Polymer Bulletin 2, 613–618 (1980)

Polymer Bulletin

On the Possibility of Estimating Weak Interactions of Macromolecules in Solutions from the Experimental Viscous Flow Activation Energies Data

E. P. Varfolomeeva, V. Ya. Grinberg and V. B. Tolstogusov

Institute of Organoelement Compounds, USSR Academy of Sciences, Vavilov St. 28, Moscow B-312, USSR

Summary

The initial viscosity and activation energy in viscous flow of the systems: water(W)-casein(C)-polysaccharide(PS) (gum arabic(G),dextran(D),dextran sulfat (DS)) have been determined for various ionic strengths corresponding to total or limited thermodynamic compatibility of macrocomponents. Excess activation energy ΔH_{η}^{E} due to the protein-polysaccharide interactions has been calculated. It is positive for systems with total compatibility and negative for systems with limited compatibility. Moreover,it yields information on type of the protein-polysaccharide interactions. Negative ΔH_{η}^{E} means that repulsive forces are dominant,while positive ΔH_{η}^{E} means that attractive forces are dominant. Since the properties of the systems W-C-D and W-C-DS are similar, it is believed that C-D complexes can possibly be formed with an energy$\sim$ 2 kT(10 mJ/g).

Introduction

According to the Flory-Huggins theory, the thermodynamic compatibility of two polymers (2 and 3) in a common solvent (1) depends strongly on the configurational energy Δe_{23} characterizing their interactions (SCOTT,1949; TOMPA,1949). In the case of total compatibility, we have $\Delta e_{23} < 2kT$,whereas for limited compatibility with a threshold point$\sim$5%, $\Delta e_{23} \simeq 40$ kT. It is hardly possible to determine such low energies from microcalorimetric data,because it involves the measurement of heat of mixing ca. 1 -100 mJ/g which is the limit of this method's potentiality (MARON andFILISCO,1972).

0170-0839/80/0002/0613/$01.20

Low configurational energies can be determined from the thermorheological data. According to the activation theory of viscosity of simple liquids extended semi-empirically to liquid mixtures (GLASSTONE et al.,1941),the activation energy in viscous flow of a multicomponent mixture is equal to

$$\Delta H_\eta = \sum_i x_i \Delta H_{\eta i} + \Delta H_\eta^E \qquad (1)$$

where x_i and $\Delta H_{\eta i}$ are the molar fraction and activation energy of the i-th component, ΔH_η^E is the excess activation energy due to the interactions of the mixture components.

For many binary mixtures of low-molecular liquids, ΔH_η^E has been found to coincide with the excess heat of mixing (to a constant factor) which is directly related to the configurational energy of interactions of the mixture components (POWELL et al., 1941). This method permits the determination of configurational energy ~1 kT.

The aim of this paper is to examine the feasibility of estimating weak interactions of macromolecules in solutions from the thermorheological data,using by way of example the systems W-C-PS(G,D, DS) with total or limited compatibility of macrocomponents. For limited compatibility systems the experiments were carried out in the one-phase region.

Casein in aqueous solution at pH 6-11 exhibits limited compatibility with gum arabic and total compatibility with dextran and dextran sulfate at low ionic strength ($I \ll 0.01$). Compatibility of casein with dextran and dextran sulfate sharply decreases when $I \gg 0.25$ and $I \gg 1.0$,respectively (ANTONOV et al.,1975;1977).

For pH > 4.9 and low ionic strength,soluble protein-DS complexes are formed as a result of electrostatic interaction of local charges of opposite signs. In a medium with high ionic strength they decompose owing to weaker electrostatic interaction (TOMPSON and MAc KERNAN,1961;TSANG and TOMPSON ,1965;WAINERMAN et al.,1975). Similarity of the influence of ionic strength on complexation and compatibility of casein and dextran sulfate suggests that the affinity of one of these polymers to the other is a measure of their compatibility.

