite dilution for a mixture of ILs from thermodynamic aspects as it relies on optimized molecular structure as the only information; no experimental data is needed [9].

The predicted activity coefficient values obtained through COSMO-RS using different or modified parameterization have been done by Banerjee group to predict potential ILs for separation of sulfur compounds (thiophene, BT and DBT), by means of selectivity, capacity and performance index at infinite dilution. In the first study, they selectively screened out 264 suitable ILs (from 24 anions and 11 cations) and found that smaller sized cations have higher selectivity, but lower capacity and vice versa [10]. They identified that for fluorinated anions, the removal of sulfur compound (thiophene) increases with the increase of the van der Waals volume. While a smaller cation with a sterically shielded large anion gave high extraction efficiency. In a second study they screened out 168 suitable ILs based on the permutations of 28 anions and 6 cations, and found that the cation without aromatic ring combined with anions having sterical shielding effect such as thiocyanate, acetate and chloride proved to be the most favorable ILs [11]. However, their predictions were not consistent with the literatures. This shows that COSMO-RS has a limitation to some extent. For example, COSMO-RS may not be able to represent the  $\pi$ - $\pi$  interaction effect which has resulted in inconsistent result between prediction and experiment. Therefore, there is a need to introduce new predictive approach for selecting appropriate ILs for desulphurization via interaction mechanism.

#### 1.2. Interaction mechanism in extractive desulphurization

ILs consist of complex ions with multiple types of interaction, where each solute molecule will possess somewhat different solute-solvent interactions due to the various acidic, basic, electron donating and electron withdrawing properties. There are several possible contributing mechanism theories in extractive desulphurization as listed in **Figure 2**.

- Aromatic ring current effect (i.e.,  $\pi$ - $\pi$  interaction and CH- $\pi$  interaction) occurs between aromatic-type-cation of ILs and aromatic sulfur compound.
- Electrostatic field effect (i.e., Columbic interaction) occurs when bonding between the anion and cation of ILs becomes weaker because of their structures (most probably due to the length of substituted alkyl side-chain on the cation), which makes it more easier for insertion or interaction of aromatic sulfur compound in/with ILs.
- Hydrogen bonding effect occurs due to the H-bond donation of cation part of ILs to the sulfur atom of aromatic sulfur.
- Anion effect.
- Dilution effect.

The CH- $\pi$  interaction between the imidazolium cation and aromatic ring of sulfur compound becomes one of the major mechanisms during sulfur extraction as indicated by chemical quantum simulation [10, 11] and NMR observations [12]. By using quantum chemical calculation approach (namely ab initio calculations correlated with experimental results), it was suggested that the positively charged atoms of the imidazolium cation can be the most approachable to the negatively charged atoms of the sulfur compounds, producing a maximal Columbic interaction [13, 14]. On the other hand, the formation of hydrogen bonding between acidic hydrogen of the imidazolium cation and the sulfur compound is weak due to poor Hbond acceptor by the sulfur compound, but becomes stronger with increasing alkyl side-chain length. The anion and dilution effects (the dilution of ILs by sulfur compound insertion) are not the dominant factors in determining the absorption capacity and selectivity of sulfur compounds in model oil/imidazolium based-ILs systems [12, 15, 16].

Meanwhile, the specific  $\pi$ - $\pi$  interaction due to aromatic current effects was first predicted between imidazolium cation and sulfur compound (thiophene) using NMR analysis approach [12]. The aromatic current effect is largely affected by the size of the cation itself and the length of alkyl side-chain substituted on the cation. Since then, it was predicted by many researchers that the stronger selective extraction of aromatic sulfur compounds resulted from the  $\pi$ - $\pi$ interaction between the imidazolium-based ILs and aromatic sulfur ring [17–21].

There was also a suggestion that  $\pi$ - $\pi$  interaction between the unsaturated bonds of sulfur and the imidazole ring leads to the formation of liquid clathrate. Liquid clathrate is a semi-ordered liquid formed by associative interactions between ILs and aromatic sulfur compounds which



Figure 2. Possible contributing theories of interaction mechanism in extractive desulphurization by ILs.

separate the cation-anion packing interactions to a sufficient degree resulting in the formation of localized cage-structures; in this case ILs are trapping the aromatic sulfur compounds. With too little interaction, the ILs are simply completely miscible or immiscible with the aromatic sulfur compound, whereas, if the cation-anion interaction of ILs are too great, then crystallization of the ILs occurs [22–25]. Since the aromatic sulfur compounds e.g. DBT, BT, 3-methylthiophene are conjugated structure, the lone pairs on the sulfur atom or the  $\pi$ -electrons on the aromatic sulfur compound ring preferentially insert into the molecular structure of the ILs. The steric effect between the interacting compounds also influences the interaction mechanism involved [26, 27].

