Thermochimica Acta, 123 (1988) 271–283
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

HEATS OF DILUTION OF WATER-SOLUBLE POLYMER SOLUTIONS *

HIDEYUKI AZUMA, KAZUO HANADA, YONEHARU YOSHIKAWA, YOSHIHIRO BABA and AKIHIRO KAGEMOTO

Department of Chemistry, Osaka Institute of Technology, Asahi-ku, Osaka 535 (Japan)

(Received 24 March 1987)

ABSTRACT

In order to obtain information about the effects of water on water-soluble polymers, the heats of dilution of poly(acrylic acid)–water and poly(acrylic acid)–ethyl alcohol systems were measured at 298.15 ± 0.002 K with a specially constructed automatic microcalorimeter. The results obtained show that the heat of dilution is endothermic for the water system and exothermic for the ethyl alcohol system.

In order to confirm the endothermic and/or exothermic heats of dilution of those systems, the excess volume of mixing of the systems was also measured at 298.15 ± 0.01 K using a densimeter. The sign of the excess volume for the ethyl alcohol system, but not for the water system, was in good agreement with that of the interaction heat parameter estimated by calorimetry. To obtain further information about the interaction, the interaction energies of the systems were calculated by means of ab initio molecular orbital (MO) calculations.

The result obtained is about -12 kJ mol^{-1} for the ethyl alcohol system, suggesting that the interaction mode between poly(acrylic acid) and ethyl alcohol molecules may be based on the hydrogen bond between the COOH group in the chain of poly(acrylic acid) and the OH in the ethyl alcohol molecule from the agreement of the heats of dilution with the excess volume of mixing and/or ab initio MO calculations. However, for the water system, the interaction energy obtained is positive and its value is very large.

INTRODUCTION

It is most important in the study of DNA and proteins to obtain information about the relationship between the structure and properties of the biopolymeric molecules. However, this relationship is very difficult to analyse exactly because biopolymeric molecules have a complicated structure which is also remarkably influenced by water, the presence of ions, pH etc. as environmental parameters.

In a previous paper [1], in order to obtain information about the effects of water molecules, we measured the heats of dilution of the poly(ethylene

---

* Paper presented at the Sino-Japanese Joint Symposium on Calorimetry and Thermal Analysis, 5–7 November 1986, Hangzhou, People's Republic of China.

0040-6031/88/$03.50 © 1988 Elsevier Science Publishers B.V.

oxide)–water system and estimated the interaction heat parameter between the polymer and the solvent. No information, however, was obtained about the effect of water on the polymer chains.

In this paper, in order to obtain information about the effects of water on water-soluble polymer solutions instead of on biopolymeric molecules, we measured the heats of dilution and the excess volume of mixing of poly(acrylic acid) (PAAc) in water-soluble polymer–water, polymer–ethyl alcohol and polymer–(water–ethyl alcohol) mixture systems with an automatic flow microcalorimeter at 298.15 ± 0.002 K and with a densimeter at 298.15 ± 0.01 K respectively.

To obtain further information about the interaction, interaction energies of the above systems were calculated by means of ab initio MO calculations. We shall discuss the interaction between polymer and solvent by combining the heat of dilution results with those of the excess volume and/or ab initio MO calculations.

APPARATUS AND PROCEDURE

The measurement of the heat of dilution of a polymer solution is very difficult to carry out experimentally, because the enthalpy change generated by mixing is very small and long times are required to reach thermal equilibrium. Therefore, accuracy, reliability and rapidity of measurement of the heats of dilution of polymer solutions are required. To solve the various problems mentioned above, a flow microcalorimeter equipped with a computer which satisfied the requirements of the various problems was built in such a way that the heat generated on mixing can be automatically compensated by the heater in the sample and/or reference cells and the temperature difference between the sample cell and the reference cell can usually be kept constant.

A block diagram of the automatic flow microcalorimeter is shown in Fig. 1, and a block diagram of the heat compensation circuit is also shown as an inset (a). As seen in Fig. 1(a), the heat compensation circuit consists of two operational amplifiers (for amplification and integration) followed by diodes which can distinguish exothermic or endothermic heat changes. For example, if the heat generated by mixing is exothermic, this calorimeter system is designed to compensate the temperature difference between the sample cell and reference cell by heating in the reference cell.

