

# Desulfurisation of oils using ionic liquids: selection of cationic and anionic components to enhance extraction efficiency

John D. Holbrey,<sup>\*,a</sup> Ignacio López-Martin,<sup>a</sup> Gadi Rothenberg,<sup>b</sup> Kenneth R. Seddon,<sup>a</sup> Guadalupe Silvero,<sup>c</sup> and Xi Zheng<sup>a</sup>

<sup>a</sup> QUILL, School of Chemistry and Chemical Engineering, The Queen's University of Belfast, Belfast BT9 5AG, Northern Ireland, UK. Tel: +44 28 90975422; E-mail: quill@qub.ac.uk

<sup>b</sup> Van 't Hoff Institute for Molecular Sciences, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

<sup>c</sup> Departamento de Química Orgánica, Universidad de Extremadura, Avenida de la Universidad, 10071 Cáceres, Spain.

## QSPR analysis of solvent group contributions to extraction

Explaining the differences in the extraction of DBT by the different ionic liquids is challenging. Factors such as the size/shape/aromaticity and/or charge distribution are the important criteria. Both [C<sub>4</sub>mim]<sup>+</sup> and [C<sub>4</sub>py]<sup>+</sup> cations contain ten non-hydrogen atoms, compared to eleven for [C<sub>4</sub><sup>3</sup>mpy]<sup>+</sup> and [C<sub>4</sub><sup>3</sup>mpy]<sup>+</sup> and twelve for the [C<sub>4</sub><sup>34</sup>dmpy]<sup>+</sup> and [C<sub>4</sub><sup>35</sup>dmpy]<sup>+</sup> cations, which may lead to the small relative increase in affinity for aromatic components. However the methyl group is not usually considered to have a significant inductive effect on aromatic rings. Similarly, the presence, or absence, of aromaticity may not be the only feature of importance; [C<sub>4</sub>mpyr]<sup>+</sup> also contains ten non-hydrogen atoms, but in contrast is neither flat nor an aromatic cation.

Quantitative structure-property relationship (QSPR) approaches were used with some success in predicting the physical properties of ionic liquids.<sup>1-7</sup> A QSPR analysis of the partitioning data was used to identify whether a correlation could be obtained, and which, if any, of the resulting descriptors could be related to the extracting ability of the ionic liquids. The study focused on the influence of the cation using data from twelve ionic liquids with the common bis{(trifluoromethyl)sulfonyl}amide anion (**4**, **8**, **10**, **14**, **18-20** from Table 2 and five additional ionic liquids<sup>†</sup>). Geometry optimised minimum energy conformations of the ionic liquid cations were computed using restricted Hartree-Fock *ab initio* calculations with the 6-31/G(d) split valence basis set on Gaussian 03.<sup>8</sup> Our previous experience, and that of others, shows this to be a good trade-off between computational cost and quality of the results. CODESSA<sup>9</sup> was then used to derive *ca.* 350 constitutional, topological, geometrical, electrostatic, quantum chemical, and thermodynamic molecular descriptors for each ion, and to perform the statistical analyses in the descriptor space.

An initial series of one-, two- and four-parameter correlations were screened using the heuristic method<sup>10</sup> implemented in CODESSA. Descriptors were discarded based on the following criteria: bad or missing values, Fischer F-criterion < 1, insignificant contribution (1-parameter correlation  $r^2 < 0.1$ ), Student's *t* criterion < 0.1, or duplicate descriptors (2-parameter intercorrelation  $r^2 \geq 0.85$ ), the one with higher 1-parameter  $r^2$  being retained. The initial set of ~350 separate descriptors was thus reduced to 37. The best one-parameter regressions involved the following descriptors (coefficient,  $r^2$ ): Minimum valency of a C atom [ $V_C^{min}$ ] (+, 0.845), hydrogen bonding donor ability weighted by total surface area [ $HDSA_f^f$ ] (-, 0.715), number of aromatic bonds [ $N_{ar}$ ] (+, 0.668), maximum valency of a C atom [ $V_C^{max}$ ] (+, 0.612), and minimum partial charge [ $Q'_{min}$ ] (+, 0.606). Using the same criteria and the "leave-one-out" validation method, the best two-parameter correlations ( $r^2$ ,  $cvr^2$ ) were:

$$+N_{ar} - P_{\sigma-\sigma} \quad (0.869, 0.814)$$

$$- P_{\sigma-\sigma} - \mu_c \quad (0.859, 0.735)$$

$$- HDSA_f^f + IC_1^s \quad (0.855, 0.693)$$

$N_{ar}$ : Number of aromatic bonds

$P_{\sigma-\sigma}$ : Maximum  $\sigma-\sigma$  bond order

$\mu_c$ : Total point-charge component of the molecular dipole

$HDSA_f^f$ : Hydrogen bonding donor ability weighted by total surface area

$IC_1^s$ : Structural information content (order 1)

For the four-parameter correlation, the collinearity criteria (2-parameter intercorrelation) was changed to  $r^2 \geq 0.95$  to allow a higher number of descriptors to be used (76) with which to construct the model. The best correlation found ( $r^2 = 0.9924$ ,  $cvr^2 = 0.9848$ ):

$$\%_{Extract} = -2.2157(WPSA_2) + 1.5243(WPSA_1) + 5.4943e03(FPSA_3) + 4.2820e02(R_A^C) - 1.4512e02$$

$R_A^C$ : maximum 1-electron reactivity index for a C atom

and the second best correlation ( $r^2 = 0.9917$ ,  $cvr^2 = 0.9655$ ):

$$\%_{Extract} = -2.3152(WPSA_2) + 1.5591(WPSA_1) + 5.7090e03(FPSA_3) + 5.4466 IC_2 - 1.6494e04$$

$IC_2$ : Average information content (order 2)

both contain the same first three descriptors, with the fourth term changing from maximum 1-electron reactivity index for a C atom to the average information content (order 2).

