

## Supporting Information

### SI:A - Fundamental equations for the analysis of solubilization

In this section, we summarise the basic relationships used in the analysis of experimental data throughout the Supporting Information. According to the Kirkwood-Buff (KB) theory of solutions, the dependence of the pseudo-chemical potential of cellobiose,  $\mu_c^*$ , on salt concentration can be expressed as:<sup>1,2</sup>

$$-\frac{1}{RT} \left( \frac{\partial \mu_c^*}{\partial c_s} \right)_{T,P} = \frac{G_{cs} - G_{cw}}{1 + c_s(G_{ss} - G_{sw})} \quad (\text{A1})$$

The symbols used above have been defined in the main text. First we explain how  $\left( \frac{\partial \mu_c^*}{\partial c_s} \right)_{T,P}$  can be determined from the experimental solubility data. To this end, let us start from the free energy of transfer of a solute (cellobiose) molecule,  $\Delta\mu_c^*$ , from a pure water phase to an aqueous salt solution phase, defined as

$$\Delta\mu_c^* = \mu_c^* - \mu_c^{*0} \quad (\text{A2})$$

where  $\mu_c^*$  and  $\mu_c^{*0}$  express the pseudo-chemical potentials of the solute c at a fixed position in aqueous salt solution and in pure water, respectively. This  $\Delta\mu_c^*$  can be calculated directly from the cellobiose solubility in solution ( $c_c$ ) and pure water ( $c_c^0$ ) as

$$\Delta\mu_c^* = -RT \ln \frac{c_c}{c_c^0} \quad (\text{A3})$$

Since, according to Eq. (A2),  $\mu_c^* = \Delta\mu_c^* + \mu_c^{*0}$ , in which  $\mu_c^{*0}$  and  $c_c^0$  do not depend on the salt concentration, Eq. (A1) can be rewritten in the following form:

$$\left( \frac{\partial \ln c_c}{\partial c_s} \right)_{T,P} = \frac{G_{cs} - G_{cw}}{1 + c_s(G_{ss} - G_{sw})} \quad (\text{A4})$$

We have also identified the two contributions to solubilization. The first is the preferential salt-cellobiose affinity:<sup>1</sup>

$$\frac{1}{c_s} \left( \frac{\partial \Delta \mu_c^*}{\partial \mu_s} \right)_{T,P,c_c \rightarrow 0} = - (G_{cs} - G_{cw}) \quad (\text{A5})$$

And the second contribution is the salt self-association, given as:

$$\frac{c_s}{RT} \left( \frac{\partial \mu_s}{\partial c_s} \right)_{T,P,c_s \rightarrow 0} = \frac{1}{1 + c_s(G_{ss} - G_{sw})} \quad (\text{A6})$$

In the following, we explain how these two contributions have been evaluated from the experimental data available in the literature.

## SI:B – Preferential affinity

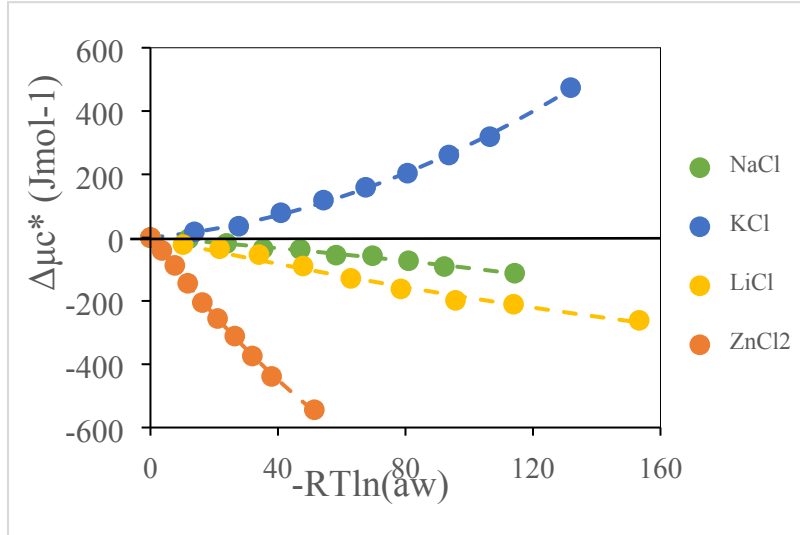
Now we evaluate the preferential affinity,  $(G_{cs} - G_{cw})$ , from experimental data using Eq. (A5). (Note that the “preferential interaction parameter” used historically literature refers to  $(G_{cs} - G_{cw})$ . Here, however, we focus on the comparison between the two KBIs).<sup>3</sup>  $G_{cs} - G_{cw}$  is a measure of a solute’s affinity with the “co-solvent” relative to that with a “solvent”. To obtain this from the dependence of  $\Delta \mu_c^*$  on water activity,<sup>4</sup> Eq. (A5) should be rewritten using the following thermodynamic relationship:

$$\frac{1}{c_s} \left( \frac{\partial \Delta \mu_c^*}{\partial \mu_s} \right)_{T,P,c_c \rightarrow 0} = - \frac{1}{c_w} \left( \frac{\partial \Delta \mu_c^*}{\partial \mu_w} \right)_{T,P,c_c \rightarrow 0} \quad (\text{B1})$$