For the calibration of the new automatic microcalorimeter, the heat of dilution of an aqueous sucrose solution was measured at 298.15 ± 0.002 K. The result obtained was in good agreement with that in the literature [2] (accuracy ±2%), suggesting that the new microcalorimetric system can be operated accurately. Except for the automatic heat compensation, the microcalorimetric system was similar to those reported previously [3].

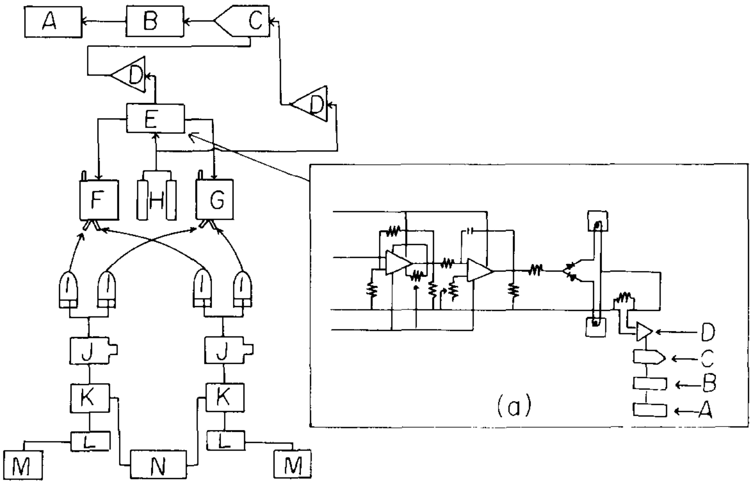


Fig. 1. Block diagram of the automatic flow microcalorimeter: A, cathode ray tube display; B, computer; C, analog/digital converter; D, d.c. amplifier; E, compensating circuit; F, sample cell; G, reference cell; H, thermomodule; I, cylinder; J, stepping motor; K, stepping motor driver; L, frequency supply; M, frequency counter; N, regulated power supply. The inset (a) shows the compensating circuit.

To determine the volume fraction of polymer and the volume change on mixing, the density is measured at 298.15 ± 0.01 K with a digital precision densimeter (DMA 601, Anton Paar, Austria).

Ab initio MO calculations were carried out with the IMSPACK [4] and Gaussian 80 [5] programs. The structure of propionic acid as a model of acrylic acid and ethyl alcohol were optimized with a STO-3G minimal basis set [6]. The structure of water was referred to the experimental value [7].

The hydrogen-bonding energy ΔE_{HB} was calculated as follows:

$$\Delta E_{\mathrm{HB}} = E(\mathrm{X{-}Y}) - [E(\mathrm{X}) + E(\mathrm{Y})] \tag{1}$$

where $E(\mathrm{X{-}Y})$, $E(\mathrm{X})$ and $E(\mathrm{Y})$ are the total energies of the X–Y hydrogen-bonding system and X and Y molecules respectively.

MATERIALS

The samples used as the water-soluble polymers in this study were poly(acrylic acid)s purchased from Scientific Polymer Products (USA). Their molecular weights are about 2.0×10^3, 5.0×10^3, 1.7×10^5 and 2.5×10^5 respectively.

The solvents used are water and ethyl alcohol. These solvents were purified by standard methods [8].

RESULTS AND DISCUSSION

Heat of dilution

The heats of dilution of PAAc–water and PAAc–ethyl alcohol systems were measured at 298.15 ± 0.002 K with the automatic flow microcalorimeter.

The heat of dilution of the water system is endothermic, while that of the ethyl alcohol system is exothermic. As shown in a previous paper [9], the heat of dilution $\Delta\overline{\mathrm{Hd}}$ is related to the initial volume fraction of the polymer ϕ_2 and to the final volume fraction ϕ_2' as follows:

$$\Delta\overline{\mathrm{Hd}} = RT\phi_2\phi_2'\Delta n_1\chi_{\mathrm{H}} \tag{2}$$

where the interaction heat parameter χ_{H} is not dependent on the concentration. When χ_{H} depends linearly on the concentration according to the equation $\chi_{\mathrm{H}} = \chi_1 + \chi_2\phi_{\mathrm{a}}$, then

$$\frac{\Delta\overline{\mathrm{Hd}}}{(RT\phi_2\phi_2'\Delta n_1)} = \chi_1 + \chi_2\phi_{\mathrm{a}} \tag{3}$$

where ϕ_{a} is the average volume fraction before and after dilution and Δn_1 is the number of moles of solvent added.

