

EFFECT OF TEMPERATURE ON DISSOLUTION ENTHALPY FOR HUMIC ACIDS IN WATER

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Abstract

The aim of this work was to study dissolution and solubility of humic acids in water. Systems were studied using solution calorimetry. Thermodynamics data of humic acids were determined in aqueous solutions in the temperature range from 298.15 K to 318.15 K. We compared two types of humic acids and influence of temperature. These HAs were isolated from two different organic origin - compost and South Moravian lignite. HAs was isolated from South-Moravian lignite from the mine Mír (locality Mikulčice, Czech Republic) and compost which was obtained from the composting plant in Náměšť n. Oslavou, Czech Republic. Isolation of HAs was performed according to the procedure recommended by the International Humic Substances Society (IHSS).

Keywords: Humic acid, dissolution, enthalpy, solution calorimetry

1. INTRODUCTION

Enthalpy change for dissolution of solids ($\Delta_{\text{sol}}H$) is an important characteristic of solute-solvent interaction [1]. We can use solution calorimetry everywhere in the field of chemistry. It is non-invasive, non-destructive method which can be utilized, for example, for determining the enthalpy of dissolution, polymorphism, degree of crystallinity/amorphous content, characterization of interactions, to investigate the stability of supersaturated systems, to study the formation of liposomes with phospholipids, photoreactivity and sorption processes [2, 3].

The thermodynamic function, which characterizes the total energetic effect of the solute-solvent interactions, is the solvation enthalpy, $\Delta_{\text{solv}}H$. This function is connected with the standard dissolution enthalpy of a solid solute, $\Delta_{\text{sol}}H^\circ$ by a simple relation (1), [1]:

$$\Delta_{\text{solv}}H = \Delta_{\text{sol}}H^\circ + H(\text{crystal lattice}) \quad (1)$$

In this study, we used semi-adiabatic solution calorimeter. These methods involve typically crushing of a glass ampoule containing the sample in a solvent chamber and measuring the released heat while stirring the solution [4].

Humic substances are well known to be one of the most important soil constituents. They are the principal components of soil organic matter and have indispensable roles for soil and the environment in general. Due to their colloidal and polyfunctional character, these substances play important roles in the mobility and bioavailability of nutrients and contaminants in the environment and can be considered as natural nano-colloids [5]. They determine the pH buffering capacity and cation exchange capabilities in natural waters and soils [6, 7]. Study of thermodynamics and dissolution results improves our knowledge about reactivity of humic substances and how these substances can behave in nature and aquatic systems.

2. MATERIALS AND METHOD

2.1. Materials

Humic acids were isolated from South-Moravian lignite from the mine Mír (locality Mikulčice, Czech Republic), compost was obtained from the composting plant in Náměšť n. Oslavou, Czech Republic. Isolation of HAs was performed according to the procedure recommended by the International Humic Substances Society (IHSS).

2.2. Methods

Solution calorimetry.

The enthalpy of solution ($\Delta_{\text{sol}}H$) of humic acids was measured with the precision solution calorimeter of the TAM III Thermal Activity Monitor (TA Instruments Inc.). The measurement temperatures were 25 ± 0.0001 °C, 30 ± 0.0001 °C and 35 ± 0.0001 °C. The volume of the vessel was 100 mL, and the stirrer speed was 500 rpm. Measurements with sample amounts of approximately 100 mg were performed. The calorimeter was calibrated with KCl (analytical grade, > 99.5%, Merck). The TAM Assistant software v0.9 and SolCal version 1.2 was used for the data analysis.

3. RESULTS AND DISCUSSION

In **Figure 1** typical output from the measurement of solution calorimetry for dissolution of lignite HA at 35 °C is shown. Green circle indicates the effect of the breakage of the ampoule with the sample of humic acids. From these data we can calculate the value of enthalpy. As can be seen the slope of curve increases in this points which indicates that studied reactions are exothermic. Values of enthalpy are negative, which corresponds to exothermic origin of reactions.