The same cannot be said confidently about the influence of ionic strength on the compatibility of casein and dextran because only some indirect information is available to show that proteins exhibit affinity to dextran at low ionic strength and lose it if $I \geq 0.25$ (ANTONOV et al.,1979).

Experimental

Materials

Sodium salt of Hammersten casein with pH 7.2("Olaine",USSR;$[\eta]$= 0.12 dl/g at I=0.15; $M_{\eta D} \approx 670$ kD);gum arabic (Merck;$[\eta]$=0.155dl/g in 0.2 M NaCl; $M_{\eta} \approx 500$ kD);dextran T-500 ("Pharmacia";$[\eta]$=0.53dl/g; M_W=480 kD); dextran sulfate ("Pharmacia";$[\eta]$=4.7dl/g at pH 7.2 and I=0.01; M_W =980 kD); tris-(hydroxymethyl)aminomethane,NaCl, HCl.

Preparation of Solutions

Sodium salt of casein and polysaccharide were dissolved separately in a "tris"-buffer with pH 7.2 at room temperature. The ionic strength of buffer was controlled by introducing NaCl.Solutions of protein and polysaccharide of equal weight concentrations (c_2 and c_3)were mixed in different weight ratios. Prior to measurements,the solutions were centrifugated at 6000 g for 30 minutes.

Method

The viscosity (η) was measured in a Couette type precision rotary viscosimeter,Model VMV-03N (Special Design Bureau of the Institute of Petroleum Chemical Synthesis, The USSR Academy of Sciences) at shearing stresses of τ =0.1-10 dyn/cm^2 and temperatures of 25-70°C. Temperature fluctuations in the viscosimeter did not exceed $\pm$ 0.1°C. The initial viscosity (η_0) was found by extrapolating the linear curve $\lg\eta_0(\tau)$ to at least $\pm$ 2% accuracy. The value of ΔH_η was determined from the Arrhenius-Frenkel-Eyring equation to $\pm$ 0.8 kJ/mol accuracy:

$$\eta_o(T) = A\ \exp(\Delta H_\eta/RT) \qquad (2)$$

The value of ΔH_η^E was determined at $c_2+c_3=c_s$=const for various $y_2=c_2/c_s$, from the equation:

$$\Delta H_\eta^E(y_2) = \Delta H_\eta(y_2) - (y_2\,\Delta H_{\eta 2}(c_2) + (1-y_2)\,\Delta H_{\eta 3}(c_3)) \qquad (3)$$

where $\Delta H_{\eta i}$ (i=2,3) is the activation energy of protein or polysaccharide solution. This equation is virtually equivalent to Eq(1). Substitution of y_i for x_i does not involve any significant error. The activation energy $\Delta H_{\eta 2}$ of casein solution is almost constant up to about 5% concentration and thereafter increases rapidly at higher concentrations. In the concentration range studied ($c_3 \leqslant 15\%$) the activation energy $\Delta H_{\eta 3}$ of all polysaccharide solutions was the same as the activation energy of water. In view of these data, we took c_s=5% in the determination of ΔH_η^E, because $\Delta H_{\eta i}(c_i \leq 5\%)$ — const (i= 2,3). Under these conditions, however, ΔH_η^E found for W-C-D system at I=0.01 was comparable with the ΔH_η determination error. Therefore ΔH_η^E of this system was determined at c_s=10% with due regard for the dependence $\Delta H_{\eta 2}(c_2)$ (Fig.1, i=2).

Results and Discussion

The values determined for ΔH_η^E (y_2) are listed in Fig.2. Curves 1-3 relate to limited compatibility systems (W-C-G at I=0.01, W-C-D at I=0.25, W-C-DS at I=1.0), while curves 5 and 4 to total compatibility systems (W-C-D and W-C-DS at I=0.01). In the first case ΔH_η^E is negative, while in the second case it is positive. Interestingly, the maximum positive ΔH_η^E for the W-C-DS system at I=0.01 is observed at $y_2 \approx 0.9$, which according to direct measurements corresponds to the limiting bonding of protein with dextran sulfate (GUROV et al., 1978). Fig.3 shows the dependence of ΔH_η^E on the ionic strength for W-C-DS system at $y_2 \approx 0.9$, which corresponds to the maximum of curve 4 (Fig.2). This plot shows that the decomposition of C-DS complexes and decrease of the compatibility of casein and dextran sulfate, caused by an increase in the ionic