By using the experimental data, χ_{H} was determined for each system. The results obtained are summarized in Table 1 and shown in Fig. 2, where $\Delta\overline{\mathrm{Hd}}/\Delta n_1$ is plotted against $RT\phi_2\phi_2'$. According to eqn. (2), $\Delta\overline{\mathrm{Hd}}/\Delta n_1$ must vary linearly with $RT\phi_2\phi_2'$. As seen in Fig. 2, these plots are not linear, demonstrating that χ_{H} depends on the concentration of polymer. In order to obtain accurate values of χ_1 and χ_2, the least-squares treatment of the data was carried out according to eqn. (3). The results obtained are listed in Table 2 and shown in Fig. 3, where χ_1 is plotted against the logarithm of the molecular weight of the polymer. As seen in Fig. 3, the values of χ_1 in dilute aqueous solutions decrease with an increase in the molecular weight of the polymer. The same dependence of χ_1 on the molecular weight has been found for the aqueous poly(ethylene oxide) solution reported previously [1] and this tendency seems to be explained qualitatively using the equation derived previously [10]:

$$\chi_1 = \frac{Z(Z-2)\Delta W M_0^{1/2}}{RT(2/3)^{3/2}\alpha^3 M^{1/2}} \tag{4}$$

where Z, α and ΔW are the coordination number, the expansion factor and the interaction energy of Hildebrand–Scott [11] respectively. M_0 and M are molecular weights of the repeating unit of the polymer and of the polymer respectively. From eqn. (4), χ_1 in aqueous solution is proportional to $M^{-1/2}$ and decreases with an increase in the molecular weight of the polymer and is in good agreement with experimental values. However, the dependence of χ_1

TABLE 1

The heats of dilution of poly(acrylic acid) (PAAc) in water and/or ethyl alcohol solutions

$\phi_2 \times 10^2$	$\phi_2' \times 10^2$	$\Delta\overline{\mathrm{Hd}}/\Delta n_1$ (J mol^{-1})	χ_H
PAAc($\overline{\mathrm{Mw}}$ = 2000)–water system			
2.73	1.91	0.227	0.18
2.73	1.64	0.199	0.18
2.73	1.36	0.514	0.17
2.73	1.09	0.129	0.18
5.59	3.36	0.671	0.14
5.59	2.80	0.568	0.15
5.59	2.24	0.468	0.15
5.59	1.68	0.361	0.16
5.59	1.12	0.250	0.16
8.56	5.59	1.450	0.11
8.56	5.14	1.270	0.12
8.56	4.28	1.100	0.12
8.56	3.42	0.913	0.13
8.56	2.57	0.729	0.13
PAAc($\overline{\mathrm{Mw}}$ = 5000)–water system			
3.46	2.77	0.324	0.32
3.46	2.42	0.285	0.14
3.46	1.73	0.205	0.14
3.46	1.38	0.164	0.14
3.46	1.04	0.131	0.15
3.46	0.69	0.085	0.14
7.39	6.65	1.480	0.12
7.39	5.91	1.270	0.12
7.39	5.18	1.100	0.12
7.39	4.44	0.942	0.12
7.39	3.70	0.803	0.12
7.39	2.96	0.658	0.12
7.39	2.22	0.519	0.13
7.39	1.48	0.367	0.14
10.7	7.48	2.190	0.11
10.7	6.41	1.900	0.11
10.7	5.34	1.590	0.11
10.7	4.27	1.320	0.12
10.7	3.20	1.040	0.12
PAAc($\overline{\mathrm{Mw}}$ = 170000)–water system			
3.34	2.34	0.234	0.12
3.34	2.00	0.200	0.12
3.34	1.67	0.170	0.12
3.34	1.34	0.140	0.13
3.34	1.00	0.109	0.13
6.09	4.26	0.761	0.12
6.09	3.66	0.642	0.12
6.09	3.05	0.542	0.12
6.09	2.44	0.443	0.12

TABLE 1 (continued)