Into the form:<sup>2</sup>

$$- \frac{1}{c_w} \left( \frac{\partial \Delta \mu_c^*}{\partial (-RT \ln a_w)} \right)_{T,P,c_c \rightarrow 0} = (G_{cs} - G_{cw}) \quad (\text{B2})$$

In order to evaluate the differentiation on the L.H.S. of Eq. (B2), the  $^{RT\ln a_w}$  dependence of  $\Delta\mu_c^*$  has been fitted using the polynomial function shown in Table B, and compared with the experimental data (Figure B).



**Figure B:** Polynomial fitting of  $\Delta\mu_c^*$  plotted against  $-RT\ln a_w$ . The fitting equation and the parameters are summarized in Table B. The solubility data from Liu et al. have been used to calculate the  $\Delta\mu_c^*$  through Eq. (A3),<sup>5</sup> and  $a_w$  was obtained from Robinson and Stokes' osmotic coefficient data through Eq. (B3).<sup>6</sup>

**Table B:** Fitting parameters for differentiation of Eq. (B2). The fitting equation:

$$\Delta\mu_c^* = a(-RT\ln a_w)^2 + b(-RT\ln a_w).$$

Salt	$a$	$b$
KCl	0.019	-1.007
NaCl	-0.002	0.748
LiCl	0.003	2.183
ZnCl <sub>2</sub>	0.024	-13.170

The term involving the water activity,  $RT \ln a_w$ , was calculated directly from the osmotic coefficient using the following well known relationship:<sup>6</sup>

$$RT \ln a_w = \phi \ln x_w \quad (\text{B3})$$

The individual KB integrals contributing to the preferential affinity ( $G_{cs} - G_{cw}$ ) can be determined independently, by complementing it with the partial molar volume  $V_c$  of cellobiose in the presence of the salts, which can be expressed as

$$G_{cw} = -V_c - c_s V_s (G_{cs} - G_{cw}) \quad (\text{B4})$$

where  $V_s$  is the partial molar volume of the salt ion.

### SI-C Salt self-aggregation

The second contribution to solubilization is the preferential self-aggregation of salts in the bulk solution,  $G_{ss} - G_{sw}$ , that reduces the solubilization efficiency. This preferential self-aggregation of salts can be obtained from salt solution osmotic coefficient data in the following manner:

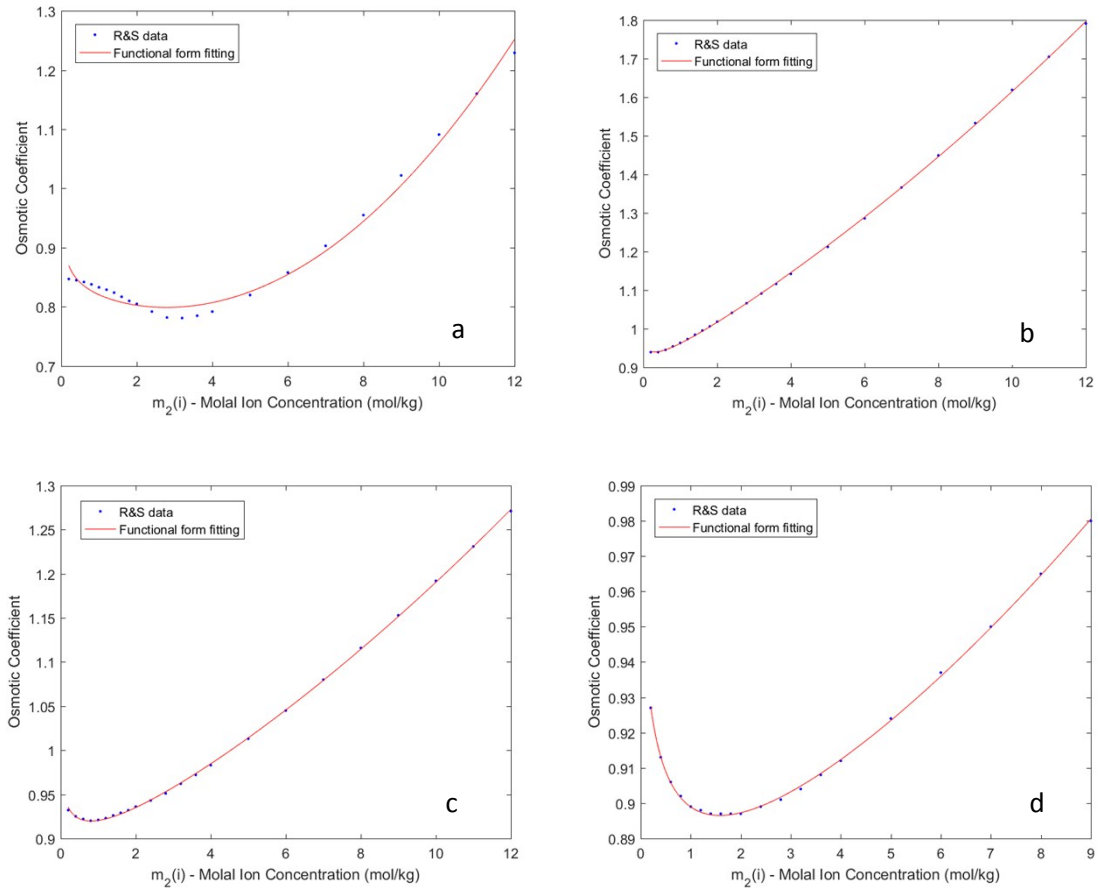
$$\frac{1}{1 + c_s (G_{ss} - G_{sw})} = c_s \left( \frac{\partial \ln m_s}{\partial c_s} + \frac{\partial \ln \gamma_s^m}{\partial m_s} \frac{\partial m_s}{\partial c_s} \right) \quad (\text{C1})$$

