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HEATS OF DILUTION OF WATER-SOLUBLE-POLYMER SOLUTIONS (II) - HEAT INTERACTION PARAMETERS OF AQUEOUS HYDROXYPROPYLCELLULOSE AND GELATIN SOLUTIONS DETERMINED BY MEANS OF FLOW MICROCALORIMETER -

MASAKI MAEDA, YOSHITAKA YAMAMOTO, YOSHIHIRO BABA,
AND AKIHIRO KAGEMOTO*

Laboratory of Chemistry, Department of General Education,
Osaka Institute of Technology,
Asahi-ku, Osaka 535, Japan

SUMMARY

In order to obtain information about the intermolecular interaction between the water-soluble-polymers, we measured the heats of dilution of hydroxypropylcellulose(HPC)-water and gelatin-water systems at 298K by the flow microcalorimeter. The heat of dilution for gelatin-water system proved to be exothermic and the heat interaction parameter χ_1, determined by Van Laar equation was estimated to be about -1.00. However, the heat of dilution of HPC-water system moves from the exothermic to the endothermic with an increase of HPC concentration and χ_1-value in dilute solution was estimated to be about -0.91. We found that the interaction between gelatin and water depends linearly on the gelatin concentration, but for HPC-water system, the interaction depends considerably on the HPC concentration.

From the results of these interactions, the hydrophilic effect of these water-soluble-polymers for water was the order of gelatin > HPC.

We will discuss the hydrophilic and hydrophobic interactions from the results of heats of dilution.

INTRODUCTION

One of the most interesting areas in biopolymers is to inform the interaction between biopolymer and small molecule, and the behaviours of the water surrounding biopolymer or the hydrated biopolymeric molecule accompanying the functional development of

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* To whom correspondence should be addressed

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life. No information, however, has been obtained for water effect.

In the previous papers, we measured the heats of dilution of the water-soluble-polymers such as poly(ethylene oxide)(ref.1) and poly(acrylic acid)s(ref.2) in aqueous solutions at 298 K by means of microcalorimetry and the heat interaction parameter was estimated to be negative(exothermic). The fact that the enthalpy parameter was negative may be expected the existence of the consolute temperature. And also, in order to obtain information about the thermodynamic quantity from the consolute temperature, we studied the lower critical solution temperature of the aqueous poly(ethylene oxide)(ref.3) and hydroxypropylcellulose(HPC)(ref.4) solutions by solution type of differential thermal analysis, and the heat interaction parameter was estimated to be -1.86 for poly(ethylene oxide) and 0.49 for HPC.

Recently, to obtain information about the intermolecular interaction for water-soluble-polymer in the concentrated solutions, the phase states of the gelatin-HPC mixture were studied by the new instrument of DTA equipped with laser and polarization microscope(ref.5). We found that HPC in ternary solutions with various HPC concentrations at a given concentration of gelatin(15 wt%) was enclosed by gelatin at low concentration of HPC and vice versa at high concentration of HPC and the mixture of HPC-gelatin forms the different liquid crystal compared with the lyotropic and choresteric liquid crystals of HPC(ref.6). It is considered that the hydrophilic and hydrophobic effects may play an important role for forming the liquid crystal of the mixture of HPC-gelatin.

As one of the approach to obtain information about the mechanism of the formation of the liquid crystal for the mixture of HPC-gelatin, the heats of dilution of HPC-water and gelatin-one systems were measured at 298.15 ± 0.005 K by a flow microcalorimeter and heat interaction parameters were estimated.

We will discuss the hydrophilic and hydrophobic interactions from the heat interaction parameter estimated by the heat of dilution in this paper.

EXPERIMENTAL

Samples used in this study were hydroxypropylcellulose($\overline{Mw} = 6.0\times10^4$, Scientific Polymer Co.Ltd., USA) and gelatin($\overline{Mw} = 1.0\times10^5$, Sigma Co.Ltd., USA), respectively.

Water as solvent used in this study was passed through the reverse osmotic membrane, distilled and deionized by ion-exchange resin.

A calorimeter used in this study was a flow microcalorimeter equipped with UV spectrometer.

RESULTS AND DISCUSSION

The heats of dilution, $\overline{\Delta H}_d$ of hydroxypropylcellulose(HPC)- and gelatin-water systems were measured at 298.15 ± 0.005 K by a flow microcalorimeter equipped with the UV spectrometer. These heats of dilution proved to be exothermic, demonstrating that the interactions between HPC and/or gelatin and water may exist.

The results obtained are listed in Table I. However, it is very interesting that $\overline{\Delta H}_d$ for HPC-water system converts from negative value to positive one with increasing the HPC concentration.