$\phi_2 \times 10^2$	$\phi'_2 \times 10^2$	$\Delta\overline{Hd}/\Delta n_1$ (J mol^{-1})	χ_H
PAAc($\overline{Mw}$ = 170000)–water system			
8.86	5.32	1.330	0.11
8.86	4.43	1.090	0.11
8.86	3.55	0.882	0.11
8.86	2.66	0.660	0.11
PAAc($\overline{Mw}$ = 250000)–water system			
2.10	1.68	0.068	0.08
2.10	0.84	0.034	0.08
2.10	0.63	0.023	0.07
2.81	2.25	0.128	0.08
2.81	1.97	0.104	0.08
2.81	1.69	0.081	0.07
2.81	1.41	0.064	0.66
2.81	1.12	0.052	0.07
2.81	0.84	0.037	0.06
3.53	2.82	0.264	0.11
3.53	2.47	0.198	0.09
3.53	2.47	0.198	0.09
3.53	2.12	0.148	0.08
3.53	1.77	0.127	0.08
3.53	1.41	0.089	0.07
3.53	1.06	0.070	0.08
3.53	0.71	0.043	0.07
4.26	3.83	0.434	0.11
4.26	1.70	0.127	0.07
4.26	0.85	0.062	0.07
6.47	4.53	0.977	0.13
6.47	3.88	0.770	0.12
6.47	3.24	0.577	0.11
6.47	2.59	0.447	0.11
6.47	1.94	0.310	0.10
6.47	1.29	0.206	0.10
6.47	0.65	0.094	0.09
7.21	3.61	0.843	0.13
7.21	2.88	0.626	0.12
7.21	2.16	0.430	0.11
7.21	1.44	0.279	0.11
7.21	0.72	0.129	0.10
PAAc($\overline{Mw}$ = 250000)–ethyl alcohol system			
2.53	1.86	−0.516	−0.45
2.53	1.60	−0.350	−0.35
2.53	1.43	−0.282	−0.31
2.53	1.27	−0.321	−0.41
2.53	1.01	−0.274	−0.43
2.53	0.76	−0.106	−0.22
2.53	0.59	−0.096	−0.26
2.53	0.42	−0.078	−0.30
3.21	1.82	−0.580	−0.40
3.21	1.61	−0.485	−0.38

TABLE 1 (continued)

$\phi_2 \times 10^2$	$\phi_2' \times 10^2$	$\Delta\overline{Hd}/\Delta n_1$ (J mol^{-1})	χ_H
PAAc($\overline{Mw}$ = 250000)–ethyl alcohol system			
3.21	1.28	−0.445	−0.44
3.21	0.96	−0.410	−0.54
3.21	0.75	−0.301	−0.51
3.21	0.54	−0.125	−0.29
3.21	0.21	−0.073	−0.43
3.43	1.94	−0.738	−0.45
3.43	1.72	−0.863	−0.61
3.43	1.37	−0.674	−0.58
3.43	1.03	−0.479	−0.55
3.43	0.80	−0.379	−0.56
3.43	0.57	−0.296	−0.61
3.97	2.91	−1.780	−0.62
3.97	2.51	−1.530	−0.62
3.97	2.25	−1.620	−0.73
3.97	1.99	−1.540	−0.79

on molecular weight cannot be explained quantitatively due to a lack of information about the expansion factor α.

The reason why the χ_1 parameter of the ethyl alcohol is exothermic and that of the aqueous solution is endothermic must be clarified. An endothermic system in an aqueous solution is attributable to the fact that the energy of isolation of a hydrogen atom from the COOH group in PAAc molecules is larger than the interaction energy between the COO$^-$ group of PAAc and

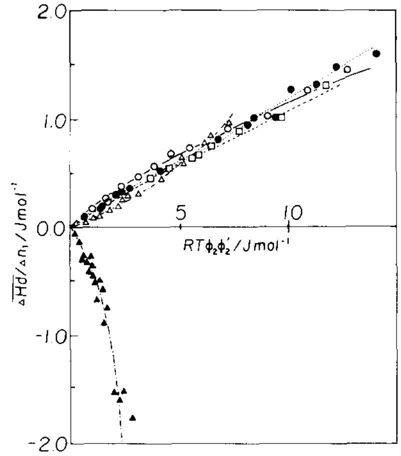


Fig. 2. Plots of $\Delta\overline{Hd}/\Delta n_1$ against $RT\phi_2\phi_2'$ for PAAc–water systems using polymers of different molecular weights (○, $\overline{Mw} = 2.0\times10^3$; ●, $\overline{Mw} = 5.0\times10^3$; □, $\overline{Mw} = 1.7\times10^5$; △, $\overline{Mw} = 2.5\times10^5$) and for PAAc–ethyl alcohol systems (▲, $\overline{Mw} = 2.5\times10^5$).

