Title: SelinfDB: a Database of Selectivity at Infinite Dilution for Liquid-Liquid Extraction

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Abstract: One of the most acute health and environmental concerns nowadays is 3R (Reduction, Reuse, Recycle) of organic solvents. Existing technology of solvent separation can be either expensive or inefficient, particularly in case of the azeotrope separation. Ionic liquids (ILs) have already shown potential in liquid-liquid extraction of organic solvents due to their high structural variability. However, it is not always known which IL is going to be efficient in a particular separation task and experimental screening for Selective ILs can be expensive and time-consuming. The preferable alternative is to use Selectivity at infinite dilution (S_∞). In this study, the database for S_∞ was developed by computationally processing activity coefficients at infinite dilution (IDACs) from free available sources. S_∞ was compared to experimental values of Selectivity, where possible, and results show that there is an ≈80% chance that a "selective" IL, according to S_∞, will be selective in liquid-liquid extraction. The results were analysed with respect to the chemical classes of azeotrope components, showing quite a difference in S_∞ to Selectivity translation. An example of structure-property analysis was given, to illustrate the usefulness of the database for understanding the effects of structure on S_∞ and design of new ILs for breaking particular two-component systems. The SQL database is freely available online and can be used for the intelligent search for better liquid-liquid extractants.

1 Introduction

The world at the beginning of the 21st century is facing an increasing need to address environmental concerns. The widely accepted 3Rs strategy (Reduce, Reuse and Recycle) is aimed at reduction of the environmental footprint of industrial processes. Additionally, the depletion of natural oil and gas is a challenge for the synthesis of large quantities of organic compounds in the future. When it is not possible to Reduce the use of organic solvents, Recycling and Reusing in industry and research is essential for sustainability, as well as, for decreasing the pollution levels.[1, 2] The substances of interest must be separated from each other in order to recycle the waste and achieve maximum possible purity. The standard separation technique is distillation, which is inefficient on azeotropes. There are other techniques that are suitable for separation of those mixtures, *e.g.,* extractive distillation, azeotropic distillation, pressure swing

distillation, or liquid extraction.[3] While being relatively efficient, these approaches require the addition of a third component, usually a volatile organic compound. Such approach shows several disadvantages both from the economic and environmental point of view, *i.e.*, toxicity, flammability or complex solvent recovery processes. Nowadays, a viable alternative to volatile organic solvents is Ionic liquids (ILs).[4] ILs are composed solely by ions and have melting temperatures below 100ºC.[5] Generally, ILs present low flammability hazard,[6] have negligible vapour pressure at standard working conditions,[7] excellent solvent properties[8] and moderate viscosities.[9] Most importantly, ILs have high structural variability which, in principle, makes it possible to design an IL capable of separating most azeotropic mixtures. One of the least expensive methods for azeotrope separation is liquid-liquid extraction and ILs have been widely used for it [10-13]. The method relies on the immiscibility between two liquid phases and it is used to separate a dissolved component (solute) from its diluent (raffinate phase) by its transfer into a second component (extraction phase) liquid phase. The equilibrium in extraction can be characterized by the values of distribution coefficient, β, and selectivity, S. These parameters are widely used in assessing the solvent feasibility in the liquid–liquid extraction and are defined as follows:

$$\beta = \frac{x_{solute}^{extraction\ phase}}{x_{solute}^{raffinate\ phase}} \quad (1)$$

$$S = \left(\frac{x_{raffinate}^{raffinate\ phase}}{x_{raffinate}^{extraction\ phase}}\right) \times \left(\frac{x_{extract}^{extraction\ phase}}{x_{extract}^{raffinate\ phase}}\right) \quad (2)$$

, where x is the mole fraction of a particular component in a particular phase. Selectivity also indicates the ease of extraction of a solute from the raffinate phase and higher selectivity corresponds, theoretically, to fewer stages required for a given separation and less raffinate in the extract.[14] Mole fractions are determined from liquid-liquid equilibria experiments at a particular temperature and pressure. The experiment requires varying ratios of extracting agent and mixture components, which makes selectivity determination rather challenging.

One of the thermodynamic parameters that reflects the ability of a chemical to be dissolved is the chemical potential, i. e. the energy that can be absorbed or released due to a change of the particle number of the given species, e.g. in a chemical reaction or phase transition (eq. 3).

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \quad (3)$$

, where μ is the chemical potential, U is the internal energy, N is the number of particles, S is the entropy, V is the volume[15].

High chemical potentials are associated with unfavourable processes, since most systems tend to minimize their internal energy. In case of dissolution, the chemical potential of the solute (1) in the ideal solution is characterized by equation 4

$$\mu_1^{ideal} = \mu_1^o + RTln\ x_1 \quad (4)$$

where, μ_B^o is the chemical potential of pure liquid 1 and $x_1$is the mole fraction of liquid 1 in the solution.