Table I Heat of dilution at 298 K

$10^2\cdot\phi_2$	$10^3\cdot\phi_2'$	$\frac{10^4\cdot\Delta n_1}{\text{mol}}$	$\frac{10^5\cdot\overline{\Delta H}_d}{\text{J}}$	x_H
(a) gelatin-water system				
0.81	4.05	1.11	-0.83	-0.92
0.81	4.86	0.89	-1.10	-1.27
0.81	6.47	0.44	-0.71	-1.23
1.02	1.02	2.00	-0.38	-0.73
1.02	2.04	1.78	-0.84	-0.92
1.02	3.06	1.56	-1.05	-0.87
1.02	4.08	1.33	-1.34	-1.04
1.02	5.10	1.11	-1.40	-0.98
1.02	6.12	0.89	-1.33	-0.97
1.24	3.71	1.56	-1.80	-1.02
1.24	4.94	1.33	-1.94	-0.96
1.24	8.65	0.67	-1.60	-0.90
1.24	11.10	0.22	-0.90	-1.18
(b) HPC-water system				
0.81	4.04	1.11	-0.59	-0.62
0.81	5.66	0.67	-0.47	-0.66
1.07	2.13	1.78	-0.80	-0.71
1.07	3.20	1.56	-0.94	-0.80
1.29	1.29	2.00	-1.04	-0.45
1.29	5.17	1.33	-1.49	-0.55
1.29	6.46	1.11	-0.68	-0.82
1.47	5.87	0.89	-0.56	-0.29
1.47	8.81	1.33	0.20	0.05
1.47	11.74	1.78	1.90	0.25
1.47	13.21	2.00	2.80	0.29
2.26	9.03	0.89	1.11	0.25
2.26	11.29	1.11	1.84	0.29
3.03	6.06	1.78	2.17	0.27
3.03	9.09	1.56	2.89	0.27

As reported previously(ref.7), the heat of dilution, $\overline{\Delta H}_d$ is related to the initial volume fraction of the polymer, ϕ_2 and the final volume fraction, ϕ_2' as follow;

$$\overline{\Delta H}_d = RT\phi_2\phi_2'\Delta n_1\chi_H \qquad (1)$$

where χ_H is the heat interaction parameter which is not dependent on the concentration of polymer, and Δn_1 the number of mole of solvent added, respectively. By using the experimental data listed in Table I and Eq. (1), the plots of $\overline{\Delta H}_d/\Delta n_1$ against $RT\phi_2\phi_2'$ are carried out and shown in Fig. 1a and 1b. As seen in Fig. 1a, the plot of $\overline{\Delta H}_d/\Delta n_1$ against $RT\phi_2\phi_2'$ for gelatin-water system is a linear, suggesting that χ_H is not dependent on the concentration of gelatin. and the solubility of gelatin for water is good(exothermic). While, the plot of $\overline{\Delta H}_d/\Delta n_1$ against $RT\phi_2\phi_2'$ for HPC-water system is shown in Fig. 1b. $\overline{\Delta H}_d$ moves from the exothermic to the endothermic with an increase of the HPC concentration. It is worth noting that the critical concentration, ϕ_c from the exothermic to the endothermic direction with increasing the HPC concentration may exist, suggesting that the hydrophilic effect by the hydrogen bonding between OH of hydroxypropyl group of HPC and water in dilute solution contributes the solubility of HPC. However, with an increase of the concentration of HPC, the hydrophobic effect between HPC and water becomes the larger and then the endothermic of $\overline{\Delta H}_d$ appears. It is demonstrating that χ_H depends considerably on the concentration of HPC by the cooperative action of the hydrophilic and hydrophobic interactions.

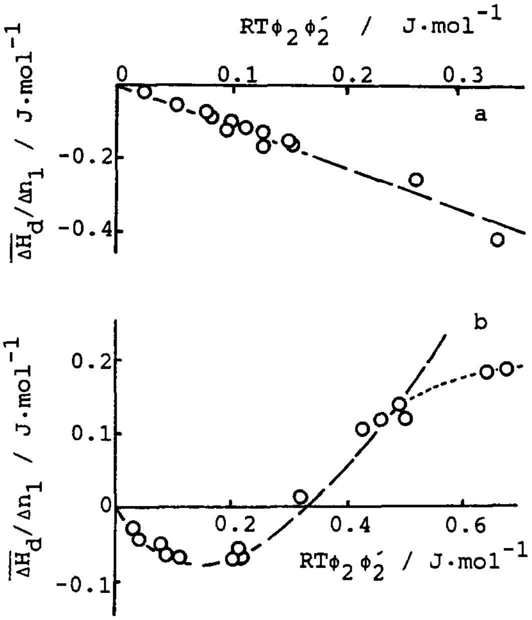

Fig. 1 Plots of $\overline{\Delta H}_d/\Delta n_1$ against $RT\phi_2\phi_2'$
a: gelatin-water system
b: HPC-water system

