# The Heat of Dilution of Poly(vinyl acetate) in Benzene and Methyl Ethyl Ketone

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In our previous papers[1-4] we have measured the heats of dilution of atactic polystyrene,[1] *cis*-polybutadiene,[2] poly(ethylene oxide),[3] and polymethyl methacrylate[4] solutions; derived the interaction parameter between the polymer and solvent, and found that the interaction heat parameter, $\chi_H$, is considerably dependent not only on the concentration of the polymer, but also on its molecular weight. In order to confirm this fact for other polymer solutions, the heats of dilution of poly(vinyl acetate) (PVAc) with the degrees of polymerization of 480, 1480, and 2450, and also the heat of mixing of the monomer of PVAc, were measured at 25.0±0.01°C using a twin micro-calorimeter, with methyl ethyl ketone (MEK) and benzene as solvents.

The heats of dilution of the polymer solutions were measured over the concentration range from 0.2 to 0.08 in the volume fraction of the polymer, by adding a successive of 10-m*l* and 30-m*l* portions of the solvent to a solution of a known concentration. The data obtained are shown in Table 1.

The benzene solution is endothermic, while the MEK solution is exothermic.

As has been shown in previously published paper,[1] the heats of dilution, $\Delta\overline{H}_d$, are related to the initial volume fraction of the polymer, $\phi_2$, and the final one, $\phi_2'$, as follows:

$$\Delta\overline{H}_d = \boldsymbol{R}T\chi_H\phi_2\phi_2'\Delta n_1 \qquad (1)$$

when the interaction heat of parameter, $\chi_H$, is not dependent on the concentration, or

$$\Delta\overline{H}_d/\boldsymbol{R}T\phi_2\phi_2'\Delta n_1 = \chi_1 + \chi_2(\phi_2+\phi_2')/2 \qquad (2)$$

when the $\chi_H$ parameter depends linearly on the concentration, according to the equation that $\chi_H=\chi_1+\chi_2\phi_2$.

In these equations $\Delta n_1$ is the number of moles of the solvent added.

By using the experimental data listed in Table 1 and Eq.(1), the interaction heat parameter, $\chi_H$, has been obtained for each dilution process of each system; these parameters are given in the last column of Table 1.

According to Eq.(1), $\Delta\overline{H}_d$ must vary linearly with $\phi_2\phi_2'\Delta n_1$. However, these plots are not linear, as may be seen in Figs. 1 (a) and (b), indicating that $\chi_H$ depends on the concentration.

This tendency has been confirmed by plotting the $\Delta\overline{H}_d/\phi_2\phi_2'\Delta n_1$ against the average volume fraction $(\phi_2+\phi_2')/2$ for each system according to Eq. (2). In order to obtain the accurate values of $\chi_1$ and $\chi_2$, the least-squares treatment of the data was carried out according to Eq. (2); the results are shown in Table 2.

In a good solvent the $\chi_H$ parameter is considerably dependent on the concentration, while in the poor solvent, benzene, it is not.

Such a tendency can be explained according to the dilution theory of polymer solutions by Flory,[5] and

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1) A. Kagemoto, S. Murakami and R. Fujishiro, This Bulletin, **39**, 15 (1966).

2) A. Kagemoto, S. Murakami and R. Fujishiro, *ibid.*, **39**, 1814 (1966).

3) A. Kagemoto, S. Murakami and R. Fujishiro, *Makromol. Chem.*, **105**, 154 (1967).

4) A. Kagemoto, S. Murakami and R. Fujishiro, This Bulletin, **40**, 11 (1967).

