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Enthalpy of Sorption by Glassy Polymers

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ABSTRACT

Thermodynamics and molecular mechanisms of sorption of gases and liquids by glassy polymers and are still not fully understood. In particular, the enthalpy of sorption (or mixing) in the glassy state – a parameter crucial for understanding the thermodynamics of sorption is not properly described by existing approaches. In this work, we propose a thermodynamic theory that describes the effect of the glass transition on the enthalpy of sorption. Firstly, a rigorous thermodynamic expression for the sorption enthalpy is presented, and then equations applicable for practical calculations are derived using certain approximations. The theory presented here is tested on the experimental water sorption data on starch and cellulose. The equations describing the hydration enthalpy are in excellent agreement with experimental data. Remarkably, the glass transition-induced apparent heat capacity change for water in carbohydrate polymers turned out to be negative. Being counterintuitive, this result can however be supported by re-evaluation of the literature data on heat capacities of the starch-water system.

1. INTRODUCTION

Glassy state is very common in synthetic and natural polymers and also in low-molecular weight compounds. Despite many decades of intensive research and importance for practical applications, properties of the glassy state are still not fully understood. Perhaps one of the least clear aspects of the glassy state is sorption of gases and liquids by glassy materials. It is known from experimental studies that glassy polymers absorb higher amounts of absorbates compared to what can be expected from the properties of the same materials in rubbery state. Moreover, a pronounced sorption-desorption hysteresis is observed in glassy materials. The first approach proposed for description of sorption of gases by glassy polymers is the dual-mode theory^{1,2}. In this approach, the total absorbed amount is given as a sum of Langmuir isotherm and Henry's law terms, where the former corresponds to "hole filling". The concept of hole filling however contradicts experimental data on comparison between sorption of water and nitrogen in biopolymers, such as cellulose³. In particular, cellulose absorbs two orders of magnitude more water than nitrogen, indicating that the holes (corresponding to the size of gas molecules) are not initially present in the material, but are created by the absorbed gas.

Among other theories used for description of sorption of gases by glassy materials, one can mention a model that considers glass as a system with mechanical deformation⁴. In this approach, sorption into elastic solid is presented as consisting of two processes: solid deformation followed by mixing with the penetrant. Another theory is based on the statistics of gas dissolved in a solid matrix with sites that can be occupied at most one solute molecule⁵. The dual-mode theory can be obtained as a particular case of this approach and the authors suggest that "preexisting holes" are not needed for validity of the expression of dual-mode theory. Among more recent models, one can mention the nonequilibrium thermodynamics for glassy

polymer (NET-GP) approach in combination with lattice fluid equation of state⁶. This model was used to analyze the effect of sample history on the sorption properties⁶.

Probably the most established approach for description of sorption in the glassy state is the free-volume theory⁷⁻⁹. Unlike the dual-mode theory, it does not assume existence of holes, but rather considers specific volumes of liquid and glassy polymers. For description of sorption isotherms, the free volume theory uses the Flory-Huggins equation modified with an additional term dependent on the heat capacity difference and the glass transition temperature of the polymer-penetrant mixture⁸. An expression for sorption enthalpy was also obtained using this approach and it correctly predicts more exothermic enthalpy of dissolution of a gas in a glassy polymer compared to a rubbery polymer.

The sorption enthalpy is a key parameter for understanding the interactions of a gas or liquid with a polymer in a glassy state. When expressed as the enthalpy of mixing $\Delta H^m = \Delta H^{\text{sorp}} - \Delta H^{\text{cond}}$, (where ΔH^{cond} is the enthalpy of condensation of gas into pure liquid) it characterizes the deviations of the polymer – penetrant system from the ideal behavior. Accurate measurements of sorption enthalpies is however a great experimental challenge. Usually the enthalpies are measured from the temperature dependences of vapor pressures of the penetrants. The differentiation procedure results in relatively high uncertainties in the enthalpies and typically no concentration dependences of the enthalpies are reported from such measurements. This situation has however been changed when the method of sorption calorimetry has been proposed¹⁰. The main feature of the method is the simultaneous measurement of the sorption isotherm and the sorption enthalpy with high resolution. Sorption calorimetry has been applied for studies of water sorption by natural^{3, 11-13} and synthetic¹⁴ polymers, proteins¹⁵⁻¹⁷ and other substances. One of the most interesting results obtained in these studies was an observation that

