

## **Comments on the interpretation of thermodynamic data on swollen hydrogels**

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### Summary

As a reply to the paper of Bowstra et al. (1) the authors summarize their earlier conclusions (2,3,4) concerning the interpretation of data on sorption equilibrium, heats of mixing and heat capacities of water-swollen gels. Two unavoidable premises of correct interpretation are emphasized: (1) accounting for the physical states of the polymer before and after mixing with water, (2) correct choice of the thermodynamic criterion for the stability of water structure and of its interaction with the polymer.

Bowstra et al.(1) found a negative heat of mixing of poly(hydroxyethyl methacrylate) (PHEMA) with water. They used this result for explaining the heat of melting deficit usually encountered in heat capacity measurements of water-swollen hydrophilic gels below 0°C. In a discussion they paraphrased, loosely but not very accurately, the conclusions of our papers (2,3), writing that on the basis of our finding of  $C_p - 0$  we affirm that "no strong interaction occurs between water and polymer" and against this supposed assertion of ours they placed their conclusion that "...a strong enthalpic interaction occurs between a part of the water and the polymer". We feel compelled to show here the non-distorted conclusions of our work (2,3) and to call attention to our another paper (4) (not cited in ref.1), in which we presented the heats of mixing of PHEMA with water five years ago.

In our paper (2,3) we presented the heat capacities of water-swollen gels of poly(hydroxyethoxyethyl methacrylate) (PHEOMA) and poly(hydroxyethyl acrylate)(PHEA); in contradistinction to PHEMA (with  $T_g \sim 370$  K), both these polymers are viscoelastic at room temperature. We concluded that "the structure or bonds (of water) with polar groups of the polymer are thermally labile, similar to the structure of hydrogen bonds in liquid water; hence in this case water cannot be strongly bound". By this statement we objected to an intuitive opinion that the bond of water to hydrogels is so strong as to be virtually irreversible, manifesting itself e.g. by the so-called nonfreezing water. In addition, we analyzed in detail the

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possible causes of the general finding of the heat of melting deficit. We have also shown that the heat of melting obtained by integration of the  $C_p$  melting peak corresponds to the transformation of water from the solid state to the liquid mixture with the polymer and differs from the heat of melting by the respective heat of mixing. In the paper (4), evidently omitted by Bowstra (1), we presented the changes of Gibbs energy, enthalpy and entropy on mixing of PHEOEMA and PHEMA with water, calculated from our experimental data on the heats of mixing and on sorption isotherms. In a discussion we have shown that the molecular origin of the heat and entropy of mixing with PHEMA, as a glassy (i.e., internally nonequilibrium and thermodynamically unstable) polymer, is in principle different from that with PHEOEMA, which is a viscoelastic (equilibrium and from the thermodynamic point of view liquid) polymer. In the case of PHEMA almost the whole heat effect is due to transformation between two physical states and has no direct relation to the hydrophilicity of the polymer. It is therefore not advisable to confront data for PHEMA with those for PHEOEMA in the way used in ref.1. Generally, the thermodynamic parameters of water related to the glassy polymer must not be used as a basis for considerations about the state of water in sufficiently swollen, i.e., elastic gels. From ref.4 it follows further that the appropriate criterion for the strength (i.e. stability) of the bond of water to polymer is the change of Gibbs energy, whereas the partial heat capacity of water in polymer is an indicator of this stability with increasing temperature (2,3). The enthalpy and entropy changes can indicate some degree of immobilization or structure formation. In the case of both polymers studied, for different reasons in each case, the enthalpy and entropy increments to Gibbs energy compensate extensively each other. Accordingly, what is called in ref.1 "a strong enthalpic interaction" does not in fact represent a really strong, thermodynamically stable bond.

### References

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