## 2. Selection of ILs for extractive desulphurization

Preliminary selection and screening of suitable ILs by relying on physical, chemical and thermodynamic properties have been intensively investigated and reported in literatures. However, the reported predictive tools for selecting potential ILs are still not satisfactory, as these tools still lack the capability to identify the correct combination of cations and anions matchup for a particular application; this needs further investigations.

#### 2.1. Predictive approach

Due to the enormous number of possible combinations of cations and anions to produce ILs, an accurate prediction for a particular application is necessary. Predictive approach will reduce cost and time as opposed to trial and error using experimental work. One of the predictive approaches is COSMO-RS which is based on quantum chemistry approach. Recently this approach is being applied especially in predicting physical, chemical and thermodynamic properties plus interaction mechanism of potential ILs [25-28]. A recent study which employed COSMO-RS was carried out by Banerjee group, in which different or modified parameterization were used to predict potential ILs for diesel desulphurization, by means of selectivity and capacity at infinite dilution. They selectively screened out 168 suitable ILs (from 28 anions and 6 cations) mostly for extracting thiophene, BT and DBT from simulated diesel composition [11– 29]. The attempted investigation via COSMO-RS showed that 4-ethyl-4-methylmorpholinium gave the best performance for desulphurization in combination with anions such as thiocyanate (CNS), acetate (CH<sub>3</sub>COO), bis(trifluoromethylsulfonyl)imide (NTf<sub>2</sub>) and triflate (CF<sub>3</sub>SO<sub>3</sub>). However, their predictions did not match well with the experimental results from the literatures; for instance Holbrey et al. who reported that (CF<sub>3</sub>SO<sub>3</sub>) and (NTf<sub>2</sub>) anions showed poor results in removing DBT from *n*-dodecane phase, while Wang et al. indicated that (CH<sub>3</sub>COO) anion gave average performance in removing thiophene from *n*-heptane phase.

#### 2.2. Experimental approach

The screening of appropriate combination of cation/anion for ILs was first attempted by Bosmann and co-worker. They justified that from three types of cations ([emim], [bmim] and

ILs	Experimental description	
[3-mebupy][N(CN) <sub>2</sub> ]	DBT (%)	GC-analysis
$[bmim][C(CN)_3]$	86	Extraction condition
[4-mebupy][N(CN) <sub>2</sub> ]	86	Speed: 1200 rpm
[4-mebupy][SCN]	85	Time: 15 min
[bmim][N(CN) <sub>2</sub> ]	84	Vol. Ratio: 1/1
[bmim][SCN]	77	
[emim][N(CN) <sub>2</sub> ]	70	
[omim][BF <sub>4</sub> ]	57	
[opv][BF <sub>4</sub> ]	70	
[beim][DBP]	66	
[bmim][DBP]	63	
[eeim][DEP]	62	
$hpv1[BF_4]$	62	
[omim][DMP]	59	
[emim][DEP]	57	
[obim][DBP]	57	
[beim][DEP]	55	
[oeim][DEP]	54	
[emim][DMP]	54	
[hmim][DMP]	54	
[hbim][DBP]	51	
[bbim][DBP]	50	
[heim][DEP]	47	
[bmim][DMP]	47	
$[bpv][BF_4]$	41	
[mmim][DMP]	44	
[emim][DBP]	33	
[bmim][BF <sub>4</sub> ]	32	
Hansmeier et al., Green chemistry	16	
[C <sub>4</sub> mim][BF <sub>4</sub> ]	DBT (%)	GC-MS and HPLC
$[C_4 mim][OcSO_4]$	47	Extraction condition;
$[C_4 mim][CF_3SO_3]$	63	Time: 60 min
$[C_4 mim][PF_6]$	50	Settling: 15 min
$[C_4 mim][NTf_2]$	53	Temp.: 40°C
[C <sub>4</sub> mim][SCN]	50	(equal volume ratio)
[C <sub>4</sub> mim][CH <sub>3</sub> CO <sub>2</sub> ]	66	
$[C_4py][NTf_2]$	61	
$[C_4py][BF_4]$	55	
$[C_4^4 mpy][NTf_2]$	43	
$[C_4^4 mpy][BF_4]$	76	
$[C_4^4 mpy][SCN]$	70	
$[C_4^4 mpy][CF_3SO_3]$	79	
$[C_4^3 mpy][NTf_2]$	72	
$[C_4^{3}mpy][BF_4]$	77	
[C4 <sup>3</sup> mpy][SCN]	70	
$[C_4^{3}mpy][CF_3SO_3]$	83	
$[C_4^{2,4} dmpy][NTf_2]$	69	
$[C_4^{2,3}dmpy][NTf_2]$	83	
[C <sub>4</sub> mpyrr][NTf <sub>2</sub> ]	81	
Holbrey et al., Green Chemistry	47	
	<i>n</i> -dodecane	