the hydration enthalpy (the partial molar enthalpy of mixing of water H_1^m) in the dry polymer limit was around -18 kJ/mol for several carbohydrate polymers independently on their properties such as presence or absence of ionic groups^{3, 12, 13}. The dependence of the hydration enthalpy on water content was however different for different polymers. Even though the absence of the effect of ionic groups on hydration enthalpy was explained by *ab initio* quantum calculations¹², there is no theory that describes the dependence of the hydration enthalpy on water content and the “universal” hydration enthalpy value in the dry limit.

In this article, we propose a thermodynamic theory that describes the effect of glass transition on the enthalpy of sorption. In our approach, we do not use extrathermodynamic or structural assumptions and derive a model that contains only thermodynamic parameters that can be obtained from measurements of thermodynamic properties. The text below is organized as follows. A rigorous thermodynamic expression for the mixing enthalpy is derived in sections 2.1-2.2. Then in sections 2.3 and 2.4, equations applicable for practical calculations are derived using linear approximations for heat capacities and the Gordon-Taylor approximation for the glass transition temperature. Finally, in section 3.1 and 3.2 the equations are applied for description of experimental data on hydration of starch and cellulose.

2. THERMODYNAMIC THEORY OF MIXING ENTHALPY IN GLASSY POLYMERS

2.1. Thermodynamic cycle of glass transition

We consider a thermodynamic cycle consisting of two isothermal and two non-isothermal steps starting from the initial state (labeled as “0” in Figure 1) characterized by a certain initial temperature T and zero concentration of solute. The transition from “0” to “3” corresponds to sorption in the glassy state at constant temperature T and final solute amount n_1 . According to

the cycle, the same final state can be achieved by heating the polymer above its glass transition temperature T_{g2} , isothermal mixing at this temperature and subsequent cooling back to initial temperature T (Figure 1).

Figure 1. The thermodynamic cycle. The blue curve shows the glass transition temperature as a function of the solute content.

Let n_1 be the number of moles of solute in the mixture in the final state. Then, the final concentration of solute will be

$$w_1 = \frac{M_1 n_1}{M_1 n_1 + M_2 n_2} \quad (1)$$

Here, M_1 and M_2 are the molar masses of the solute and polymer, respectively. During all steps of the cycle, the number of moles of polymer n_2 remains constant.

The non-isothermal path $0 \rightarrow 1 \rightarrow 2 \rightarrow 3$ consists of three stages (see Figure 1), and each of them is characterized by the corresponding enthalpy increment. On the first stage (heating of the two pure components up to the glass transition temperature of the polymer T_{g2}), the enthalpy increment is given by

$$\Delta H_{01} = n_2 \int_T^{T_{g2}} C_{p2}^{g0} dT + n_1 \int_T^{T_{g2}} C_{p1}^{l0} dT \quad (2)$$

where C_{p1}^{l0} is the molar heat capacity of water in the liquid state, C_{p2}^{g0} is the molar heat capacity of the pure polymer in the glassy state.

On the second stage (gradual mixing), the enthalpy of the system receives an increment

$$\Delta H_{12} = \int_0^{n_1} H_1^{m,l}(T_{g2}) dn_1 \quad (3)$$

where $H_1^{m,l}(T_{g2})$ is the partial molar enthalpy of mixing at the transition temperature T_{g2} .

On the third stage of the first cycle (cooling the mixture down to the initial temperature T), the enthalpy increment is

$$\Delta H_{23} = (n_1 + n_2) \int_{T_{g2}}^T C_p dT \quad (4)$$

where C_p is the molar heat capacity of the mixture.

