IUFoST 2006
DOI: 10.1051/IUFoST:20060665

Determining the State Diagram of a frozen aqueous solution by stepwise DSC: validating the method

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Abstract

Differential Scanning Calorimetry (DSC), while an important calorimetric technique, well able to identify temperatures of significance, suffers from the drawback of uncertain instrumental thermal lags. As a result, the enthalpy-temperature profile is distorted. This is most evident upon inspection of DSC traces of the phase transition of a pure substance, such a smelting.. While the melting occurs at constant temperature, the DSC trace appears to show melting over a temperature range. It is therefore dangerous to overanalyze the apparent dependence of enthalpy upon temperature obtained from any scanning DSC technique. Stepwise DSC (Kerr and Reid, 1994), which determines total heat flow in a series of small steps between isothermal holding conditions provides a more accurate enthalpy-temperature profile. Stepwise DSC has been applied to the determination of the state diagrams of some aqueous carbohydrate solutions. Validation has been provided by calculating the enthalpy-temperature curve for each individual sample, expressed in terms of the enthalpy per standard mass of solute per step, and comparing the results for solutions of different concentration..

Glucose, maltose and sucrose solutions of initial concentration 10, 20, 30, 40% solute by mass have been studied. The results show that, in a warming protocol, solutions of the same solute produce results that track up to the point at which no further ice is present in the particular sample under study. This confirms that the unfrozen phase, in the presence of ice, is the same for all starting compositions held at the same subfreezing temperature, and thus confirms the validity of the technique. The enthalpy difference per gram solute for different solutions correlates well with the difference in water content per gram solute. Using a simple procedure, the amount of ice present at each subfreezing temperature can be calculated for each sample, and hence the unfrozen phase composition can be calculated. The plotted state diagrams provide greater confidence in the melting curve, and also on the location of the lower temperature transitions associated with amorphous state transformations.

Keywords DSC , aqueous, phase diagram, frozen

Introduction

Conventional differential scanning Calorimetry (DSC), unfortunately, provides only a distorted representation of the heat flows, and hence enthalpies, as a function of temperature as a sample is heated or cooled. This is apparent if one considers the traces obtained for melting of a pure material. Phase diagrams, therefore, are usually obtained from a multiplicity of experiments on a range of concentrations of the solution of interest. In theory, if the distortions of the conventional DSC scan could be eliminated, information could be obtained from the true temperature dependence of the enthalpy. It should also be noted that the distortions of the typical scan, evidenced by the distorted shape of a pure melting peak, provide evidence that a DSC does not provide a linear response record of the thermal event it is assumed to be tracking. This throws doubt upon the efficacy of techniques such as modulated DSC that incorporate linear transform mathematics into their data analysis routines..

A power compensated DSC, such as those marketed by Perkin Elmer Inc, can be operated in an alternative heating mode, in which alternate temperature jumps and isothermal holds are applied. If total heat flow is monitored, and also if the isothermal hold time is long enough to re-establish steady state, then each of these 2-stage cycles can be repeated many times, producing a program of small temperature steps between isothermal plateaus. The net heat flow for each of these “step and hold” instructions can be measured and recorded. Assuming each step to be 1K, then a plot can be made of step heat flow against temperature. A baseline can be produced by using empty pans, and , by subtraction, the step heat flow for any sample can be plotted as a function of temperature (Kerr and Reid 1994) The resulting data prove to be a good measure of the effective heat capacity of the sample for each 1K step. The cumulative sum is thus a plot of the sample enthalpy increase from the starting temperature. The data obtained for aqueous glucose, sucrose and maltose confirm that this is indeed the case, and these data have been analyzed to validate the appropriateness of this procedure to study the enthalpies associated with the heating (and melting) process.

Reference

Kerr, W.L., and D.S. Reid. Nov. 1994. The use of stepwise differential scanning calorimetry for thermal analysis of foods. Thermochimica Acta 246(2):299-308.