 Table 1. Results of DBT removal using some ILs in extractive desulphurization.

[omim]) with [BF<sub>4</sub>] as anion and seven types of anions ([PF<sub>6</sub>], [CF<sub>3</sub>SO<sub>3</sub>], [BF<sub>4</sub>], [Cl], [MeSO<sub>4</sub>], [MeSO<sub>3</sub>] and [OSO<sub>4</sub>]) with [bmim] as cation, [omim] and [OSO<sub>4</sub>] depicted better extractability for DBT removal. It was later proved that the combination of these cation-anion, [omim][OSO<sub>4</sub>] has high viscosity at ambient conditions. Further work was carried out which indicated that [bmim][OSO<sub>4</sub>] has the best extractability of some sulfur compounds (Eβer et al.; Nie et al.). Later, Holbrey and co-worker screened out 20 ILs for extracting DBT and revealed that 1-butyldimethylpyridinium bis(trifluoromethylsulfonyl)imide ([bdmpy][NTf<sub>2</sub>]) yielded the highest DBT removal (83%) from *n*-dodecane. Recently, [bmim] tricyanomethane ([C(CN)<sub>3</sub>] has been found to yield higher DBT removal (86%) as compared to previous works [28, 29]. The result of both research studies are summarized in **Table 1**.

## 3. Extractive desulphurization

When a separation by distillation is ineffective or very difficult, liquid–liquid extraction (LLE) is one of the main alternatives to be considered. Close boiling point mixtures or substances that are unstable at the temperature of distillation, even under a vacuum condition, may often be separated by extraction which utilizes the chemical differences instead of vapor pressure differences. One of the major uses of extraction is to separate petroleum products that have different chemical structures, but have about the same boiling range. In liquid–liquid extraction, two phases must be brought into good contact to permit transfer of solute and then be separated [29, 30].

Extraction is a process in which a liquid mixture (of normally two species that contain the solute and the feed carrier) is contacted in a mixer with a third liquid (normally the solvent) that is immiscible or nearly immiscible with the feed carrier component. When the liquids are contacted, the solute is transferred from the feed carrier into the solvent. It is because during mixing process, bonds between solute and feed carrier are broken and possible new bonds are formed between solute and solvent. The energy, which may or may not be required in breaking the bonds between the solute and feed carrier or in forming the bonds between the solute and solvent, depends on the type of interaction.

The combined mixture is then allowed to settle into two phases that are then separated by gravity in a decanter. When a solute transfers from one phase to another, the transfer rate generally decreases with time until the second phase is saturated with the transferred solute, holding as much as it can hold at the prevailing process condition. When the concentrations of the solute in each phase no longer changes with time, the phases are said to be at equilibrium. The effectiveness of any of the separation processes described depends on both how the solute is distributed between the phases at equilibrium and on the rate at which the system approaches equilibrium from its initial state. The extract is the layer of solvent plus extracted solute and the raffinate is the layer from which the solute has been removed from the feed carrier substance [31, 32].

Recently, ILs has been applied in the petrochemical industry especially in catalytic processes, extractive distillation and LLE process for example upgrading heavy oils for desulphurization.

Their negligible vapor pressure allows the extracted product to be separated from the ILs through low pressure distillation with potential energy savings. In addition, as a result of their negligible vapor pressure, they are able to be regenerated for reuse.

The use of ILs for selective extraction of sulfur compounds from diesel is first described by Bosmann et al. in 2001 [33]. Based on the initial idea to extract the sulfur compound by chemical interaction, the extraction of DBT with Lewis and Brønsted acidic ILs was majorly investigated. They indicated that such Lewis-acid based interactions enhance the extraction power of ILs that permit complex formation of sulfur compound and ILs. They also identified that extraction of actual diesel is much more complicated due to the complex chemical composition of diesel which includes many different sulfur compounds and other impurities like organic nitrogen and oxygen compounds [34].