Under this representation of the dissolution process, the chemical potential of the solute in the solution can never be higher than the one of the pure substance. This fact contradicts many experimental findings. Thus, the formula describing chemical potential of the real solution, requires the use of the activity coefficient (γ_1) (eq. 5).

$$\mu_1 = \mu_1^o + RTln\ x_1\gamma_1 = \mu_1^o + RTln\ x_1 + RTln\ \gamma_1 \quad (5)$$

As the mole fraction of the solute increases, so will the chemical potential of the solution, until the further dissolution becomes unfavourable. This representation might be the best to describe the process, however its use is limited, since γ_1 may be dependent on x_1 as well. Thus, many researchers resorted to the simplified representation under the infinite dilution concept: a state of solution, in which adding more solvent does not result in the change in concentration. In that case, the $RTln\ x_1$ term of the eq. 5 is negligible and the activity coefficient becomes independent of the solute concentration, what is known as the infinite dilution activity coefficient (IDAC).

$$ln\ \gamma_\infty = \frac{\mu_1 - \mu_1^o}{RT} \quad (6)$$

Thus, IDAC (γ_∞) can be used as an indicator of a system's energy gain/loss as a result of dissolution. Different substances can be compared in terms of how favourable their dissolution in the same solvent is.

This is an alternative selectivity assessment, namely the selectivity at infinite dilution (S_∞) approach, which represents the selectivity when concentration of the extracting agent is much higher than the ones of solute and raffinate. The value of S_∞ is calculated according to equation 7:

$$S_\infty^{12} = \frac{\gamma_\infty^2}{\gamma_\infty^1} \quad (7)$$

, where γ_∞ are the IDACs of a solute (1) and a raffinate (2) in the extracting agent. IDACs are determined from gas chromatography retention data using the expression proposed by Cruickshank et al.[23] and Everett[24]:

$$ln\gamma_{1,z}^\infty = ln\left(\frac{n_z\ RT}{V_n P_1^0}\right) - P_1^0 \times \frac{B_{11} - V_1^0}{RT} + \frac{2B_{13} - V_1^\infty}{RT} \times J \times P_0 \quad (8)$$

, where $\boldsymbol{n_z}$is the mole number of the solvent stationary phase component inside the column, $\boldsymbol{R}$ is the ideal gas constant, $\boldsymbol{T}$ denotes the temperature of the oven, $\boldsymbol{V_n}$ is the net retention volume, $\boldsymbol{B_{11}}$ refers to the second virial coefficient of the solute in the gaseous state at temperature $\boldsymbol{T}$, the molar volume of the solute is denoted by $\boldsymbol{V_1^0}$, $\boldsymbol{B_{13}}$ represents the mutual virial coefficient between the solute 1 and the carrier gas helium (index 3), $\boldsymbol{V_1^\infty}$ represents the partial molar volume of the solute at infinite dilution

in the solvent (extracting agent) and $\boldsymbol{P_1^0}$ is the probe vapor pressure at temperature $\boldsymbol{T}$. The factor $\boldsymbol{J}$ amends for the influence of the pressure drop alongside the column. The formula is applied to calculate IDAC for both solute and raffinate. Gas chromatography allows to measure IDACs of many organic substances for the same solvent, generating much more potential selectivity data, than experimental selectivity determination.

Selectivity at infinite dilution has been originally used in extractive distillation as a derivative from the Scatchard-Hildebrand theory of regular solutions[16]. The theory already establishes some limitations for the use of activity coefficients for selectivity assessment, such as

- the interaction between molecules in solution are regulated strictly by Van der Waals' forces

-the entropy change on forming the solution has the same value as for an ideal solution.

Thus, the use of S_∞ for systems that can form H-bonds might result in assessment errors. Despite limitations, S_∞ has been widely used for suggestion of extractants for extractive distillation [17-19]. Although this is the intended use of S_∞ [16], the fundamental aspect of IDAC as an estimator of solute's chemical potential, presented in the equation 6, does not seem to be restricted to the extractive distillation process in particular and may be used to assess selectivity in liquid-liquid extraction in general. This assumption is even more plausible considering that UNIQUAC[20], a well-known model used in the description of phase equilibria from activity coefficients, is commonly used to predict the phase behavior of multicomponent chemical mixtures both at vapor-liquid and liquid-liquid equilibria[21, 22].

Thus, it is important to investigate how well the selectivity at infinite dilution translates into selectivity determined by actual liquid-liquid extraction selectivity ($\boldsymbol{S}$). Comparison of $\boldsymbol{S_\infty}$ and $\boldsymbol{S}$,[25] as well as, using $\boldsymbol{S_\infty}$ to select the most efficient solvent for the separation [26] was previously done, however the comparison was done only for two-component systems of aromatic hydrocarbons + aliphatic hydrocarbons and $\boldsymbol{S_\infty}$ was calculated from IDAC values predicted by COSMO-RS[27], rather than experimental IDACs. The comparison has shown some concordance and a potential for the use of $\boldsymbol{S_\infty}$ to suggest efficient extracting agents. In this work we verified if this can be extrapolated to systems composed of chemicals that belong to other classes. Another issue with using $\boldsymbol{S_\infty}$, is the lack of a standardized, easily accessible database that provides the researcher an opportunity to compare $\boldsymbol{S_\infty}$ of known solvents and make a guided decision about the optimal choice of the extracting agent with respect to a particular system. Without that, the only option is to browse through multiple articles that presented IDACs in different solvents and compare IDACs manually. An attempt to make the data search easier was done by Paduszyński[28] and Dortmund Data Bank (DDBST GmbH)[29], who collected IDAC datasets for IL and non-IL solvents, respectively. However, upon manually finding the right IDACs from the datasets, one would still need to calculate all $\boldsymbol{S_\infty}$ manually.

The goals of this study are to create a free online database of selectivity at infinite dilution for both IL and non-IL solvents and to compare S_∞ vs S for as many systems as possible.