The second path represents isothermal mixing of n_1 number of moles of solute with n_2 number of moles of polymer, so that the enthalpy of the system receives an increment

$$\Delta H_{03} = \int_0^{n_1} H_1^{m,g}(T) dn_1 \quad (5)$$

where $H_1^{m,g}(T)$ is the partial molar enthalpy of mixing at the initial temperature.

Under the assumption of thermal equilibrium, we have $\Delta H_{03} = \Delta H_{01} + \Delta H_{12} + \Delta H_{23}$, from where it immediately follows that

$$\Delta H_{03} - \Delta H_{12} = \Delta H_{01} + \Delta H_{23} \quad (6)$$

Where the transition shown in eq 4, can be further divided into two steps:

$$\Delta H_{23} = -(n_1 + n_2) \left(\int_{T_{gm}}^{T_{g2}} C_p^l dT + \int_T^{T_{gm}} C_p^g dT \right) \quad (7)$$

2.2. Partial molar enthalpy of mixing

Now, by using Leibniz's rule for differentiation, we differentiate both sides of eq 6 with respect to the variable parameter n_1 and derive for the difference between enthalpies of sorption in the glassy and the liquid states $\Delta H_1^m = H_1^{m,g}(T, n_1) - H_1^{m,l}(T_{g2}, n_1)$ the following equation:

$$\begin{aligned} \Delta H_1^m = & \int_T^{T_{g2}} C_{p1}^{l0} dT + (n_1 + n_2) \left(C_p^l(T_{gm}) - C_p^g(T_{gm}) \right) \frac{\partial T_{gm}}{\partial n_1} \\ & - \int_{T_{gm}}^{T_{g2}} \left(C_p^l + (n_1 + n_2) \frac{\partial C_p^l}{\partial n_1} \right) dT - \int_T^{T_{gm}} \left(C_p^g + (n_1 + n_2) \frac{\partial C_p^g}{\partial n_1} \right) dT \quad (8) \end{aligned}$$

Note that formulas 2 and 7 were utilized in deriving eq 8.

2.3. Approximation for the heat capacity of mixing

Most often, accurate experimental data on heat capacities of liquid and especially glassy mixtures are not available. Therefore, following the established practice for calculations of heat capacities and heat capacity changes for mixtures^{18, 19}, we assumed linear dependencies of heat capacities on compositions:

$$C_p^l = C_{p1}^{l0} x_1 + C_{p2}^{l0} x_2, \quad C_p^g = C_{p1}^{g0} x_1 + C_{p2}^{g0} x_2 \quad (9)$$

where $x_1 = n_1/(n_1 + n_2)$ and $x_2 = n_2/(n_1 + n_2)$ are the mole fractions of solute and polymer, respectively. The heat capacities with superscript “0” can be either heat capacities of pure substances, or (see discussion below) apparent heat capacities of the substances $C_{pi}^\emptyset$.

Differentiating eqs 9 with respect to the number of moles n_1 , we readily find

$$\frac{\partial C_p^l}{\partial n_1} = \frac{n_2}{(n_1 + n_2)^2} (C_{p1}^{l0} - C_{p2}^{l0}), \quad \frac{\partial C_p^g}{\partial n_1} = \frac{n_2}{(n_1 + n_2)^2} (C_{p1}^{g0} - C_{p2}^{g0}) \quad (10)$$

Using the fact that differentiation of eq 1 gives following result:

$$\frac{dw_1}{dn_1} (n_1 + n_2) = w_1 w_2 + w_2^2 \frac{M_1}{M_2} \quad (11)$$

we can write

$$\Delta H_1^m = \int_T^{T_{gm}} \Delta C_{p1}^0 dT + \frac{\partial T_{gm}}{\partial w_1} \Delta C_p(T_{gm}) \left(w_1 w_2 + w_2^2 \frac{M_1}{M_2} \right) \quad (12)$$

where

$$\Delta C_p(T_{gm}) = x_1 \Delta C_{p1}^0(T_{gm}) + x_2 \Delta C_{p2}^0(T_{gm}) \quad (13)$$