The descriptors identified from the one-, two- and four-parameter correlations indicate that the size, shape and aromaticity of the cation are important. However, with such a small number of observations (12), chance correlations are likely if the number of screened variables is large.<sup>11</sup> Notably, it should be recognised that  $WPSA_1$ ,  $WPSA_2$  and  $FPSA_3$  from the four parameter correlations are all related parameters describing weighted positive charge size and distribution (suggesting that the cation size has a significant correlation with extraction ability). Topliss and Edwards suggest that all duplicate descriptors with intercorrelation  $r^2 > 0.8$  should be discarded for the final modelling, which also dramatically reduces the likelihood of chance correlations since the number of descriptors screened is reduced.

When the four-descriptor correlation was rescreened using a more stringent rejection criterion for duplicate descriptors (2-parameter intercorrelation  $r^2 \geq 0.80$ ), it reduced the descriptor pool to 31. The best regression correlation, shown in Fig 5 ( $r^2 = 0.9835$ ,  $cvr^2 = 0.9452$ ) was:

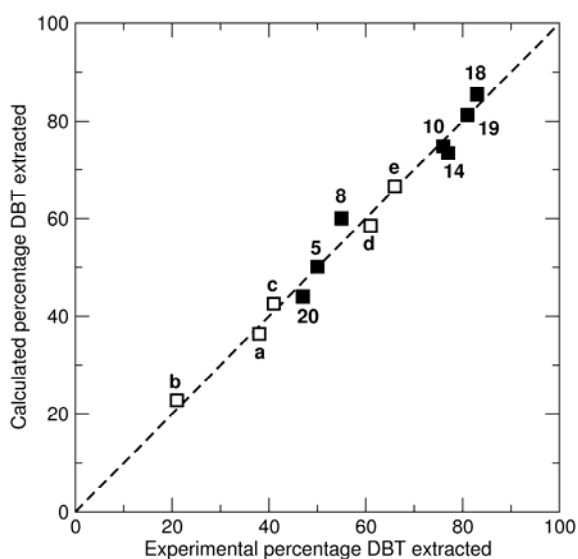
$$\%_{Extract} = 2.9504e01(\epsilon_{HOMO-1}) - 1.3835e04 (P_{\sigma-\sigma}) - 7.9048e02 P^C_{AB} - 1.2512e02(S_{YZ}^r) + 1.5082e04$$

$\epsilon_{HOMO-1}$ : HOMO-1 energy (2<sup>nd</sup> ionisation potential)

$P_{\sigma-\sigma}$ : maximum  $\sigma$ - $\sigma$  bond order

$P^C_{AB}$ : minimum ( $>0.1$ ) bond order for a C atom

$S_{YZ}^r$ : YZ shadow/YZ rectangle



**Fig. 5** Comparison of experimental and calculated percentage DBT extraction from the regressional analysis ( $r^2 = 0.9835$ ,  $cvr^2 = 0.9452$ ) for the ionic liquids **4**, **8**, **10**, **14**, **18-20** and five additional ionic liquids; **a**,  $[CH_3OC_2H_4mim][NTf_2]$ ; **b**,  $[NMeBu(CH_2CH_2OH)_2][NTf_2]$ ; **c**,  $[HOEtmmor][NTf_2]$ ; **d**,  $[C_4^4CNpy][NTf_2]$ ; **e**,  $[C_6^4CNpy][NTf_2]$ .

With this correlation, the best interpretation of the descriptors is that the extraction is governed by a combination of solute-solvent interactions with the aromatic system ( $\epsilon_{HOMO-1}$ ,  $P_{\sigma-\sigma}$ ,  $P^C_{AB}$ ) and is also controlled by the topology of the cation, with larger-flatter cations (ZY shadow/XY rectangle) performing best. However, these criteria can also be interpreted in a number of alternative ways: for example, in order to obtain a larger/flatter cation, additional carbon atoms can be added (pyridinium, methylpyridinium, dimethylpyridinium, *etc.*) which increases the number of carbon atoms and the reduction in sigma-sigma bond order all as intercorrelated descriptors.

Given the small number of observations, caution must be exerted when interpreting these results. Yet, where overall conclusions can be drawn, they point towards transfer interaction ability, aromaticity and the shape of the molecule as being influential with this extraction process and suggest that ionic liquids containing cations with greater aromatic character, for example containing polyaromatic cations, would give enhanced extraction. Ionic liquids containing a polyaromatic quinolinium and isoquinolinium cations are known, but tend to have relatively high melting points, a common feature of the larger ring structure.<sup>12,13</sup> Two examples, 1-butylisoquinolinium

bis{(trifluoromethyl)sulfonyl}amide (mp 56 °C), and 1-butyl-6-methylquinolinium bis{(trifluoromethyl)sulfonyl}amide (mp 47 °C) were prepared and tested for extraction of DBT at 60 °C. Both ionic liquids performed exceptionally well giving 80 % extraction ( $K_D = 4$ ) with 1-butylisoquinolinium bis{(trifluoromethyl)sulfonyl}amide and 90 % extraction ( $K_D = 9$ ) for 1-butyl-6-methylquinolinium bis{(trifluoromethyl)sulfonyl}amide, consistent with the QSPR predictions.

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