Electronic Supporting Information for

Thermodynamics of Cellulose Dissolution in an Imidazolium Acetate Ionic Liquid

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Test of the solution calorimeter

The dissolution of potassium chloride into water is a process that has been recommended by NIST as a test reaction for solution calorimeters. In order to test the solution calorimeter, we have measured the heat of dissolution of KCl in water at 298.15 K.

KCl used for the test of the calorimeter was provided by Sigma Aldrich with a 0.99 mass fraction purity. The sample was dried overnight at 383 K before the measurements were carried out. The water used as solvent was three-times distilled in an all-quartz system.

0.1000 g of KCl were dissolved in 25 mL of water at T = (298.15 ± 0.001) K thus forming a solution with a concentration of 0.050 mol kg^{-1}. After all the necessary mass corrections due to buoyancy, the average enthalpy of dissolution of KCl, determined from two independent tests was (234.0 ± 1.1) Jg^{-1}. The temperature profile of the solution calorimeter during this measurement is represented in Figure S1. The recommended value of the enthalpy of dissolution of KCl is of 235.86 Jg-1 – a value 0.8% higher than that determined herein.

The difference found is acceptable and is explained by different effects[1,2,3]: i) the concentration of the solution herein (0.05 mol kg^{-1}) is half of that used to measure the recommended value; ii) the water was not degased prior to the determination of the heat of dissolution; iii) the salt used is not as pure as the the one recommended by NIST.

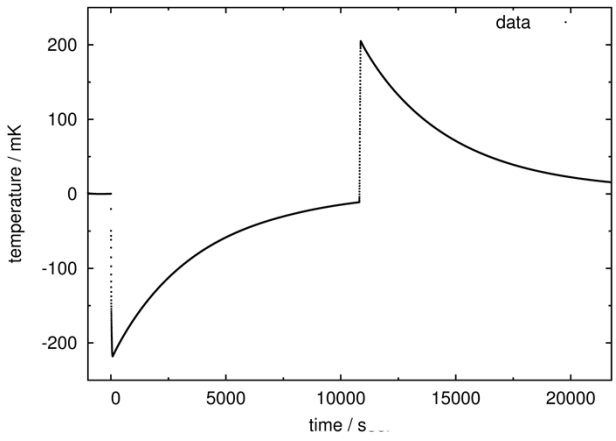

Figure S1. Temperature profile of the solution calorimeter when 0.100 g of KCl are dissolved in 25 mL of tridistilled water at 298.15 K.

Detailed experimental results

The details of the experiments done in the dissolution calorimeter are listed in Table S1.

Experiment number	Temperature (°C)	MCC mass (mg)	Volume of ionic liquid (mL)	Enthalpy of dissolution (J/g)
1	80.0	112.8	25.0	139.7
2	80.0	101.0	24.9	124.1
3	80.0	98.0	25.0	132.6

Table S1: Enthalpy of dissolution of cellulose in the pure ionic liquid as determined by independent experiments.

The experimental temperature profiles were fit to equation (7) in order to determine the heat of dissolution and the two characteristic times – that corresponding to the dissolution and the one attributed to the thermal relaxation of the calorimeter. The values calculated for each experiment are listed in Table S2. In Figure S2 are represented the details of three typical fits corresponding to the dissolution of a sample of water in $[C_2C_1Im][OAc]$; a sample of dried MCC in pure $[C_2C_1Im][OAc]$; and a sample of dried MCC in a 50/50 mole solution of $[C_2C_1Im][OAc]$ + DMSO.

	dissolution			Calibration (10J)		
	τ_d (s)	τ_c (s)	A (mk)	τ_d (s)	τ_c (s)	A (mk)
H_2O in $[C_2C_1Im][OAc]$	11.7	1531	157.8	23	1543	153.1
MCC in $[C_2C_1Im][OAc]$	35.4	1725	219.5	23	1520	168.9
MCC in $[C_2C_1Im][OAc]$/DMSO	16.7	1980	175.7	22	1540	157.6

Table S2: Examples of parameters of the fitting for dissolution and calibration

The τ_d corresponds to the characteristic time of the dissolution while τ_c represents the relaxation of the calorimeter. A is the pre-exponential factor of equation (7) of the manuscript. If the value at T_∞ is different from T_0 the difference (in mK) is added to the pre-exponential factor. For example, in the third experiment of the dissolution of MCC in $[C_2C_1Im][OAc]$/DMSO, T_∞ is 10mk lower than at T_0.

