



Cite this: *Chem. Commun.*, 2015, 51, 4485

Received 22nd December 2014,
Accepted 5th February 2015

DOI: 10.1039/c4cc10249e

www.rsc.org/chemcomm

Thermodynamics of cellulose dissolution in an imidazolium acetate ionic liquid†

J.-M. Andanson, A. A. H. Pádua and M. F. Costa Gomes*

The heat of dissolution of cellulose in one imidazolium acetate ionic liquid was determined experimentally. The value of $-132 \pm 8 \text{ J g}^{-1}$ indicates that the dissolution is exothermal thus confirming energetically favourable cellulose–ionic liquid interactions but indicating that an increase in temperature does not thermodynamically favour the dissolution process.

Natural cellulose cannot be dissolved in usual solvents under mild conditions. This fact prevents many possible applications of this cheap and abundant natural polymer.¹ In 2002, Swatloski *et al.*² reported that ionic liquids could dissolve high amounts of cellulose at moderate temperatures. These molten salts, liquid below 100 °C, are thermally stable and non-volatile, decreasing the risk of pollution and facilitating recycling.³ Ionic liquids based on acetate or chloride anions, combined with small alkylimidazolium cations, were found to be the most promising as they could dissolve large amounts of cellulose (>15 wt%).^{4,5}

Acetate-based ionic liquids, being less viscous, seem to present some advantages over chloride-based ionic liquids, namely improved mass transport and faster kinetics of dissolution.⁶ It was recently demonstrated that the addition of co-solvents, like dimethyl sulfoxide, DMSO, to 1-butyl-3-methylimidazolium acetate, [C₄C₁Im][OAc], significantly decreases the time necessary for the cellulose dissolution.⁷ DMSO does not interact with the polymer in solution, its role being just to increase the fluidity of the medium.⁸

As is the case for other polymers, cellulose dissolution in ionic liquids seems to be controlled kinetically. The thermodynamics of the dissolution process are rarely treated specifically, even when arguments involving molecular interactions or hydrogen bond formation are used to explain the behavior of cellulose in the presence of ionic liquids.⁹ The dissolution of high molecular weight polymers is always associated with small positive entropy

changes, therefore the enthalpy term is crucial to evaluate the free energy of dissolution and thus the solubility of the polymer.¹⁰

It seems thus capital to characterize the thermodynamics of cellulose dissolution in ionic liquids if novel solvents or operating conditions are to be suggested. Dissolving crystalline polymers in molecular solvents is generally an endothermic process¹¹ indicating that polymer–solvent interactions are not favorable enough to compensate the loss of polymer–polymer and solvent–solvent interactions during dissolution. In this case, increasing the temperature thermodynamically favors dissolution. The opposite is expected when dissolution is exothermic. In this work, we have measured the heat of dissolution of cellulose in the ionic liquid 1-ethyl-3-methylimidazolium acetate, [C₂C₁Im][OAc], and in a 50/50 mol% mixture of [C₂C₁Im][OAc] with DMSO.

In this work, MicroCrystalline Cellulose (MCC) from Sigma-Aldrich was used after drying it under vacuum (10⁻⁴ bar) at 80 °C for 24 hours. 1-Ethyl-3-methylimidazolium acetate – [C₂C₁Im][OAc] >98% from Iolitec was used as a solvent after being kept under vacuum (10⁻⁴ bar) during several days prior to usage. DMSO (dimethyl sulfoxide, >99.9%, from Fluka) was used as a co-solvent.

The heat of dissolution was measured using a precision solution semi-adiabatic solution calorimeter equipped with a 25 mL dissolution vessel and housed in a TAM III thermostat from TA instruments. All the experiments were performed at 80 °C. The quantities of both the microcrystalline cellulose (MCC) and of the solvent were determined gravimetrically. Special care was taken during the preparation of the MCC sample by filling the glass ampoule under a flow of nitrogen, drying the MCC already inside the ampoule, sealing the ampoule after drying the MCC (also under a flow of nitrogen) using an epoxy resin resistant to the ionic liquid at the temperatures of the experiment.