2 Materials and Methods

2. 1 Using IDACs to calculate S_∞

The source of IDACs for ILs is the Electronic supplementary information (ESI) of the Paduszyński article[28], particularly Table S4 from the excel file. IDACs for non-IL solvents have been extracted from the Dortmund Data Bank (Dortmund DB)[29]: Data has been manually collected from Dortmund DB webpages dedicated to particular systems into separate files. Then, the data from all Dortmund DB files were merged and processed in R version 3.4.4.[30] Data processing required standardizing names of chemicals and data columns. Both ILs and non-ILs data had duplicates, *i. e.* several data entries with the same combination of solute, solvent and temperature value (temperature rounded to 1 K). The deduplication of data was done as follows: if the difference between minimum and maximum values among duplicates for the combination is higher than 20%, then all duplicates for this combination are discarded, otherwise the arithmetic mean of the IDAC values for the combination is calculated and used further. In the next step, if IDAC for "compound 1" in solvent (IL or non-IL) and IDAC for "compound 2" exist for the same solvent at the same temperature, then S_∞^{12} and S_∞^{21} of the solvent at this temperature for extracting "compound 1 from compound 2" and "compound 2 from compound 1" were calculated according to eq. 7. Then, S_∞^{12} data for ILs and non-ILs were merged. Since the order of magnitude is more important, than the actual value in distinguishing between selectivities, it was decided to use the decimal logarithm ($\log_{10}[S_\infty]$) to describe selectivity data further. This revealed one concerning detail about using $\log_{10}[S_\infty]$ as an indicator of good extraction capacity – it is possible to get a high ($\log_{10}[S_\infty]$. ≥ 1) selectivity value by dividing very big IDAC by a smaller, yet big IDAC. An illustrative example is the case of the IDAC of methanol dissolved in hexadecane[31], at 293 K (83.76), whereas IDAC of water dissolved in hexadecane[32] is 1153.9. The $\log_{10}[S_\infty^{\mathbf{methanol/water}}]$ of hexadecane at 293 K is 1.14, indicating that it should be a good extracting agent. However, the dipole moments for water and methanol are 1.85 and 1.70, respectively[33], whereas hexadecane must have a dipole moment ≈0 due to its symmetry and similar electronegativity of hydrogen and carbon atoms. This makes extraction of methanol from water by hexadecane highly unlikely. Thus, a big IDAC warning was added to $\log_{10}[S_\infty]$ data if the IDAC of solute was higher or equal to 10. The final dataset was exported from the R environment to a csv file, which was uploaded onto a MySQL database (MySQL database server v. 5.7.31).

The csv file was submitted in 4 batches, due to data size restrictions, via phpMyAdmin on cPanel[34]. The database consists of 9 fields, including an auto-incremented primary key (Table S1 of Supporting information).

A website has been created to host the database using WordPress 5.4.2. It consists of 4 public pages and 1 posting page. Public pages are:
- **Homepage.** Gives basic description of the database, links to other pages
- **Browse SelinfDB.** The page for querying the database.
- **DB.** A page that displays query results (inactive unless browsing is completed).
- **IL codes translation.** Dictionary that translates IL codes needed for querying into ILs IUPAC names.

The posting page is used to inform the users about the database updates. PHP language (v. 7.3.6) scripts were used for communication between SQL and HTML.

2.2 Checking how well S_∞ translates into S

The importance of $\log_{10}[S_\infty]$ is defined by its ability to translate into experimental selectivity ($\log_{10}[S]$). The selectivity at infinite dilution for azeotropes in ref. [14] was compared to all available experimental data (Table 1).

Table 1 Sources of S vs S_∞ comparison. [a]This code is identical to the one in[28]. T_∞ is the temperature for $\log_{10}[S_\infty]$ values, $T_{exp.}$ is the temperature for $\log_{10}[S]$.

Azeotrope	IL code (SelinfDB)[a]	IL code (article)	T_∞	T_{exp}	Ref.
benzene+cyclohexane	IM-2,1_SCN	[C2mim][SCN]	298	298	[26]
benzene+cyclohexane	IM-2,1_DCA	[C2mim][N(CN)2]	323	298	[26]
benzene+cyclohexane	IM-2,1_AC	[C2mim][Ac]	313	298	[26]
benzene+cyclohexane	IM-2,1_NTF2	[C2mim][Tf2N]	313	298	[26]
ethanol+ethyl acetate	IM-2,1_BF4	[emim]BF4	323	298	[35]
ethanol+ethyl acetate	IM-2OH,1_BF4	[C2OHmim]BF4	303	298	[35]
2-propanol+water	IM-4,1_NTF2	[bmim][Tf2N]	323	323	[36]
1-propanol+water	IM-4,1_NTF2	[bmim][Tf2N]	323	323	[37]
ethanol+water	IM-4,1_NTF2	[bmim][Tf2N]	323	323	[38]
benzene+cyclohexane	IM-4,1_Cl	[BMIM]Cl	358	339	[39]
benzene+cyclohexane	IM-4,1_SO4-1	[BMim][MSO4]	313	298	[40]
benzene+cyclohexane	IM-2,1_BF4	[C2Mim][BF4]	313	298	[41]
1-butanol+water	IM-8,1_NTF2	[OMIM] [Tf2N]	333	298	[42]
1-butanol+water	PIP-4,1_NTF2	[bmPIP][NTf2]	318	298	[43]
1-butanol+water	PIP-2O1,1_NTF2	[COC2mPIP][NTf2]	318	298	[43]
1-butanol+water	PYR-2O1,1_NTF2	[COC2mPYR][NTf2]	318	298	[43]
benzene+cyclohexane	IM-2,1_PO2-O2,O2	[C2mim][DEP]	313	313	[44]
benzene+cyclohexane	IM-1,1_PO2-O1,O1	[C1mim][DMP]	303	298	[44]
butanone+ethanol	IM-4,1_PF6	[BMIM][PF6]	313	298	[45]
butanone+2-propanol	IM-4,1_PF6	[BMIM][PF6]	313	298	[45]
methanol+n-heptane	IM-8,1_CL	C12H23N2,Cl	313	298	[46]
ethanol+hexane	IM-2,1_SO4-2	[EMIM][EtSO4]	303	298	[47]
ethanol+hexane	IM-4,1_SO4-1	[BMIM][MeSO4]	313	298	[48]
ethanol+hexane	IM-8,1_PF6	OMIM PF6	313	298	[49]
ethanol+hexane	IM-6,1_BF4	[Hmim][BF4]	343	298	[50]