#### 3.1. Extractive desulphurization on model oil

As mentioned previously, due to the limited efficiency of HDS towards aromatic sulfur compounds, a number of research have been focused on extracting them, mainly thiophene, BT, DBT and their derivatives. By using various types of ILs through various anion/cation combinations, some researchers have found that extraction process alone could remove up to 86% sulfur in model oil and 30% in actual diesel, which due to the steric hindrance of various sulfur compounds [25]. There are various types of model oil that have been investigated including aliphatics (*n*-hexane, *n*-heptane, *n*-octane, *n*-dodecane) and aromatics (toluene). In evaluating desulphurization performance, besides removal percentage, sulfur partition coefficient ( $K_N$ ) gives a better insight in terms of explaining the relationship between ILs amount and its structure against desulphurization performance [25, 27].  $K_N$  is defined as the ratio of sulfur concentration on weight basis in ILs to sulfur concentration in hydrocarbons, which the higher  $K_N$  the better the desulphurization performance of that ILs [33, 34].

Taib and Murugesan [35] in their report said that at ambient condition operation, sulfur compounds with  $C_5$  aromatic ring were observed to favorably absorb over  $C_6$  aromatics sulfur, while sulfur with non-aromatic structures were poorly absorbed by imidazolium-based ILs. Eßer and co-worker reported in their article that, even though the concept of extraction in desulphurization seemed feasible, but selective extraction of nitrogen-containing compounds and aromatic hydrocarbons still needs further investigation. Although quite a few researchers preferred pyridiniumbased [36] and ammonium based ILs [37] for extractive desulphurization, it seems that the extraction ability is less promising. Some have been noticed to be comparable to imidazoliumbased ILs if the anions matchup is just appropriate [38].

#### 3.2. Extractive desulphurization on model fuel

Extractive desulphurization has been performed on model fuel containing up to 25% aromatics. Basically naphthalene, methylnaphthalene, indole, pyridine and tetralin are the most common aromatics used for preparing model fuel. The extraction efficiency is relatively high, and competing removal of aromatics and sulfur compounds was not detected based on model fuel containing *n*-dodecane/indole/DBT using [BMIm][OSO<sup>–</sup>] as extractant. Further investigations showed that ILs gave higher removal of molecules that have higher density of aromatic  $\pi$ -electrons. Cross-miscibility of the studied aromatics in the ILs produced an unwanted effect, whereby high cross-miscibility will demonstrate a loss of fuel or at least contribute to an increase of process costs [39]. However, the effect of aromatic hydrocarbons such as benzene and xylene needs further research in order to understand the selective extraction process.

#### 3.3. Extractive desulphurization on actual diesel

An approach based on extraction for removing sulfur compounds from actual diesel using ILs have been investigated by many researchers [39]. Compared to model oil or model fuel, the extraction from actual diesel is much more complicated due to its complex chemical composition including many different sulfur compounds and other impurities such as nitrogen and oxygen-containing compounds. For example, the removal of sulfur from model oil is 64% but in actual diesel this percentage is drastically reduced to 24.3% when the same ILs is applied. The obvious or most sterically hindered sulfur species would still remain in the actual diesel even though after several extraction steps. However, it has been proven that extractive desulphurization of actual diesel with ILs is still possible, although the operating expenses such as the number of theoretical extraction steps may vary in order to reach ultra-low concentration of sulfur [40].

## 4. Regeneration of spent ILs

Besides being efficient for extraction process, regeneration or recycibility of spent ILs is equally important since ILs has been recognized as environmentally benign solvent. Since ILs is quite expensive as compared to some conventional organic solvents, finding an alternative way to recycle spent ILs is the key for cost effectiveness in order to ensure the feasibility of using ILs at a larger scale application.

Undoubtedly, regeneration has become a fundamental issue from economic point of view. However, this is not only limited to the operating cost, but also concerning environmental issues such as disposal, biodegradable and toxicity. In general, ILs has a higher density compared to organic solvents or water; therefore, many ILs form separate phases when mixed with organic or aqueous solution. This behavior makes ILs as feasible for regeneration, which in turn presents potential economic viability of desulphurization process using ILs. In addition, the process is considered as being environmental benign since no waste is generated [33–40].

In conclusion, extractive desulphurization process using selective ILs as the extractant is still in need of further research, starting from screening of suitable ILs for desulphurization, synthesis of ILs, physical property analysis of ILs, single batch extraction study encompassing process optimization up to actual diesel application, and including regeneration of spent ILs.

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