The calorimeter was first filled with the ionic liquid and with a sealed glass ampoule containing a precise quantity of MCC. Both the ionic liquid and the glass ampoule stay inside the calorimeter for thermal equilibration during *circa* four hours. The glass ampoule containing the MCC is then broken against a sapphire tip and the solute is dissolved inducing a rapid change of the calorimeter's temperature. A slow thermal relaxation of

CNRS, UMR 6296, Institut de Chimie de Clermont-Ferrand, 24 avenue des Landais, BP 80026, F-63171 Aubière, France. E-mail: margarida.c.gomes@univ-bpclermont.fr

† Electronic supplementary information (ESI) available: The experimental results obtained for the test of the calorimeter and for each calorimetry experiment are reported together with the details concerning the fits of the experimental curves. See DOI: 10.1039/c4cc10249e

the calorimeter is then observed. After the dissolution, and once the base-line temperature is recovered (three hours), an electrical heat pulse of 10 J is applied to the calorimeter for calibration. Similar experimental procedures were followed for the dissolution of samples of MCC in the pure ionic liquid and in equimolar mixtures of $[C_2C_1Im][OAc]$ and DMSO. The complete list of experiment results and the details of the data treatment are given in ESI.†

The heat-balance of the semi-adiabatic calorimeter used can be expressed by eqn (1):

$$-\frac{dQ}{dt} - \frac{dQ_F}{dt} = C_p \frac{dT}{dt} + \frac{C_p}{\tau_c}(T - T_s) \quad (1)$$

where dQ/dt is the heat of dissolution, dQ_F/dt is the spurious heat (e.g. due to stirring, to the joule effect from the thermistor, ...), $C_p dT/dt$ accounts for the heat accumulated by the system (C_p is the heat capacity of the calorimeter) and the last term is related with the heat exchange of the calorimeter with the surroundings. T is the temperature of the calorimeter, T_s is the temperature of the surroundings and τ_c is the characteristic time of thermal relaxation of the calorimeter.

The term related to the spurious heat can be determined from the behavior of the system when no dissolution is taking place in the calorimeter:

$$-\frac{dQ_F}{dt} = C_p \frac{dT}{dt} + \frac{C_p}{\tau_c}(T - T_s) \quad (2)$$

When the calorimeter is in thermal steady state (stable base line), the heat capacity term is negligible and eqn (2) becomes:

$$-\frac{dQ_F}{dt} = \frac{C_p}{\tau_c}(T_\infty - T_s) \quad (3)$$

where T_∞ is the base line temperature of the calorimeter. By replacing eqn (3) in eqn (1), the heat balance of the calorimeter becomes:

$$-\frac{dQ}{dt} = C_p \frac{dT}{dt} + \frac{C_p}{\tau_c}(T - T_\infty) \quad (4)$$

The signal of a quasi-adiabatic calorimeter is thus a result of the heat effect due to the dissolution and of the heat leak to the surrounding thermostat. When the dissolution is fast, compared to the time scale of heat dissipation, the two phenomena are decoupled and the signal consists of essentially a sudden temperature jump followed by a slow exponential decay of temperature until the base line is recovered. When the timescales of the dissolution and of the heat dissipation in the calorimeter are not sufficiently different, like in the case of the dissolution of cellulose in an ionic liquid, the temperature profile of the calorimeter is a function representing the convolution of the two effects.