ethanol+hexane	IM-1,1_PO2-O1,O1	[MMIM][DMP]	343	303	51
ethanol+hexane	IM-6,1_NTF2	[HMim][NTf2]	302	298	52
ethanol+hexane	PYR-4,1_OTF	[BMpyr][TfO]	298	298	53
ethanol+hexane	IM-2,1_SCN	[Emim][SCN]	298	298	54
ethanol+hexane	PYR-3,1_NTF2	[PMpy][NTf2]	323	298	55
ethanol+heptane	IM-2,1_SO4-2	[EMIM][EtSO4]	303	298	47
ethanol+heptane	IM-8,1_PF6	OMIM PF6	313	298	49
ethanol+heptane	IM-4,1_SO4-1	[BMIM][MeSO4]	313	298	56
ethanol+heptane	IM-8,1_CL	C12H23N2,Cl	313	298	46
ethanol+heptane	PYR-3,1_NTF2	[PMpy][NTf2]	323	298	55
ethanol+heptane	PYR-4,1_OTF	[BMpyr][TfO]	298	298	55
ethanol+heptane	PYR-4,1_DCA	[BMpyr][N(CN)2]	318	298	55
ethanol+heptane	IM-1O6,1_NTF2	[C6H13OCH2MIM][NTf2]	308	313	57
ethanol+heptane	IM-2,1_TFA	[EMIM][TFA]	328	313	57
ethanol+heptane	N-8,2,2,2_NTF2	[N8,2,2,2][NTf2]	318	313	57
ethanol+heptane	IM-2,1_SCN	[C2MIM][SCN]	298	298	58
ethanol+heptane	IM-1,1_PO2-O1,O1	[MMIM][DMP]	343	298	59
ethanol+heptane	IM-6,1_BF4	[Hmim][BF4]	343	298	60
benzene+hexane	IM-2,1_SO4-2	[emim]C2H5SO4	313	313	61
benzene+hexane	IM-4,1_SO4-1	[bmim]CH3SO4	313	313	62
benzene+hexane	PY-2_NTF2	[C2py][NTf2]	313	313	63
benzene+hexane	N-2OH,1,1,1_NTF2	[N111(C2OH)][NTf2]	318	313	63
benzene+hexane	P-14,6,6,6_NTF2	[P6 6 6 14][NTf2]	298	298	64
benzene+hexane	IM-2,1_NTF2	[C2mim][NTf2]	313	298	65
benzene+hexane	IM-4,1_NTF2	[C4mim][NTf2]	303	298	66
benzene+hexane	IM-8,1_NTF2	[C8mim][NTf2]	303	298	66
benzene+hexane	IM-12,1_NTF2	[C12mim][NTf2]	318	298	66
benzene+hexane	PY-4,1[4]_BF4	[4MBpy][BF4]	323	313	67
benzene+hexane	IM-4,1_NO3	[Bmim][NO3]	303	298	68
benzene+hexane	IM-8,1_NO3	[Omim][NO3]	303	298	68
benzene+heptane	IM-4,1_NO3	[Bmim][NO3]	303	298	68
benzene+heptane	IM-8,1_NO3	[Omim][NO3]	303	298	68
benzene+heptane	IM-2,1_SO4-2	[EMim][ESO4]	303	298	69
benzene+heptane	IM-4,1_BF4	[BMIM][BF4]	298	298	70
benzene+heptane	IM-4,1_SCN	[BMIM][SCN]	298	298	70
benzene+heptane	PYR-4,1_NTF2	[BMpyr][NTf2]	303	298	71
benzene+heptane	IM-2,1_SO4-8	[EMIM][OcSO4]	318	298	72
benzene+heptane	IM-6,1_BF4	[hmim](BF4)	303	298	73
benzene+heptane	IM-6,1_PF6	[hmim](PF6)	298	298	73
benzene+heptane	IM-8,1_CL	MeOctImCl	298	298	74
pyridine+heptane	MO-4,1_CCN3	[BMMOR][TCM]	318	298	75
pyridine+heptane	IM-4,1_CCN3	[BMIM][TCM]	318	298	75
pyridine+heptane	PY-4,1[4]_CCN3	[BMPY][TCM]	328	298	75
pyridine+heptane	QUINI-6_SCN	[HiQuin][SCN]	328	298	76
ethanol+tert-butylethylether	IM-2,1_SO3-1	[emim][OMs]	318	298	77
ethylacetate+hexane	IM-6,1_PF6	HMIM PF6	313	298	78
ethylacetate+hexane	IM-8,1_PF6	OMIM PF6	313	298	78
ethylacetate+hexane	IM-6,1_BF4	[Hmim][BF4]	343	298	79
ethylacetate+hexane	IM-8,1_BF4	[Omim][BF4]	298	298	79