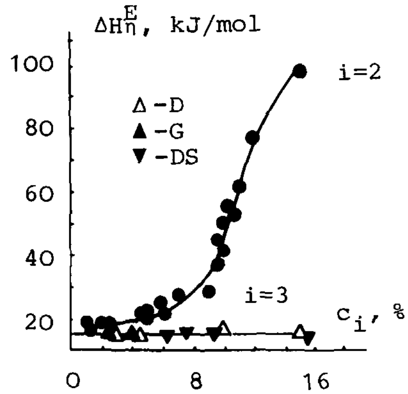

Figure 1. Concentration dependences of activation energy in viscous flow for casein (i=2) and polysaccharides (i=3) solutions (D-dextran, G-gum arabic, DS-dextran sulfate)

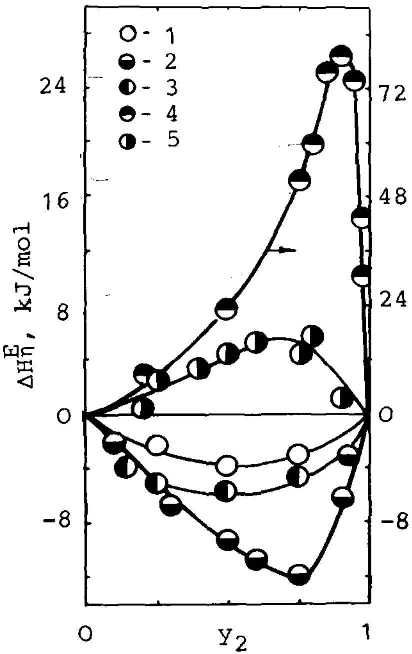

Figure 2. Dependences of excess activation energy in viscous flow on casein apparent weigth fraction (y_2) for some water-casein-polysaccharide systems with limited and total thermodynamic compatibility of macrocomponents (see text for explanations)

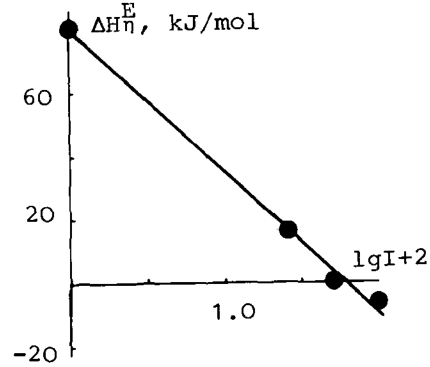

Figure 3. Dependence of excess activation energy on ionic strength for water-casein-dextran sulfate system at y_2=0.9, which corresponds to the maximum of curve 4 in Fig.2

strength, are accompanied with a decrease in ΔH^E_η from the positive to negative values.

These data are in qualitative agreement with the data obtained for binary liquid mixtures. They suggest that the parameter ΔH^E_η gives information on the type of the protein-polysaccharide interactions. A negative value of this parameter indicates that the repulsive forces dominate, while a positive value, that attractive forces dominate. Thus, there is ground to believe that the C-D complexes are possibly formed at low ionic strength. Using the maximum value of ΔH^E_η (Fig.2,5) we can make an approximate estimate of the energy of formation of these complexes (ca. 2 kT, i.e. 10 mJ/g). This is rather too low. Possibly, because of this reason, it is difficult to identify dextran-protein complexes.

The authors express their sincere graditude to Konstantinov A.A., Kondratev V.P., Chernysh M.M. (Special Design Bureau of the Institute of Petroleum Chemical Synthesis, The USSR Academy of Sciences) and Dmitrienko A.P. (Institute of Organoelement compounds, The USSR Academy of Sciences) for their invaluable help.

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Received April 4/ Accepted April 9, 198o