In the case of a slow dissolution phenomenon, it is still possible to measure the heat of dissolution after a calibration experiment performed using a heat pulse from an electrical heater. A working equation simulating the concurrent dissolution and the heat leak processes can be obtained, as long as the kinetics of the dissolution is known. In the present case, a first-order kinetics of dissolution was considered:¹²

$$-\frac{dn(t)}{dt} = \frac{n(t)}{\tau_d} \Rightarrow n(t) = n_0 e^{-t/\tau_d} \quad (5)$$

where n_0 is the quantity of solute, $n(t)$ is the amount of undissolved solute and τ_d is the characteristic time of the dissolution process. The heat of dissolution is proportional to the quantity of dissolved solute:

$$Q(t) = \Delta H[n_0 - n(t)] \quad (6)$$

By replacing eqn (5) and (6) in eqn (4) the temperature profile of the dissolution in the calorimeter can be obtained:

$$T(t) = \frac{n_0 \Delta H}{C_p} \frac{\tau_c}{\tau_c - \tau_d} (e^{-t/\tau_c} - e^{-t/\tau_d}) + T_\infty \quad (7)$$

where τ_d and τ_c are the characteristic times of dissolution and of thermal relaxation of the calorimeter, respectively; T_∞ is the temperature when the calorimeter is in equilibrium with its surrounding thermostat; C_p is the heat capacity of the calorimeter and ΔH is the enthalpy of dissolution.

The temperature profile obtained when a sample of MCC was dissolved in $[C_2C_1Im][OAc]$ is presented in Fig. 1, together with a blank experiment using an empty ampoule. The blank experiment confirms that the heat effect attributable to breaking an empty ampoule is negligible as almost no temperature change is observed in the calorimeter. In the presence cellulose, the first peak corresponds to the MCC dissolution and the second corresponds to the response of the calorimeter to a 10 J heat pulse thus serving to calibrate the heat capacity and relaxation time of the apparatus (this heat pulse also exists in the blank experiment).

In agreement with previous studies of the cellulose dissolution in this ionic liquid, done using optical microscopy,⁷ the dissolution process is relatively fast, with a characteristic time of less than one minute for the dissolution of cellulose, compared to around 30 minutes for the relaxation of the calorimeter. Further details of the characteristic times for each experiment are included in the ESI.†

It is observed that the dissolution of cellulose in $[C_2C_1Im][OAc]$ is an exothermic process and the enthalpy of dissolution is of $-132 \pm 8 \text{ J g}^{-1}$ of cellulose (an average value taken over three independent experiments). By molecular simulation, the dissolution

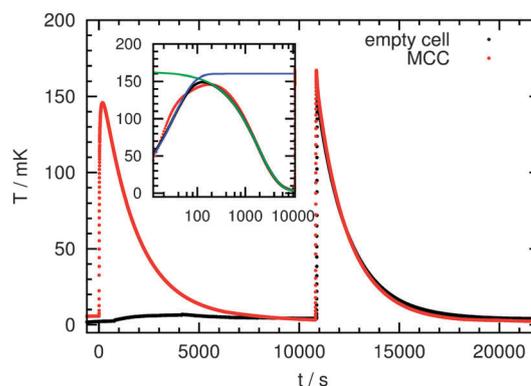


Fig. 1 Temperature profile of the solution calorimeter when an empty ampoule is broken (black curve) or a 100 mg sample of dried MCC is dissolved (red curve) at 80 °C. The temperature was recorded every 2 seconds. The inset represents the detail of the fitting used to determine the enthalpy of dissolution (details given in the ESI.†).

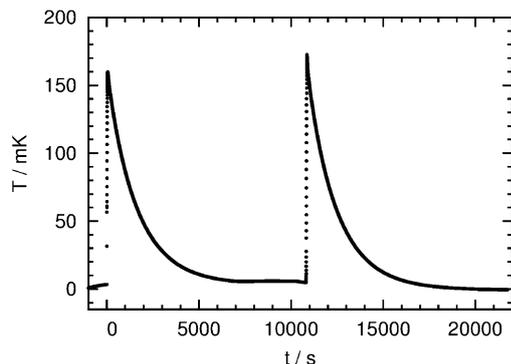


Fig. 2 Temperature profile of the solution calorimeter when 11.6 mg of water are dissolved in 25 mL of $[C_2C_1Im][OAc]$ at 80 °C.

of cellulose has been considered like the peeling of a polymer chain from a cellulose fibril and this phenomenon has also been found exothermic in an imidazolium-based ionic liquid.¹³

Because the MCC sample is difficult to dry and is very hygroscopic, the water content might affect the measured heat of dissolution. In order to assess the effect of the MCC water content on the measured heat effects, we have determined the heat of dissolution of a small sample of water in the pure ionic liquid. The temperature profile obtained is represented in Fig. 2.

