Thermochimica Acta, 119 (1987) 47–51
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

ENTHALPIES OF SOLUTION OF POLYVINYLALCOHOL IN WATER AND POLYVINYLACETATE IN DIOXANE

PETER SCHNEIDER AND ANDREAS HEINTZ

Physikalisch-Chemisches Institut der Universität Heidelberg
Im Neuenheimer Feld 253, D-6900 Heidelberg

SUMMARY

Heats of solution of Polyvinylalcohol (PVA) and Polyvinylacetate (PVAc) in Water and Dioxane have been measured by using an isothermal titration calorimeter. The χ_H- parameter of the Flory-Huggins-theory has been evaluated from the calorimetric data. The system PVA + H_2O shows negative χ_H - values and the system PVAc + Dioxane shows positive χ_H - values corresponding to exothermic and endothermic heats of dilution repectively.

EXPERIMENTAL PROCEDURE

The heat of dilution absorbed or delivered by addition of a certain amount of solvent to a well known quantity of a mixture of defined composition of polymer + solvent has been measured using a titration calorimeter (Tronac 1250). The calorimetric measurements have been conducted at 298.15 K in a quasi isothermal process. The reaction vessel (~25 ml) of the calorimeter where the dilution process takes place is shown schematically in Fig.1.
It is immersed in a large external waterbath (~100 l) (not shown in Fig.1) where the temperature is controlled to within $\pm\ 0.5 \cdot 10^{-4}$ K. By means of a precision buret (PB) titration can be conducted continuously by adding solvent with a titrant tube (TT) to the polymer solution in the reaction vessel. A Peltier cooler (PH) in the bottom of the reaction vessel removes energy from the solution at a constant rate. A controlled heater (PH) compensates for this energy and for the energy librated or absorbed by the mixing process maintaining the solution in the reaction vessel at constant temperature. This temperature is practically identical with the reference temperature in the external water bath.
The difference of the compensating heating power during and before the mixing process is a direct measure of the heat of mixing.

0040-6031/87/$03.50

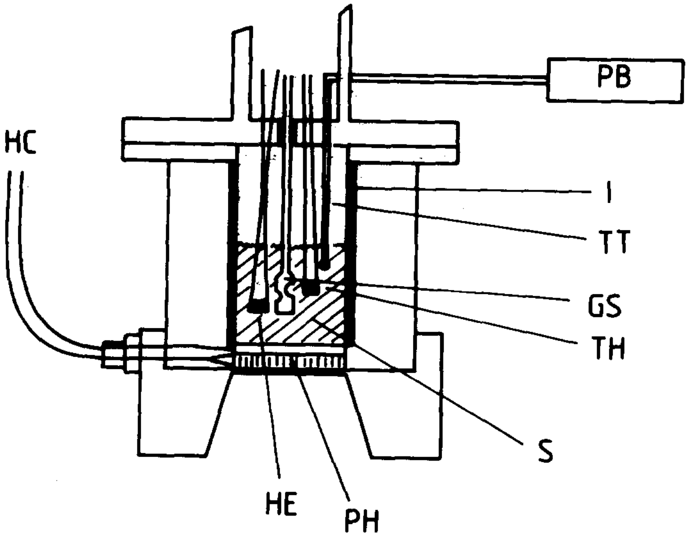

Fig.1. Schematic diagram of the calorimetric reaction vessel. HC= Heater and cooler leads, HE= Calibration heater, TT= Titrant tube, GS= Glass stirring rod, TH= Monitor and control thermistors, PB= precision buret and reservoir of solvent or solution, PH= Peltier cooler and control heater, S= Polymer solution or pure solvent, I= Heat insulation.

A glass stirring rod (GS) assures a homogeneous temperature within the solution. Using the calibration heater (HE), a well defined energy can be generated thus making the calibration of the whole system possible.

RESULTS AND DETERMINATION OF THE χ_H - PARAMETER

Integration of the heat rate of mixing over the time interval where the titration process occurs, gives the total heat of mixing ΔQ absorbed or delivered during the titration run. ΔQ is related to the partial molar enthalpy of dilution ΔH_1 by the following equation:

$$\Delta Q = \int_{\Phi_{2i}}^{\Phi_{2,f}} \Delta H_1 \, dn_1 \qquad (1)$$

where n_1 is the number of moles of component 1 (solvent H_2O or Dioxane) and Φ_{2i} and Φ_{2f} are the initial and final volume fractions of component 2 (polymer PVA or PVAc) in the reaction vessel. The definition of Φ is given by

$$\Phi_2 = \frac{w_2 \cdot v_{sp2}}{w_1 \cdot v_{sp1} + w_2 \cdot v_{sp2}} = 1 - \Phi_1 \qquad (2)$$

where $w_2 = 1 - w_1$ is the weight fraction of the polymer in the solution and v_{sp2} and v_{sp1} are the specific volumes of the polymer and solvent respectively.
Using the terminology of the Flory-Huggins-theory with

$$\Delta H_1 = \chi_H \cdot R \cdot T \cdot \Phi_2^2 \qquad (3)$$

integration of eq.(1) may be performed assuming χ_H to be a constant:

$$\Delta Q = R \cdot T \cdot \chi_H \cdot \Phi_{2i} \cdot \Phi_{2f} \cdot \Delta n_1 \qquad (4)$$

where Δn_1 is the number of moles of the solvent added to the reaction vessel during the titration process.