For practically important situation when w_1 tends to zero, this equation reduces to

$$\Delta H_1^{m0} = \int_T^{T_{g2}} \Delta C_{p1}^0 dT + \frac{\partial T_{gm}}{\partial w_1} \Delta C_{p2}^0 \frac{M_1}{M_2} \quad (14)$$

2.4. Gordon–Taylor approximation for the glass transition temperature

Recall that the Gordon–Taylor approximation is given by the simple formula

$$T_{gm} = \frac{T_{g1} w_1 + \kappa T_{g2} (1 - w_1)}{\kappa + (1 - \kappa) w_1} \quad (15)$$

where T_{g1} and T_{g2} are the glass transition temperatures of the pure substances, and κ is the

Gordon–Taylor fitting parameter. The differentiation of eq 15 yields

$$\frac{\partial T_{gm}}{\partial w_1} = - \frac{\kappa (T_{g2} - T_{g1})}{(\kappa + (1 - \kappa) w_1)^2} \quad (16)$$

Thus, eq 12 can be presented in the following form:

$$\Delta H_1^m = \int_T^{T_{gm}} \Delta C_{p1}^0 dT - \frac{\kappa (T_{g2} - T_{g1})}{(\kappa + (1 - \kappa) w_1)^2} \left(w_1 w_2 + w_2^2 \frac{M_1}{M_2} \right) \Delta C_p(T_{gm}) \quad (17)$$

3. RESULTS AND DISCUSSION

3.1. Approximation for the partial molar enthalpy of mixing of solute

For many polymer systems, molecular masses are not well defined and it is more convenient to work with heat capacities expressed per polymer mass. Then if the heat capacities are expressed in J/K/g, then we can introduce the notation

$$C_{p1}^{l0} = M_1 c_{p1}^{l0}, \quad C_{p1}^{g0} = M_1 c_{p1}^{g0} \quad (18)$$

$$\Delta c_{p1}^0(T) = \frac{1}{M_1} (C_{p1}^{l0}(T) - C_{p1}^{g0}(T)), \quad \Delta c_{p2}^0(T) = \frac{1}{M_2} (C_{p2}^{l0}(T) - C_{p2}^{g0}(T)) \quad (18a)$$

Then the change of heat capacity per mole of mixture ΔC_p can be expressed through the changes of heat capacities of pure components and mass fractions of the components as follows:

$$\Delta C_p = \Delta C_{p2}^0 + \frac{w_1(\Delta C_{p1}^0 - \Delta C_{p2}^0)}{w_1 + w_2 \frac{M_1}{M_2}} \quad (19)$$

Then, in view of eq 19, we can represent eq 17 as follows:

$$\frac{\Delta H_1^m}{M_1} = \int_T^{T_{gm}} \Delta c_{p1}^0 dT - w_2 \frac{\kappa(T_{g2} - T_{g1})}{(\kappa + (1 - \kappa)w_1)^2} (w_1 \Delta c_{p1}^0(T_{gm}) + w_2 \Delta c_{p2}^0(T_{gm})) \quad (20)$$

A practical interest represents the limit situation as w_1 tends to zero, when the difference between the enthalpies of sorption is equal to $\Delta H_1^{m0} = H_1^{m,g}(T, 0) - H_1^{m,l}(T_{g2}, 0)$ and eq 20 takes the form

$$\frac{\Delta H_1^{m0}}{M_1} = \int_T^{T_{g2}} \Delta c_{p1}^0 dT - \frac{T_{g2} - T_{g1}}{\kappa} \Delta c_{p2}^0 \quad (21)$$

A further simplification can be achieved by employing a constant approximation for the integrand:

$$\frac{\Delta H_1^m}{M_1} = \Delta c_{p1}^0(T_{gm} - T) - w_2 \frac{\kappa(T_{g2} - T_{g1})}{(\kappa + (1 - \kappa)w_1)^2} (w_1 \Delta c_{p1}^0(T_{gm}) + w_2 \Delta c_{p2}^0(T_{gm})) \quad (22)$$

Correspondingly, substituting the value $w_1 = 0$ into the above equation, we obtain for the limiting case

$$\frac{\Delta H_1^{m0}}{M_1} = \Delta c_{p1}^0(T_{g2} - T) - \frac{T_{g2} - T_{g1}}{\kappa} \Delta c_{p2}^0 \quad (23)$$