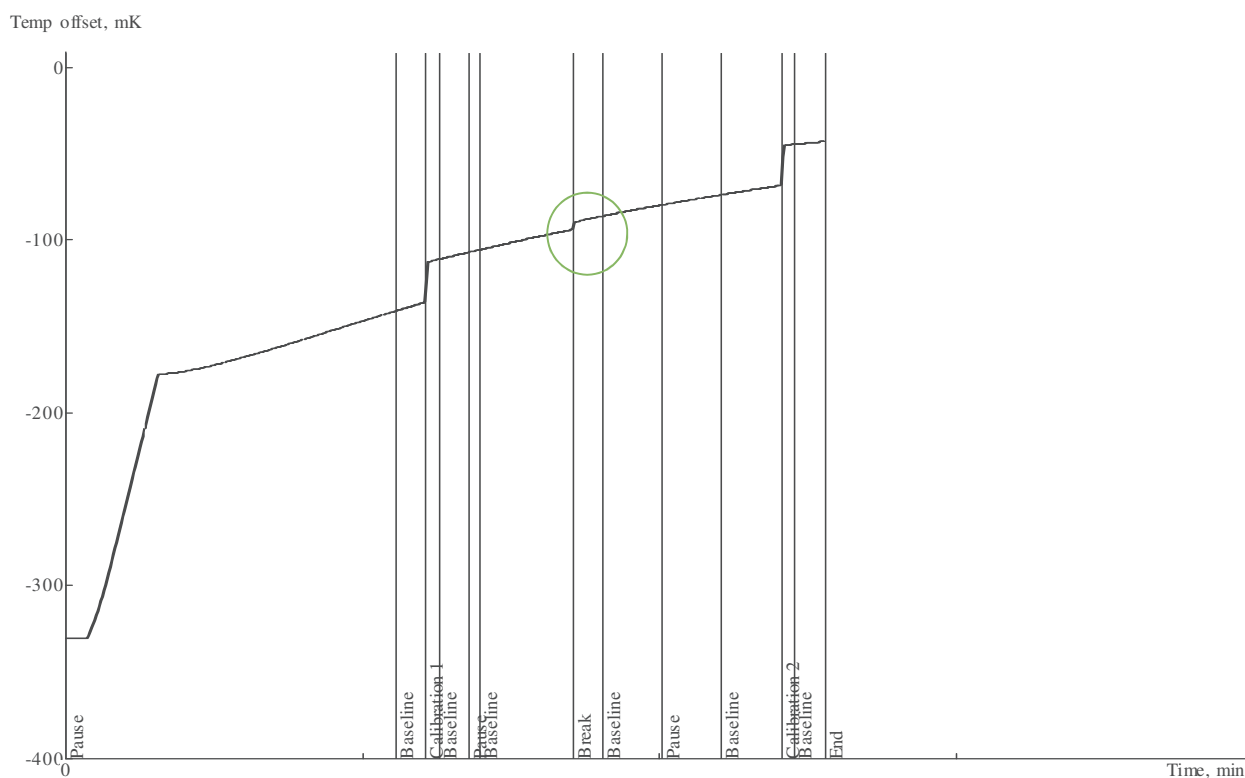


Figure 1 Result from solution calorimetry for dissolution of lignite HA at 35 °C

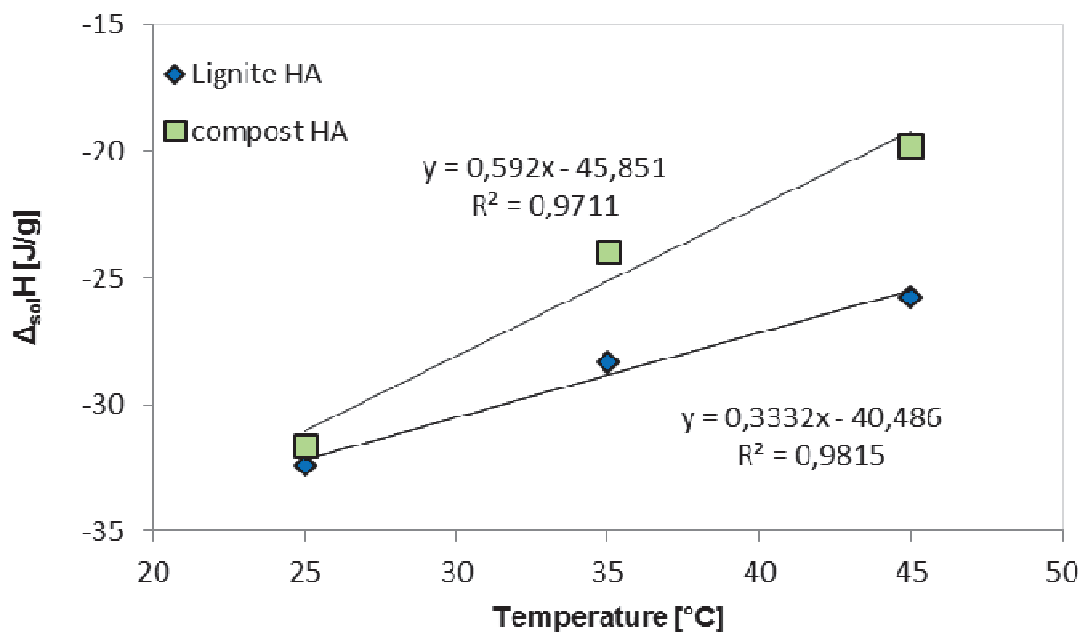


Figure 2 Dependence of dissolution enthalpy on temperature (25 °C to 45 °C)

The data for lignite HA and compost HA showed linear decrease of (the absolute value of) measured enthalpy with increasing temperature of dissolution in water, cf. **Figure 2**. As it is known, the solubility of humic acids increases with increasing temperature. This should predict and increasing enthalpy at higher temperatures. Considering the observed phenomena together with complexity of humic acids it is hard to resolve which effects predominate in dissolution of humic acids and therefore are responsible for decrease enthalpy with temperature increase. Received data are shown in **Table 1**.

Table 1 Dissolution enthalpy from solution calorimetry (TAM III, TA Instruments)

Reaction	$\Delta_{\text{sol}}H$ [J/g]	Reaction	$\Delta_{\text{sol}}H$ [J/g]
Lignite HA + water (25 °C)	-32.419	Compost HA + water (25 °C)	-31.640
Lignite HA + water (35 °C)	-28.296	Compost HA + water (35 °C)	-23.952
Lignite HA + water (45 °C)	-25.755	Compost HA + water (45 °C)	-19.870

4. CONCLUSION

The heat of dissolution of lignite humic acid, compost humic acid in water was determined experimentally. The values of dissolution enthalpies in both cases indicate that the dissolution is exothermal processes. From results we can see dependence on the temperature. With increasing temperature the decrease of dissolution enthalpy can be observed. It means that endothermic part of solution is increasing during dissolution.

ACKNOWLEDGEMENTS

This work was supported by project Nr. LO1211, Materials Research Centre at FCH BUT-Sustainability and Development (National Programme for Sustainability I, Ministry of Education, Youth and Sports).

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