The $\log_{10}[S_\infty]$ value reflects the liquid selectivity when both the solute and raffinate quantities are substantially smaller than the one of the extracting liquid. The actual liquid-liquid extraction, however, is obtained at much higher quantities of azeotrope components. Therefore, it was important to see how useful the knowledge of $\log_{10}[S_\infty]$ is to predict the experimental selectivity. One of the challenges of comparing $\log_{10}[S_\infty]$ and $\log_{10}[S]$ is that experimental $\log_{10}[S]$ is calculated from liquid-liquid equilibrium data defined by varying diverse equilibrium concentrations. Thus, $\log_{10}[S]$ of an extracting liquid applied to a two-component system of fixed composition at a particular temperature and pressure is a vector of values characterized by different liquid concentrations, contrary to the one value of $\log_{10}[S_\infty]$. In order to compare $\log_{10}[S]$ and $\log_{10}[S_\infty]$, $\log_{10}[S]$ needed to be transformed into one value. Several transformations, namely the calculation of the minimum, maximum, mean, median and mid-range values of $\log_{10}[S]$ was done for every data entry given in Table 1. Then, the root-mean-square-error (RMSE) was used to assess the deviation between $\log_{10}[S_\infty]$ and $\log_{10}[S]$, and the Pearson's product-moment correlation (r) was used to determine the possibility of correlation between them. Additionally, a classification interpretation of $\log_{10}[S_\infty]$ and $\log_{10}[S]$ comparison was applied because of temperature discrepancy between compared values and the fact that a precise selectivity value is not needed for labeling extracting solvent as “selective”, as long as that value is high enough. The interpretation was as follows: let results with $\log_{10}[S] \geq 1$ be considered Positive (“selective” IL) and results with $\log_{10}[S] < 1$ be considered Negative (“non-selective” IL) under a two-class interpretation. In that case, results with $\log_{10}[S] \geq 1$ & $\log_{10}[S_\infty] \geq 1$ will be True Positives (TP), $\log_{10}[S] < 1$ & $\log_{10}[S_\infty] < 1$ will be True Negatives (TN), $\log_{10}[S] < 1$ & $\log_{10}[S_\infty] \geq 1$ will be False Positives (FP) and $\log_{10}[S] \geq 1$ & $\log_{10}[S_\infty] < 1$ will be False Negatives (FN). The following statistics were used to assess class prediction capacity:

$$\text{Accuracy} = \frac{TP + TN}{All\ results} \tag{9}$$

$$\text{Sensitivity} = \frac{TP}{TP + FN} \tag{10}$$

$$\text{Specificity} = \frac{TN}{TN + FP} \tag{11}$$

$$\text{Precision} = \frac{TP}{TP + FP} \tag{12}$$

$$\text{Balanced Accuracy} = \frac{Sensitivity + Specificity}{2} \tag{13}$$

Additionally, we analysed the impact of side chain length of the cation and the anion type on the S_∞ of n-heptane + benzene and n-hexane + benzene from several imidazole-based ILs, to illustrate the potential of using the database to understand the structure-property relationship and facilitate the design of new ILs for breaking particular two-component systems.

3 Results

3.1 Obtaining selectivity data

There were 1028 and 41868 IDACs obtained from[29] and[28], respectively. After duplicate removal, the numbers went down to 438 and 40182. The high number of duplicates from the Dortmund DB is due to the fact that the IDAC for the same system is reported by two different hyperlinks to the same webpage – the link dedicated to solute and the one dedicated to solvent. The calculation of $\log_{10}[S_\infty]$ resulted in 1615816 $\log_{10}[S_\infty]$ data points (1246 for non-IL and 1614570 for IL solvents). $\log_{10}[S_\infty]$ data has 282 - 448 K temperature range for 249 solvents (226 IL and 23 non-IL), 5695 two-component systems and 154 unique chemicals (either solutes or raffinates). The $\log_{10}[S_\infty]$ range is [-5.05;5.05], since presence of IDACs for different solutes and same solvent at the same temperature allows calculation of two $\log_{10}[S_\infty]$, for both mixture components. The big IDAC warning is issued for 26% of data points. Chemical classes of extracting agents vary enormously: non-IL solvents are represented by benzene and its derivatives, aliphatic alcohols and heterocycles, as well as, singular representative of other classes (e. g. water, acetic acid, diethyl ether and others). ILs can be characterized by the several major classes of cations and anions, the complete list can be found elsewhere[28].