TABLE 2

Interaction heat parameters χ_1 and χ_2 in dilute solution for poly(acrylic acid)–water and poly(acrylic acid)–ethyl alcohol systems

$\overline{Mw}$	Water system		Alcohol system	
	χ_1	χ_2	χ_1	χ_2
2.0×10^3	0.20	−1.22		
5.0×10^3	0.15	−0.48		
1.7×10^5	0.13	−0.30		
2.5×10^5	0.04	0.46	−0.40	−20.72

water molecules as shown in Fig. 4(a). However, the exothermic nature of χ_1 in the alcohol system may be attributed to the formation of a hydrogen bond between COOH groups in the side chain of PAAc and OH groups in ethyl alcohol molecules, as shown in Fig. 4(b).

However, the exothermic and/or endothermic nature of these systems may be also influenced by factors such as the conformational energy change of the polymer chain and the volume change on mixing.

In order to obtain further information about the influence of ethyl alcohol on the interaction between PAAc and water molecules in aqueous solution, the heats of dilution of PAAc in water–ethyl alcohol mixtures were also measured at 298.15 ± 0.002 K by the same microcalorimeter. The data obtained for the dilution process were also analysed according to eqns. (2) and (3) respectively. The heat of dilution changes its sign from endothermic to exothermic as the proportion of ethyl alcohol in the mixed solvent increases. The results obtained are listed in Table 3 and shown in Fig. 5, where χ_1 is plotted against the volume fraction of ethyl alcohol, ϕ_3, in the mixed solvent. As seen in Fig. 5, the χ_1 value in the water-rich region is positive, demonstrating that the dehydration energy of water molecules is

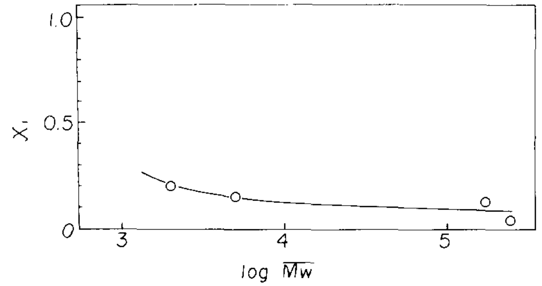
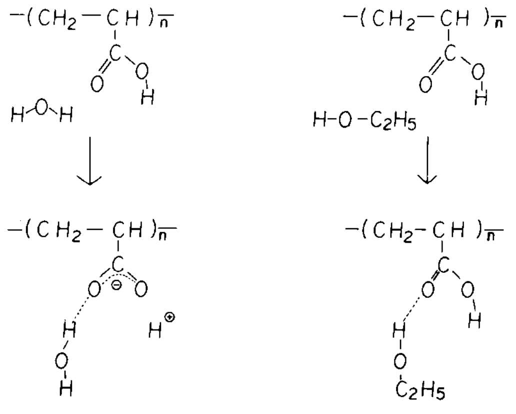


Fig. 3. Plot of the interaction heat parameter χ_1 in dilute solutions against the logarithm of the molecular weight of polymer for PAAc – water system.



(a) PAAc – H_2O (b) PAAc – C_2H_5OH

Fig. 4. Schematic interaction mode for (a) PAAc–water and (b) PAAc–ethyl alcohol systems.

TABLE 3

Interaction heat parameters of poly(acrylic acid)–(water–ethyl alcohol) mixture

ϕ_3 [a]	χ_1	χ_2
0.00	0.04	1.60
0.10	1.12	−28.93
0.20	0.06	−11.23
0.30	0.13	−1.80
0.40	−0.09	−0.07
0.50	−0.18	−7.73
0.60	−0.17	−17.22
0.70	−0.09	20.19
1.00	−0.04	−20.82

[a] ϕ_3, volume fraction of ethyl alcohol in the water–ethyl alcohol mixture.

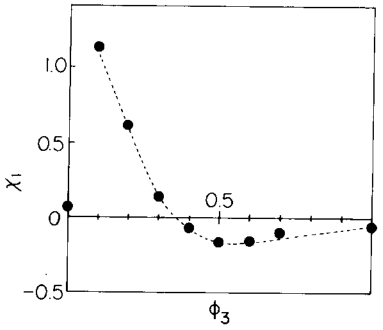


Fig. 5. Plot of the interaction heat parameter χ_1 against volume fraction ϕ_3 of ethyl alcohol in mixed solvent.

larger than the hydrogen-bonding energy between COO^- groups in the side chain of PAAc and water molecules. In the region rich in ethyl alcohol χ_1 is negative, demonstrating that the three-dimensional structure of water is presumably destroyed by the large quantity of ethyl alcohol molecules introduced into the solvent, and the hydrogen-bonding energy between COOH groups in the side chain of PAAc and the OH of ethyl alcohol in the mixed solvent is stronger than that between COO^- groups in the side chain of PAAc and water molecules.