The expressions for the partial molar enthalpy of mixing shown above, e.g. eqs 12, 20, 22 show the difference between the enthalpies that are expected in the glassy state at temperature T and in liquid at temperature T_{g2} . It can be shown that if linear approximations (eq 9) are valid, then the enthalpy change at the step $1 \rightarrow 2$ ΔH_{12} is equal to the enthalpy change at the step $0 \rightarrow 3$ in a hypothetical case of the absence of the glass transition $\widetilde{\Delta H_{03}}$. Then the values of ΔH_1^m shown above can be interpreted as the difference between the partial molar mixing enthalpy observed in the glassy state compared to hypothetical case of sorption by liquid polymer at the same temperature. Furthermore, for many systems the enthalpy of mixing in the liquid state is much lower (i.e. closer to zero) than the enthalpy of mixing in the glassy state. Hence the equations presented above can be reasonably good approximations for the partial molar enthalpies of mixing of solutes in the glassy state:

$$\Delta H_1^m \approx H_1^m \quad (24)$$

3.2. Application to experimental data

Eq 22 can be used to describe experimental data obtained by, for example, sorption calorimetry. The dependence of the partial molar enthalpy on water content in this equation is

however nonlinear, therefore a nonlinear least-squares solver implemented in MATLAB was used for fitting the experimental data. Hydration enthalpy data in the glassy regions for two starch^{11, 20} and two cellulose³ materials were selected for fitting. In all four cases the fitting was nearly perfect, see an example for acid-hydrolyzed starch in Figure 2.

Figure 2. The partial molar enthalpy of mixing of water in the acid hydrolyzed starch - water system. Black curve – experimental data¹¹, stars – experimental data points selected for fitting, red curve – fitting using eq 22.

The results of the fitting showed that identical fitting curves can be produced for different combinations of T_{g2} and Δc_{p2}^0 parameters, therefore one of these parameters should be fixed (taken from literature) and the other one obtained in the fitting procedure. We chose to fix T_{g2} , on which literature data are available for these systems. The values of Δc_{p2}^0 for starch obtained in fitting (see Table 1) are in good agreement with literature data on this polymer (0.30 J/K/g²¹),

which lends further credibility the presented approach. Moreover, obtained values of parameter k are also in good agreement with literature value of 0.1546²¹ (note that the value of κ is dependent on the form of Gordon–Taylor equation; for comparison with cases when the Gordon–Taylor factor k is associated with T_{g1} , its reciprocal value should be used, i.e., $\kappa = 1/k$).

Table 1. Fitting parameters for four different carbohydrate polymers (eq 22). Concentration range used for fitting was 0.5–12 wt% water. Values of T_{g2} are taken from literature^{21, 22}. The value of T_{g1} is 136K²³.

	T_{g2} , K	Δc_{p1}^0 , J/K/g	Δc_{p2}^0 , J/K/g	κ
Starch microspheres	568.75 ²¹	-0.702	0.305	0.185
Acid hydrolyzed starch	568.75 ²¹	-0.746	0.297	0.150
Microcrystalline cellulose	526 ²²	-0.973	0.184	0.0798
Ball-milled cellulose	478 ²²	-0.108	0.536	0.183

The value of the polymer heat capacity change obtained for microcrystalline cellulose is lower than other values. This reflects the fact that only a part of the material is in the glassy state, the rest is in crystalline state where the glass transition does not occur. Also, the value of κ for microcrystalline cellulose is lower than that for other materials, indicating stronger deviation of the glass transition curve from the straight line connecting the glass transition temperatures of the two components. This can be explained by the fact that less water is needed to plasticize the material, if only a part of it is in the amorphous state. Thus, the proportional decrease in both Δc_{p2}^0 and κ compared to fully amorphous materials cancels their effect of the hydration enthalpy

at low water contents, see eq 21, 23. This explains the observed experimental fact that the hydration enthalpy in the dry limit is constant – about -18 kJ/K/mol for several carbohydrate polymers.