3.2 Checking how well $\log_{10}[S_\infty]$ translates into $\log_{10}[S]$

$\log_{10}[S_\infty]$ vs $\log_{10}[S]$ comparison have shown significant deviation between experimental and infinite dilution values, as well as, weak or moderate positive correlations for all interpretations of experimental selectivity. The classification approach shows that, using median interpretation, both Accuracy and Balanced Accuracy of prediction is satisfactory (> 0.7). The most compelling result is the $\text{Precision}_{(\text{median})}$ of 0.81, which should be interpreted as follows: if a liquid has a $\log_{10}[S_\infty]$ that is more or equal to 1, there is an 81% chance that the liquid has a median $\log_{10}[S]$ of 1 or more (Table 2).

Table 2 Statistical assessment of $\log_{10}[S_\infty]$ vs $\log_{10}[S]$ comparison. Int. - $\log_{10}[S]$ interpretation, BA - Balanced Accuracy.

Int.	rmse	r	Accuracy	Sensitivity	Specificity	Precision	BA
min	0.87	0.4	0.64	0.83	0.5	0.53	0.67
max	0.98	0.63	0.68	0.69	0.62	0.89	0.65
mean	0.64	0.63	0.7	0.76	0.6	0.79	0.68
median	0.66	0.62	0.73	0.78	0.64	0.81	0.71
mid-extreme	0.64	0.61	0.66	0.71	0.55	0.79	0.63

Different types of azeotrope systems are predicted with different success rate. For instance, aryl + saturated hydrocarbon systems have high correlation of 0.83 between $\log_{10}[S_\infty]$ vs $\log_{10}[S]$ values, however Specificity is rather low (0.31), indicating that $\log_{10}[S_\infty]$ tends to present most ILs as selective when it comes to breaking this type of azeotropes. On the other hand, alcohol + water systems have

no correlation and $\log_{10}[S_\infty]$ predicts all ILs to be “unselective”, regardless of experimental status. Alcohol + saturated hydrocarbons have good correlation and BA of 0.7 and 0.82, respectively, as well as, a perfect Precision, *i.e.* all ILs with high $\log_{10}[S_\infty]$ have high $\log_{10}[S]$. As for ester + saturated hydrocarbon, the RMSE is the lowest for this group (0.18) and Specificity is perfect with all 4 unselective ILs predicted as unselective. Alcohol + ether, alcohol + ester and alcohol + ketone systems do not have enough examples to derive any conclusions (Figure 1).

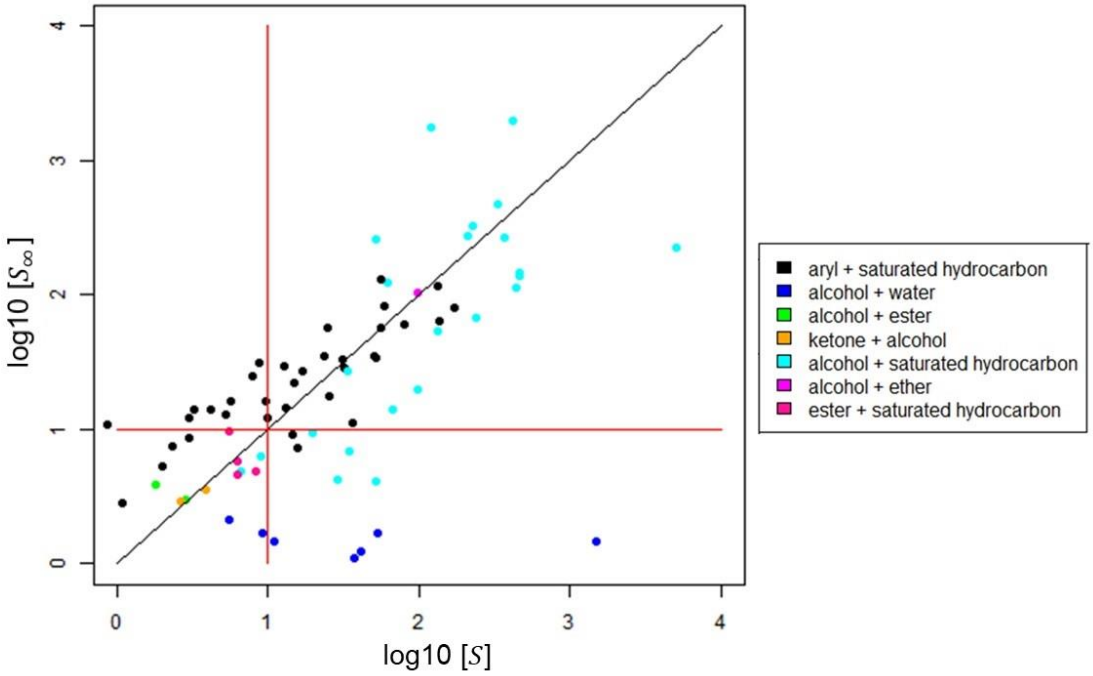

Figure 1 $\log_{10}[S_\infty]$ vs median $\log_{10}[S]$ plot. Red lines divide plot area into regions that reflect above-mentioned classification. The colors show the chemical class of the azeotrope.