Besides of these dilution experiments measurements have also been made by titrating polymer solutions to the reaction vessel containing pure solvent before the titration process starts. In this case an equation similar to eq.(4) can be obtained by considering three solutions A, B, and F characterized by the volume fractions Φ_{1A}, Φ_{1B}, Φ_{1F} respectively. F is generated by mixing A and B. The heat effect ΔQ associated with this mixing process is:

$$\Delta Q = Q_F - Q_A - Q_B \qquad (5)$$

where Q_A, Q_B, and Q_F are defined as the integral heats of solution of the polymer amounts Δn_{2A}, Δn_{2B}, and Δn_{2F} in the solvent corresponding to volume fractions Φ_{2A}, Φ_{2B}, Φ_{2F} respectively.
In the framework of the Flory-Huggins-theory the following equations are obtained with $(r_2/r_1) = v_{sp2} \cdot M_2 / v_{sp1} \cdot M_1$:

$$Q_A = \int_{\Phi_{1i}=1}^{\Phi_{1A}} \Delta H_2 \cdot dn_{2A} = R \cdot T \cdot \Phi_{1A} \cdot \Delta n_{2A} \cdot (r_2/r_1) \cdot \chi_H \tag{6}$$

$$Q_B = \int_{\Phi_{1i}=1}^{\Phi_{1B}} \Delta H_2 \cdot dn_{2B} = R \cdot T \cdot \Phi_{1B} \cdot \Delta n_{2B} \cdot (r_2/r_1) \cdot \chi_H \tag{7}$$

$$Q_F = \int_{\Phi_{1i}=1}^{\Phi_{1F}} \Delta H_2 \cdot dn_{2F} = R \cdot T \cdot \Phi_{1F} \cdot \Delta n_{2F} \cdot (r_2/r_1) \cdot \chi_H \tag{8}$$

Substituting eqs.(6-8) into eq.(5) gives:

$$\Delta Q = R \cdot T \cdot \chi_H \cdot (\Phi_{1F} \cdot \Delta n_{2F} - \Phi_{1A} \cdot \Delta n_{2A} - \Phi_{1B} \cdot \Delta n_{2B}) \cdot (r_2/r_1) \tag{9}$$

or expressed by the mass amounts Δm of polymer:

$$\Delta Q = R \cdot T \cdot \chi_H \cdot \frac{v_{sp2}}{M_1 \cdot v_{sp1}} \, (\Phi_{1F} \cdot \Delta m_{2F} - \Phi_{1A} \cdot \Delta m_{2A} - \Phi_{1B} \cdot \Delta m_{2B}) \tag{10}$$

M_1 in eq.(10) is the molar mass of solvent. Δm_{2F}, Δm_{2A}, and Δm_{2B} are the masses of polymer in the final solution, in the reaction vessel before starting the titration process, and in the solution of the buret delivered to the reaction vessel respectively.
Eq.(10) can be used for evaluating χ_H from measured values of ΔQ.
χ_H parameters obtained from dilution experiments (eq.(4)) and those obtained by titrating polymer solution to the pure solvent

(eq.(10)) are represented graphically in Fig.2.

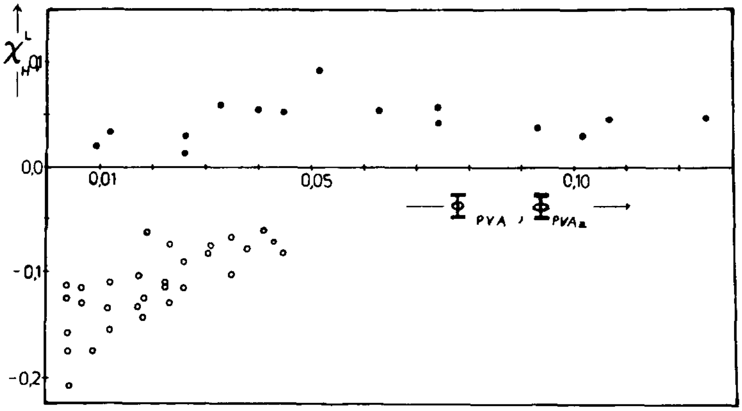

Fig.2. χ_H parameter as function of volume fractions Φ_{PVA}, Φ_{PVAc} obtained by calorimetric measurements. ● = χ_H for PVAc + Dioxane, ○ = χ_H for PVA + H_2O at 298.15 K.

The concentration range covered by the experiments is limited to relatively low polymer volume fractions according to the fact that solutions with higher polymer concentrations have too high viscosities. This causes instabilities in the temperature control system of the reaction vessel leading to oscillations of the compensating heating power of the control heater.

The results, however, show clearly that heats of dilution of PVA + H_2O are exothermic with negative χ_H parameters and those of PVAc + Dioxane are endothermic with positive χ_H parameters.

The scattering of the data and the limited concentration range do not allow to observe a significant dependence of χ_H of the volume fraction. The average value of χ_H is -0.151 ± 0.05 for PVA + H_2O and $+0.047 \pm 0.02$ for PVAc + Dioxane.