Assuming that χ_H is expressed as;

$$\chi_H = \chi_1 + \chi_2\phi_2 + \chi_3\phi_2^2 + --- \tag{2}$$

and making the same derivation as that of Eq.(1), we can obtain the following equation;

$$\overline{\Delta H}_d = RT\phi_2\phi_2'\Delta n_1\left\{\chi_1 + \chi_2\frac{(\phi_2+\phi_2')}{2} + \chi_3\frac{(\phi_2^2+\phi_2'^2)}{3} + ---\right\} \tag{3}$$

In order to find χ_1, χ_2, and χ_3, we tried to plot the $\overline{\Delta H}_d/RT\phi_2\phi_2'\Delta n_1$ against $(\phi_2+\phi_2')/2$ for each system as shown in Fig. 2a and 2b. The experimental data, however, are scattered to obtain accurate values. Therefore, we carried out the least - squares treatment of the data according to Eq.(3), and this gives the values for χ_1, χ_2 and χ_3 shown in Table II. But, χ_2- and χ_3-values for gelatin-water system are nearly zero which is independent of the gelatin concentration. While, it is worth noting that the behaviour of χ_H-parameter for HPC-water system shows transformation from negative to positive values with

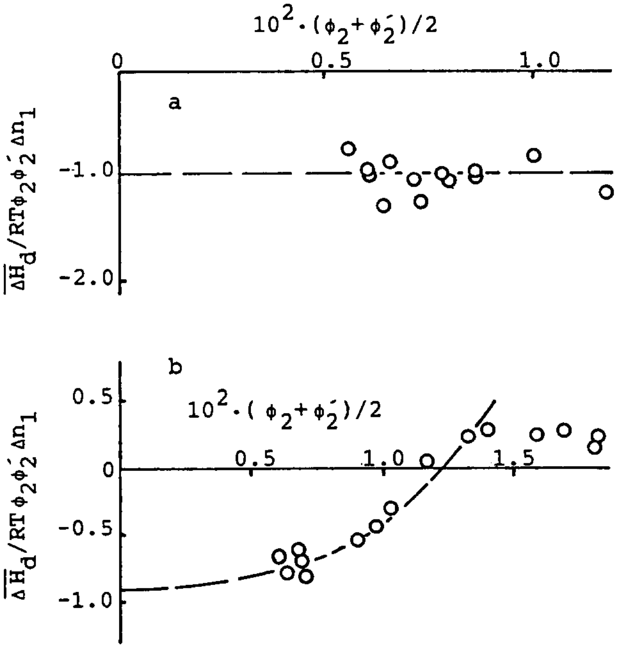

Fig. 2 Plots of $\overline{\Delta H}_d/RT\phi_2\phi_2'\Delta n_1$ against $(\phi_2+\phi_2')/2$
a: gelatin-water system
b: HPC-water system

increasing the HPC concentration. By using the values of χ_1, χ_2 and χ_3 listed in Table II, a $\overline{\Delta H}_d/\Delta n_1-RT\phi_2\phi_2'$ curve has been calculated for each system; This curve, which is shown by the solid line in Fig. 1, is in good agreement with experimental data for each system.

Table II Values of χ_1-, χ_2- and χ_3- parameters

	χ_1	χ_2	χ_3
gelatin	-1.00	$\cong$ 0	0
HPC	-0.91	2.52	$4.65\text{x}10^3$

As seen in Table II, χ_1-parameter is negative value which is independent of the gelatin concentration, suggesting that gelatin molecule from the dilute to the concentrated solutions has the large hydrophilic effect based on the hydrogen bond between >C=O and/or >N-H groups of main chain of gelatin molecule and water molecule. On the other hand, for HPC-water system, χ_1-parameter in dilute solution is negative value which has approximately the same value as well as that of gelatin-water system. This negative value in dilute solution may be based on the hydrogen bond between OH in hydroxypropyl group as side chain of HPC molecule and water molecule. But, χ_2- and χ_3- parameters which depend on the HPC concentration are positive value, demonstrating that positive value may be due to the cooperative action of the hydrophobic effect and the hydrogen bond as mentioned above with increase of the HPC concentration.

However, it is very difficult to analyze exactly the complicated interaction between HPC and water with increasing HPC concentration from our present work only.

Further study is in progress to obtain many information about the interaction between water-soluble-polymers.

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