The calculation of  $G_{ss} - G_{sw}$  via Eq. (C1) requires the evaluation of  $\frac{\partial \ln \gamma_s^m}{\partial m_s}$ . To do so, we adopt the following fitting equation for electrolyte osmotic coefficients based on a classical model by Stokes and Robinson:<sup>6</sup>

$$\phi - 1 = -\frac{\alpha \sqrt{m}}{3} \left( \frac{3}{(\beta \sqrt{m})^3} \left[ 1 + \beta \sqrt{m} - 2 \ln (1 + \beta \sqrt{m}) - \frac{1}{1 + \beta \sqrt{m}} \right] \right) + cm + dm^2 \quad (\text{C2})$$

Using the fitting parameters for Eq. (C2), summarized in Table C, we can calculate  $\frac{\partial \ln \bar{\gamma}_s^m}{\partial m_s}$  straightforwardly as follows:

$$\frac{\partial \ln \bar{\gamma}_s^m}{\partial m_s} = -\frac{\alpha}{2\sqrt{m}} \left( \frac{1}{(1 + \beta\sqrt{m})^2} \right) + 2c + 3dm \quad (C3)$$



**Figure C:** Comparison between the experimental osmotic coefficient  $\phi$  and fitting for (a) ZnCl<sub>2</sub>, (b) LiCl, (c) NaCl and (d) KCl.

**Table C:** Fitting parameters for Eq. (C2).

Salt	$\alpha$	$\beta$	$c$	$d$
KCl	0.7684	0.7492	0.0066	0.0005
NaCl	0.7076	0.7171	0.0001	0.0008
LiCl	0.8603	0.9633	0.0547	0.0016
ZnCl <sub>2</sub>	1.6940	1.3280	0.0342	0.0054

### SI-D Source of the experimental data

The experimental solubility data necessary for the calculation of cellobiose solvation free energies ( $\mu_c^*$ ) and the cellobiose-water and cellobiose-salt KBIs, have been obtained from Fig. 1 of Liu et al.<sup>5</sup> Since we could not obtain the raw solubility data, we have extracted the solubility data via pixel selection method using “Graph Data Extractor” open source software. The error bar for the experimental solubility determination were not reported in the original paper, and the error in digitalization is roughly estimated to be ca. 0.002 mol dm<sup>-3</sup> though this is dependent on the accuracy of pixel selection.

### References

- 1 J. J. Booth, S. Abbott and S. Shimizu, *J. Phys. Chem. B*, 2012, **116**, 14915–14921.
- 2 J. J. Booth, M. Omar, S. Abbott and S. Shimizu, *Phys Chem Chem Phys*, 2015, **17**, 8028–8037.
- 3 S. Shimizu, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 1195–1199.
- 4 J. J. Booth, M. Omar, S. Abbott and S. Shimizu, *Phys. Chem. Chem. Phys.*, 2015, **17**, 8028–8037.
- 5 Z. Liu, C. Zhang, R. Liu, W. Zhang, H. Kang, P. Li and Y. Huang, *Cellulose*, 2016,

23, 295–305.

6 R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworth, London, 1959.

7 Graph Data Extractor, <https://sourceforge.net/projects/graphdataextrac/>, (accessed October, 2016).