The side chain length of the cation and the anion type impact has been analysed for 11 imidazole-based ILs with main side chain length varying from 1 to 10 carbon atoms and 3 anion types, i. e. bis(trifluoromethylsulfonyl)azanide (NTF2), thiocyanate (SCN) and tetracyanoboranuide (TCB). The results for comparisons are given in Figure 2

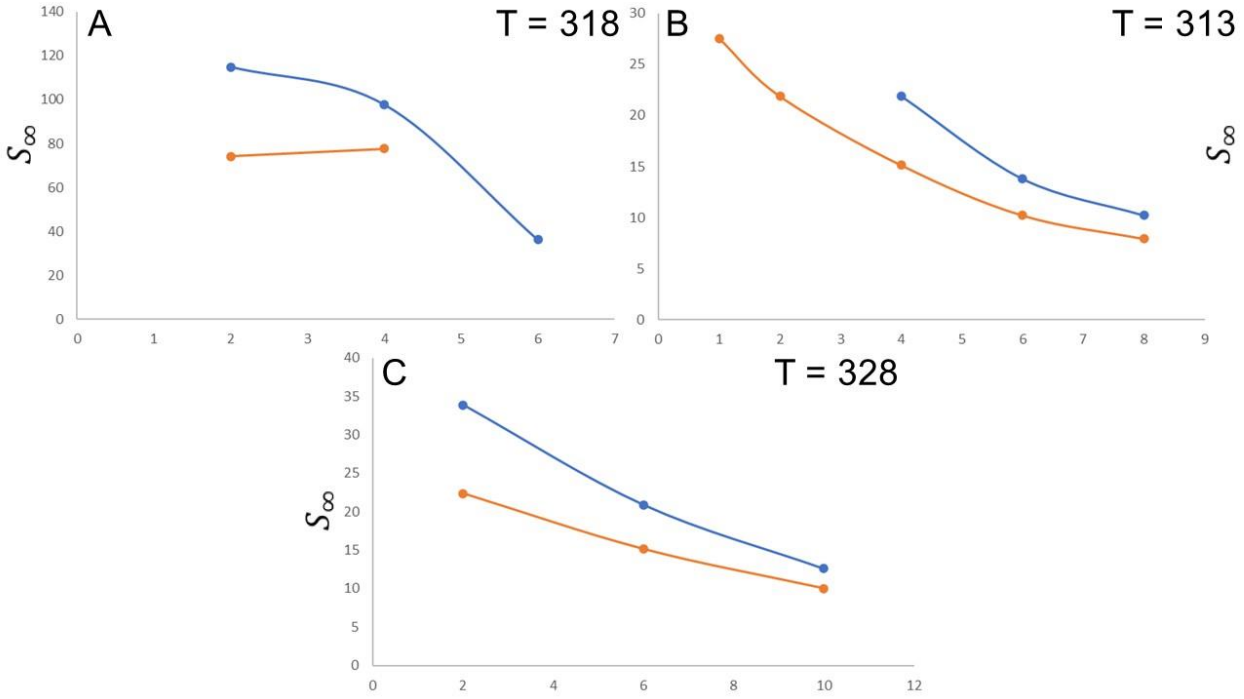

Figure 2 Example of the structure-property relationship analysis. A – SCN anion, B – NTF2 anion, C – TCB anion. X-axis is the number of carbon atoms in the main side chain. Orange is n-hexane + benzene data, blue is n-heptane + benzene data.

The analysis shows decrease in S_∞ with the increase of the alkyl chain in the majority of cases. S_∞ is higher for heptane-containing than for hexane-containing one, suggesting better azetrope-breaking capacity for the system with more hydrophobic aliphatic hydrocarbon. However, anion impact cannot be compared using data from Figure 2, since that data is given at different temperatures. Thus, anion impact was assessed at common temperature of 318K and number of carbon atom of 2 (Figure 3). The anion impact on the S_∞ of n-heptane + benzene and n-hexane + benzene systems is SCN > NTF2 > TCB.