The dissolution of water in $[C_2C_1Im][OAc]$ is also an exothermic process and a heat of dissolution of -850 J g^{-1} of water was determined in this case. We have observed that the mass variation of MCC when subject to drying was of the order of 5% but we consider that even if there is a water uptake during the loading of the cell, the maximum uncertainty associated with the enthalpy of dissolution measured herein is of $\pm 8 \text{ J g}^{-1}$ of cellulose.

It has been observed that the addition of a co-solvent like dimethyl sulfoxide, DMSO, to the ionic liquid enhances its solvent power by decreasing the time needed for dissolution, even at low temperatures.⁷ It has been proved using computer simulation that DMSO facilitates mass transport by decreasing the solvent viscosity without significantly affecting the specific interactions between cations and anions or between the ionic liquid and the polymer.

The heat of dissolution of dried MCC in 50/50 mol% mixture of $[C_2C_1Im][OAc]$ with DMSO was also determined experimentally

in this work. The temperature profile of the solution calorimeter is presented in the ESI.† The heat of dissolution measured was of -106 J g^{-1} , still an exothermic dissolution with an enthalpy comparable to that observed in the pure ionic liquid.

These results contribute to the understanding of the dissolution of cellulose in ionic liquids. Being an exothermic process means that the interactions between the ionic liquid and the biopolymer are highly favorable. It also means that an increase in temperature does not facilitate the dissolution, at least not in terms of the thermodynamics of the process. Raising the temperature increases the fluidity of the ionic liquid thus facilitating mass transport and leading to a faster dissolution of cellulose.⁷ Furthermore, we have shown that the addition of DMSO as a co-solvent does not affect dramatically the enthalpy of dissolution, thus confirming that this co-solvent does not participate significantly in the interactions between the ions and the dissolved polymer chains of cellulose.

The authors acknowledge the *Contrat d'Objectifs Partagés*, CNRS-UBP-Région Auvergne, France for the dissolution calorimeter and for the post-doctoral grant of J.-M. A.

Notes and references

- 1 A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484.
- 2 R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 4974.
- 3 N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123.
- 4 A. Pinkert, K. N. Marsh, S. Pang and M. P. Staiger, *Chem. Rev.*, 2009, **109**, 6712.
- 5 B. Zhao, L. Greiner and W. Leitner, *RSC Adv.*, 2012, **2**, 2476.
- 6 R. Rinaldi, *Chem. Commun.*, 2011, **47**, 511.
- 7 J. M. Andanson, E. Bordes, J. Devemy, F. Leroux, A. A. H. Padua and M. F. Costa Gomes, *Green Chem.*, 2014, **16**, 2528.
- 8 S. Velioglu, X. Yao, J. Devemy, G. Ahunbay, A. Dequidt, S. B. Tantekin-Ersolmaz, M. F. Costa Gomes and A. A. H. Padua, *J. Phys. Chem. B*, 2014, **118**, 14860.
- 9 B. Lindman, G. Karlström and L. Stigsson, *J. Mol. Liq.*, 2010, **156**, 76.
- 10 B. Miller-Chou and J. L. Koenig, *Prog. Polym. Sci.*, 2003, **28**, 1223.
- 11 J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe and D. R. Bloch, *Polymer Handbook*, Wiley, New York, 4th edn, 1999.
- 12 P. S. Antonel, P. A. Hoijemberg, L. M. Maiante and M. G. Lagorio, *J. Chem. Educ.*, 2003, **80**, 1042.
- 13 H. M. Cho, A. S. Gross and J. W. Chu, *J. Am. Chem. Soc.*, 2011, **133**, 14033.