For extremely fast dissolution (i.e. water dissolution in $[C_2C_1Im][OAc]$), the time of 11.7 s corresponds mainly to the time needed to mix and the time needed for the heat to reach the thermometers. The 10 J calibration corresponds to a heat of 500 mW for 20 s, which correspond to an exponential with a value of τ of 22-23 s.

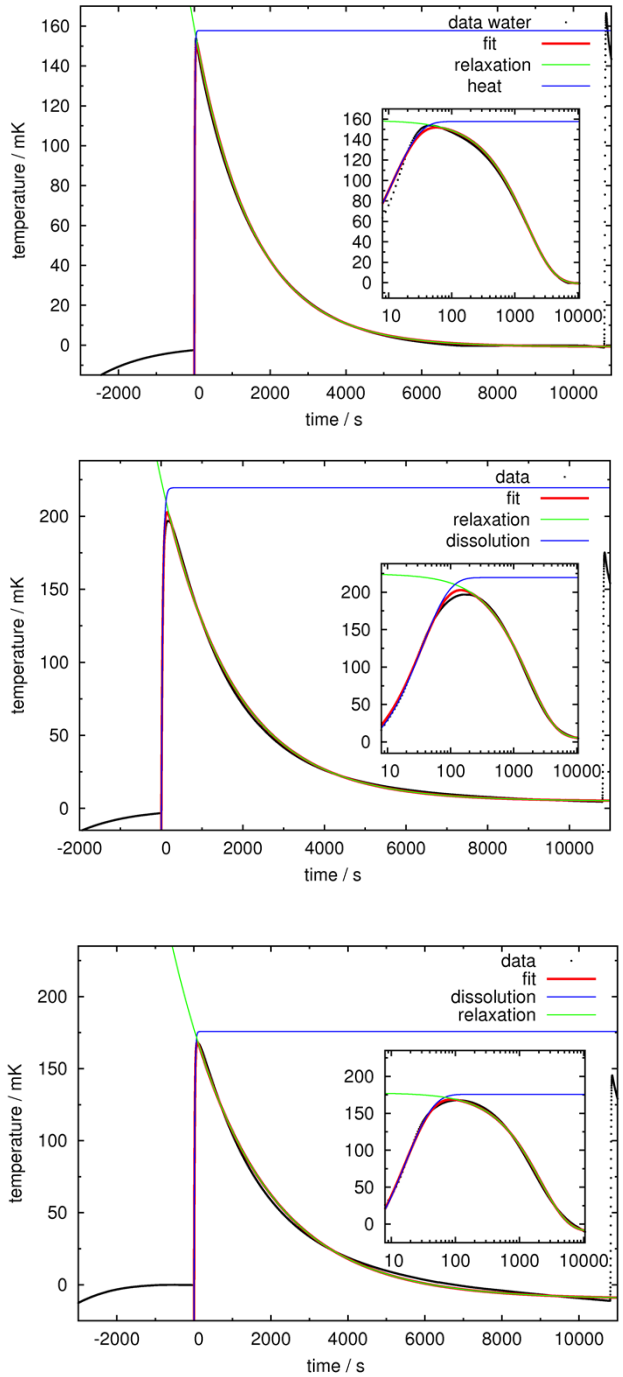

Figure S2. Temperature profiles of the solution calorimeter and fit used to calculate the heats of dissolution. Upper plot: dissolution of 11.6mg of water in 25 ml of $[C_2C_1Im][OAc]$ at 80˚C; middle plot: Dissolution of 98 mg of dry MCC in 25 ml of $[C_2C_1Im][OAc]$ at 80˚C; lower plot: Dissolution of 105 mg of dry MCC in 25 ml of an equimolar solution of $[C_2C_1Im][OAc]$/DMSO at 80˚C

References

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