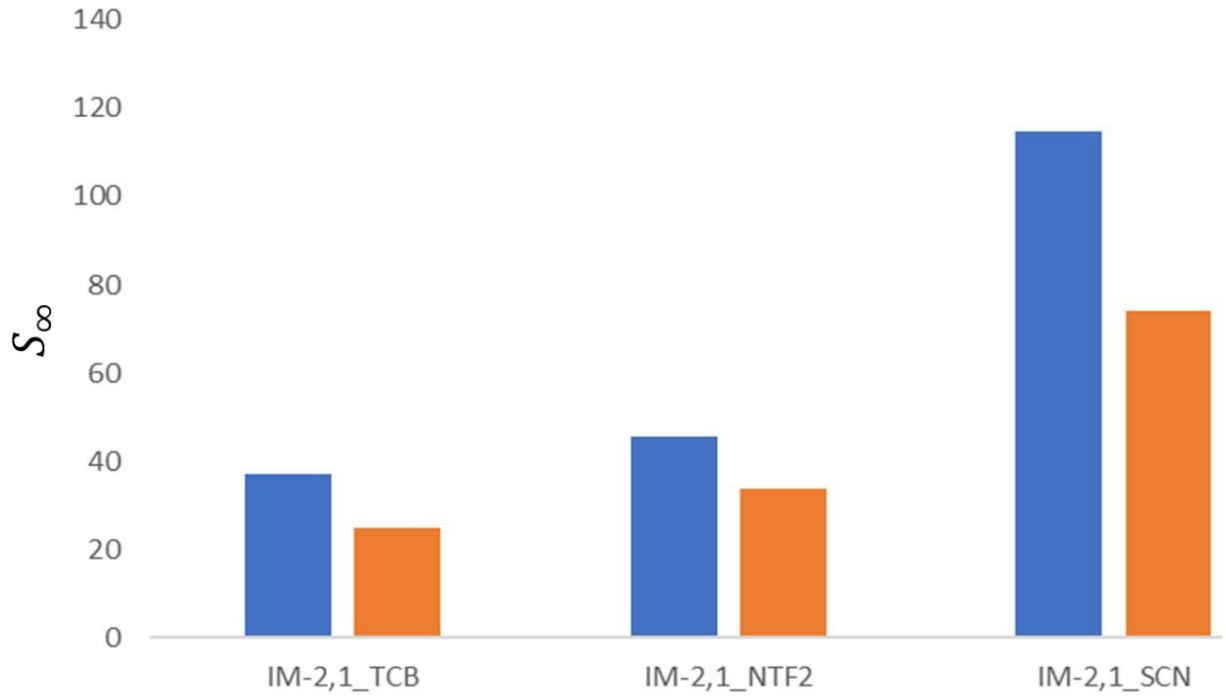

Figure 3 Example of anion impact on the S_∞. Orange is n-hexane + benzene data, blue is n-heptane + benzene data.

3.3 SQL database

The database is composed of the data points, solvents and unique components described above. The database website address is https://selinfdil.dq.fct.unl.pt/. The main page has a link to "Browse SelinfDB" page for querying. On the "Browse SelinfDB" page, the user is free to use multiple fields with case-insensitive query but it is obligatory to fill in at least one field in order to successfully retrieve data in HTML table format. The query page consists of 6 fields (Extractant, solute, raffinate, Temperature, cation, anion) that can be queried and returns values for the above-mentioned fields, as well as, the database entry ID, the decimal logarithm of selectivity at infinite dilution and the IDAC-flag as a result (Figure 4). Query results are displayed as 50 data entries per page and can be freely copied and used further for any purposes. The IDAC-flag value of 0 means that IDAC for the solute is < 10, whereas a value of 1 means it is ≥ 10. NA values are given in anion and cation fields for non-IL extractants.

A

B

Browse SelinfDB DB IL codes translation SelinfDB: The database of selectivity at infinite dilution

ID	lg [S]	Extracting Agent	Solute	Temperature[K]	Raffinate	IL-cation	IL-anion	IDAC-flag
460	0.48	Acetone	methanol	308	water	NA	NA	0
834	0.10	Sulfolane	methanol	323	water	NA	NA	0
1062	1.14	Hexadecane	methanol	293	water	NA	NA	1
8573	-0.46	IM-2,1_SO3-1	methanol	318	water	IM-2,1	SO3-1	0
13651	-0.41	IM-2,1_SO3-1	methanol	308	water	IM-2,1	SO3-1	0
13686	-0.46	IM-2,1_SO3-1	methanol	328	water	IM-2,1	SO3-1	0
13728	-0.46	IM-2,1_SO3-1	methanol	338	water	IM-2,1	SO3-1	0
13770	-0.50	IM-2,1_SO3-1	methanol	348	water	IM-2,1	SO3-1	0
33347	-0.20	IM-2,1_TFA	methanol	348	water	IM-2,1	TFA	0

Figure 4 Example of Browsing page (A) and Results page (B) of SelinfDB.

Conclusions

The investigation of the selectivity at infinite dilution dataset has suggested that only 210980 out of 1615816 (13%) of data points are possibly useful for extraction, *i.e.* $\log_{10}[S_\infty]$ of more or equal to 1 with no big IDAC warning. Therefore, the probability of finding a selective extracting agent for a liquid-liquid extraction by chance is low. Until now, the choice of an extracting agent for separations of two liquids has been mostly

based on expert judgment which can lead to synthesis and testing of chemicals unfit for this task, thus wasting a lot of time and resources. Even though SelinfDB has high quantity of experimental data, it only covers a small fraction of possible extractant/solute/raffinate/temperature combinations. The gas chromatography experiment, for determination of IDAC, must be done for extractant/solute and extractant/raffinate at the same temperature, in order to obtain S_∞ for one system, whereas choosing the best extractant requires testing of numerous compounds. This can make experimental screening for the best extractant both expensive and time-consuming. There are several theoretical approaches for IDAC predictions, such as molecular-based equations of state or Gibbs energy local composition models[28] and computational ones, such as Quantitative Structure-Property Relationship (QSPR) models[80]. One of the most efficient IDAC prediction tools at the moment is implemented in COSMO-RS, where calculations can be carried out solely on the basis of the 3D molecular conformation, obtained from ab initio electronic calculations. Therefore, the chemical structure (composition and molecular topology) is the only required input, contrary to the theoretical methods. However, there is no computational model that can predict S_∞ so far, which might be an improvement compared to the IDAC prediction approach, since predicting one endpoint, instead of two, can lead to a diminished error. It is also evident that ILs are of greater interest as extractant candidates due to the prevalence of $\log_{10}[S_\infty]$ data for ILs compared to non-ILs. Moreover, the results indicate an ≈80% chance that a "selective" IL, according to $\log_{10}[S_\infty]$, will be selective in liquid-liquid extraction. Our results with a very large dataset confirm that calculated $\log_{10}[S_\infty]$ can assist in the design of IL extractants. SelinfDB has a potential to become a source of preliminary information for the assessment of ILs and other chemicals as components of liquid-liquid extracting systems

Conflicts of interest

There are no conflicts to declare.

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Supporting Information

Table that describes the SQL structure of the database, namely fields and associated data types.

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