Excess volume

In order to obtain further information about the reason why the χ_1 parameter of the ethyl alcohol system is exothermic and that of the water system is endothermic, the excess volume of mixing of the systems PAAc–ethyl alcohol and/or PAAc-water was measured at 298.15 ± 0.01 K by using a densimeter. The results obtained are summarized in Table 4 and shown in Fig. 6, where the excess volume V^E is plotted against the volume fraction of polymer.

As seen in Fig. 6, the sign of the excess volume change for the ethyl alcohol system is comparable with the sign of the interaction heat parameter

TABLE 4

Excess volume of mixing of poly(acrylic acid)–water and poly(acrylic acid)–ethyl alcohol systems at 298 K

Solvent	Volume fraction ϕ_2	Excess volume V^E(cm^3 g^{-1})
Water	0.01217	−0.00236
	0.01128	−0.00206
	0.00994	−0.00192
	0.00867	−0.00173
	0.00718	−0.00171
	0.00581	−0.00163
	0.00445	−0.00151
	0.00301	−0.00144
	0.00164	−0.00133
	0.00034	−0.00121
Ethyl alcohol	0.00804	−0.00263
	0.01118	−0.00331
	0.01247	−0.00558
	0.01481	−0.00656
	0.01843	−0.00620
	0.02084	−0.00735
	0.02552	−0.00638
	0.02780	−0.00755

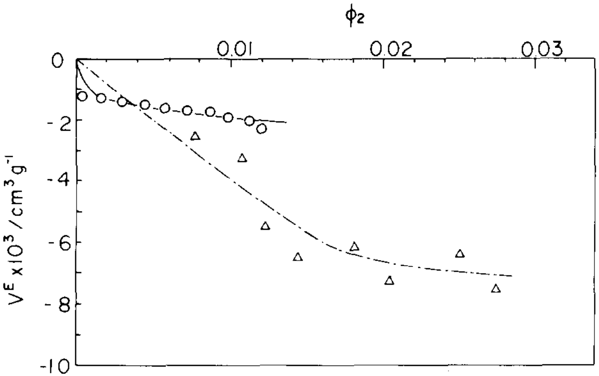


Fig. 6. Plots of the excess volume V^E against the volume fraction ϕ_2 of polymer for PAAc–water (○) and PAAc–ethyl alcohol (△) systems at 298 K.

determined by calorimetry, suggesting that the excess volume change may also play an important role in the interaction between polymer and solvent. However, the excess volume change for the water system reverses its sign compared with the sign of the interaction heat parameter obtained by calorimetry, demonstrating that for the water system, other factors such as dipole–dipole interaction, dipole–induced dipole interaction and the effect of the orientation of molecules need to be taken into consideration.

Ab initio MO calculations

The sign of the excess volume change for the ethyl alcohol system is in good agreement with that determined from calorimetry, but the signs of the corresponding values for the water system do not agree. To confirm the effects of the solvent on PAAc, ab initio MO calculations were carried out with the IMSPACK [4] and Gaussian 80 [5] programs.

For the water system, the optimized structures of interaction between propionic acid (AAc) as a model of acrylic acid and water molecules are calculated by referring to the experimental value and are shown in Fig. 7(a). As seen in Fig. 7(a), the optimized structure of AAc as a model of PAAc and water molecules may be based on the following reaction:

$$\mathrm{AAc} + H_2O \rightarrow \mathrm{AAc}^{-}\text{–}H_2O + H^+$$

Therefore the mode of interaction for the water system may be the formation of a hydrogen bond between the COO^- group of AAc and water molecules.