Interestingly, the changes of heat capacity of water obtained by the fitting procedure are negative in all four cases. This result may look counterintuitive. Indeed, the change of heat capacity of pure water during its glass transition is usually referred to as 1.94 J/K/g²⁴, although lower values also appeared in literature²⁵. This value cannot however be directly applicable to systems with low water contents, where glass transitions occur at temperatures 300-400 K higher than in pure water and dominating interactions are between polymer and water. Hence, in the linear expressions for ΔC_p , such as eq 13, the heat capacity change at low water contents has a meaning of apparent change of heat capacity ΔC_{p1}^ϕ , which can be different from the value observed in pure water ΔC_{p1}^0 .

Furthermore, the Gordon-Taylor parameter κ is sometimes interpreted in literature as the ratio of heat capacity changes²⁶:

$$\kappa = \Delta c_{p2}^0 / \Delta c_{p1}^0 \quad (25)$$

The meaning of these heat capacity changes is however unclear since the derivation was based on comparison of liquid and crystalline states²⁶. Therefore, we did not assume in the fitting procedure that κ is equal to the ratio of the heat capacity changes, but used it as an independent parameter. The change of heat capacity of water calculated from Eq 25 using values of κ and Δc_{p2}^0 , is around 1.6-2.0 J/K/g for the starch materials and 2.3-2.9 J/K/g for the cellulose materials. This indicates that Δc_{p1}^0 in Eq 25 corresponds to heat capacity change in pure water rather than to apparent heat capacity change in the material at low water content, which has negative values in the considered cases (see Table 1).

As it was mentioned above, heat capacity data for glassy polymer-solute systems are not very common in literature; one of few exceptions is data by Noel and Ring²⁷ for amorphous amylopectin. They presented a data for heat capacities in the glassy and in the liquid states at 298K, see Figure 3. We approximated both data sets by straight lines (although one should expect a linear dependence for the glassy state only at relatively low water contents and not in the whole range of concentrations since the heat capacity of pure water in the glassy state is about 1.1 J/K/g²⁴). The difference between the heat capacities is shown as a straight line in Figure 3, which can be represented by the following equation:

$$\Delta c_p = -0.940 \cdot w_1 + 0.506 \cdot w_2 \quad (26)$$

Hence $\Delta c_{p1}^\emptyset$ value of -0.940 J/K/g obtained from the data by Noel and Ring²⁷ is negative and is in a similar range as the data shown in Table 1.

Figure 3. Heat capacity in amorphous amylopectin – water system at 298K, data points graphically taken from ref²⁷. Black squares represent glassy state, blue circles – liquid state, a diamond shows a point close to the glass transition. The dashed line for ΔC_p shows the difference between heat capacities in the liquid and in the glassy states.

The theory presented here shows the origin of the exothermic heat effect of sorption by glassy polymers as well as the dependence of the sorption enthalpy on the solute content. This dependence links the isothermal calorimetric sorption data with the parameters typically used to describe glass transition behavior of polymers. Moreover, it can be used as an alternative method for evaluation of glass transition parameters when they are not experimentally accessible, due to for example, chemical degradation at high temperatures. The main area of application of the theory presented here is sorption of water (and other solutes) by polymers. In particular, keeping in mind that sorption enthalpy is the parameter that describes the change of vapor pressure with respect to temperature, equations presented here can be used for development of thermodynamic theory of the polymer glassy state alternative to the free volume theory.

4. CONCLUSIONS

- Equations describing the partial molar enthalpy of mixing of solutes with glassy polymers are derived based on thermodynamic approach
- The theoretical approach presented here is in good agreement with literature data on hydration of carbohydrate polymers
- The equations presented here allow calculations of heat capacity changes of solutes and polymers from data on enthalpy of sorption
- For water in glassy carbohydrates, the values of apparent molar heat capacity changes induced by glass transitions are negative at low water contents.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

SUPPLEMENTARY MATERIAL

Supplementary material – derivation of eq. 8 is available online.

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Graphical abstract