According to the reaction mentioned above, the total energies of interaction of the optimized structures of AAc and water molecules were calculated using eqn. (1) as described in the experimental section. The results obtained are shown in Table 5. As seen for the water system, the calculated values of ΔE_{HB} are positive, in good agreement with the sign of the heat of dilution

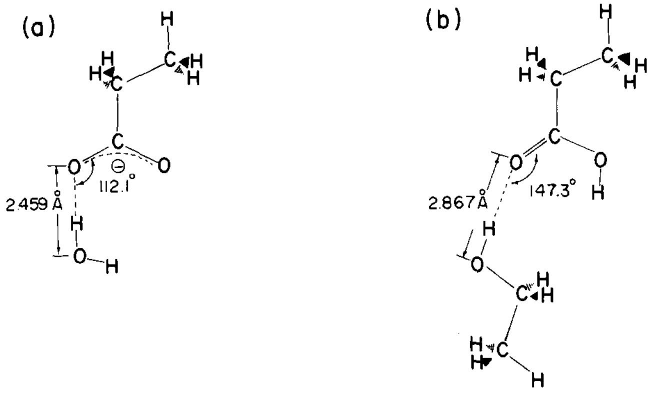


Fig. 7. The optimized structure of interaction between propionic acid as a model of PAAc and (a) water and/or (b) ethyl alcohol systems.

determined from calorimetry. However, the value of the interaction energy is very large, demonstrating that the energy of protonation of a H^+ atom in COOH group of an AAc molecule is very large.

Also, the optimized structure of interaction between AAc as a model of PAAc and ethyl alcohol molecules is shown in Fig. 7(b). As seen in Fig. 7(b), the mode of interaction between AAc and ethyl alcohol molecules assumes a hydrogen bond between the COOH group of AAc and the OH group of ethyl alcohol. Total energies of the optimized structures of AAc and ethyl alcohol molecules were also calculated according to eqn. (1) as described in the experimental part and the results obtained are summarized in Table 5.

As seen in Table 5, the sign of the heat of dilution for the ethyl alcohol system is in good agreement with the sign of ΔE_{HB} calculated according to the ab initio MO calculation, suggesting that the interaction mode between AAc and ethyl alcohol may be caused by the hydrogen bond between the COOH group of the AAc and the OH group of the ethyl alcohol molecules as shown in Fig. 7(b).

To clarify the behaviour of the PAAc–water system, further study is now in progress.

TABLE 5

Total energy E of propionic acid (AAc, X), water, ethyl alcohol (Y) and the hydrogen-bonded system (X–Y) and the hydrogen-bonding energy ΔE_{HB} due to the interaction between X and Y

System	E(X) (a.u.) [a]	E(Y) (a.u.) [a]	E(X–Y) (a.u.) [a]	ΔE_{HB} (kJ mol^{-1})
AAc–H_2O	−263.388469	−74.963062	−337.630201	1890
AAc–C_2H_5OH	−263.388469	−152.132687	−415.525744	−12

[a] a.u. is atomic unit (1 a.u. = 2624 kJ mol^{-1}).

ACKNOWLEDGEMENT

We are grateful to the Computer Center of the Institute for Molecular Science for the use of the computer.

REFERENCES

1 A. Kagemoto and R. Fujishiro, Makromol. Chem., 105 (1967) 154.
2 E.F.G. Herrington, Pure Appl. Chem., 40 (1979) 399.
3 H. Ogawa, Y. Baba and A. Kagemoto, Makromol. Chem., 182 (1981) 2495.
4 K. Morokuma, S. Kato, K. Kitaura, I. Ohmine, S. Sakai and S. Obara, IMS Computer Center Program Library, The Institute for Molecular Science Japan, 1980, Program No. 372.
5 J.S. Binkly, R.A. Whiteside, R. Krishnan, R. Seeger, P.J. DeFrees, H.B. Schlegel, S. Topiol, L.R. Kahn and J.A. Pople, Q.C.P.E., 13 (1981) 406.
6 W.J. Hehre, R.F. Stewart and J.A. Pople, J. Chem. Phys., 51 (1969) 2657.
7 A.R. Hoy and P.R. Bunker, J. Mol. Spectrosc., 74 (1979) 1.
8 J.A. Riddick and W.B. Bunger, Organic Solvents, Wiley-Interscience, New York, 1970.
9 A. Kagemoto and R. Fujishiro, Bull. Chem. Soc. Jpn., 39 (1966) 15.
10 Y. Baba, H. Katayama and A. Kagemoto, Polym. J., 6 (1974) 230.
11 J.H. Hildebrand, J.M. Prausnitz and R.L. Scott, Regular and Related Solution, Van Nostrand Reinhold, New York, 1970, Chapter 6, p. 85.