5) P. J. Flory, and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

Table 1. The heat of dilution of polyvinyl acetate solution at 25°C

I. Polyvinyl acetate - Benzene systems

| $V$ cc | $\phi_2$ | $V'$ cc | $\phi_2'$ | $\Delta\overline{H}_d$ cal | $\chi_H$ |
|---|---|---|---|---|---|
| Monomer | | | | | |
| 5 | 1.000 | 10 | 0.500 | 3.491 | 0.22 |
| 10 | 0.500 | 15 | 0.333 | 1.301 | 0.24 |
| 15 | 0.333 | 20 | 0.250 | 0.623 | 0.23 |
| 20 | 0.250 | 25 | 0.200 | 0.358 | 0.22 |
| 5 | 1.000 | 10 | 0.500 | 3.420 | 0.21 |
| 10 | 0.500 | 15 | 0.333 | 1.193 | 0.22 |
| 15 | 0.333 | 20 | 0.250 | 0.623 | 0.23 |
| $\overline{P}=480$ | | | | | |
| 10 | 0.265 | 20 | 0.128 | 0.163 | 0.074 |
| 20 | 0.128 | 30 | 0.088 | 0.065 | 0.089 |
| 30 | 0.088 | 40 | 0.066 | 0.034 | 0.090 |
| 20 | 0.212 | 30 | 0.141 | 0.141 | 0.072 |
| 30 | 0.141 | 50 | 0.085 | 0.122 | 0.078 |
| 20 | 0.197 | 30 | 0.131 | 0.138 | 0.082 |
| 30 | 0.131 | 40 | 0.098 | 0.072 | 0.086 |
| 40 | 0.098 | 50 | 0.078 | 0.045 | 0.090 |
| 50 | 0.078 | 60 | 0.065 | 0.025 | 0.076 |
| $\overline{P}=1850$ | | | | | |
| 10 | 0.220 | 20 | 0.110 | 0.087 | 0.055 |
| 20 | 0.110 | 30 | 0.077 | 0.040 | 0.072 |
| 30 | 0.095 | 40 | 0.074 | 0.032 | 0.070 |
| 30 | 0.080 | 50 | 0.050 | 0.034 | 0.065 |
| 10 | 0.196 | 30 | 0.065 | 0.125 | 0.075 |
| 10 | 0.156 | 20 | 0.078 | 0.055 | 0.070 |
| 20 | 0.078 | 30 | 0.052 | 0.017 | 0.058 |
| 10 | 0.220 | 30 | 0.077 | 0.127 | 0.058 |
| 10 | 0.156 | 30 | 0.052 | 0.072 | 0.068 |
| 30 | 0.105 | 50 | 0.063 | 0.056 | 0.065 |
| $\overline{P}=2450$ | | | | | |
| 10 | 0.196 | 20 | 0.098 | 0.053 | 0.042 |
| 20 | 0.098 | 30 | 0.065 | 0.020 | 0.048 |
| 10 | 0.092 | 20 | 0.046 | 0.011 | 0.040 |
| 30 | 0.098 | 40 | 0.073 | 0.023 | 0.049 |
| 10 | 0.151 | 20 | 0.076 | 0.036 | 0.048 |
| 40 | 0.062 | 50 | 0.050 | 0.008 | 0.039 |
| 20 | 0.085 | 30 | 0.056 | 0.014 | 0.045 |
| 30 | 0.123 | 50 | 0.074 | 0.059 | 0.050 |
| 20 | 0.176 | 30 | 0.117 | 0.052 | 0.039 |
| 30 | 0.117 | 40 | 0.088 | 0.030 | 0.045 |

II. Polyvinyl acetate - Methyl ethyl ketone systems

| $V$ cc | $\phi_2$ | $V'$ cc | $\phi_2'$ | $-\Delta\overline{H}_d$ cal | $\chi_H$ |
|---|---|---|---|---|---|
| Monomer | | | | | |
| 5 | 1.000 | 10 | 0.500 | 2.443 | −0.15 |
| 10 | 0.500 | 15 | 0.333 | 0.813 | −0.15 |
| 15 | 0.333 | 20 | 0.250 | 0.380 | −0.14 |
| 20 | 0.250 | 25 | 0.200 | 0.212 | −0.13 |
| 5 | 1.000 | 10 | 0.500 | 2.280 | −0.14 |
| 10 | 0.500 | 15 | 0.333 | 0.813 | −0.15 |
| 15 | 0.333 | 20 | 0.250 | 0.380 | −0.14 |
| $\overline{P}=480$ | | | | | |
| 10 | 0.256 | 20 | 0.128 | 0.209 | −0.098 |
| 20 | 0.128 | 30 | 0.085 | 0.060 | −0.085 |
| 30 | 0.085 | 40 | 0.064 | 0.032 | −0.090 |
| 10 | 0.205 | 20 | 0.104 | 0.122 | −0.088 |
| 20 | 0.104 | 30 | 0.068 | 0.044 | −0.095 |
| 30 | 0.086 | 50 | 0.051 | 0.045 | −0.079 |
| 10 | 0.167 | 30 | 0.055 | 0.108 | −0.090 |
| 20 | 0.237 | 30 | 0.158 | 0.244 | −0.100 |
| 30 | 0.158 | 40 | 0.059 | 0.053 | −0.087 |
| 40 | 0.156 | 70 | 0.089 | 0.239 | −0.088 |
| 10 | 0.256 | 30 | 0.085 | 0.269 | −0.094 |
| 10 | 0.256 | 40 | 0.064 | 0.301 | −0.094 |
| 10 | 0.205 | 30 | 0.068 | 0.166 | −0.091 |
| 10 | 0.205 | 50 | 0.051 | 0.211 | −0.077 |
| $\overline{P}=1850$ | | | | | |
| 10 | 0.210 | 20 | 0.105 | 0.115 | −0.080 |
| 20 | 0.105 | 30 | 0.070 | 0.036 | −0.075 |
| 10 | 0.198 | 20 | 0.099 | 0.088 | −0.069 |
| 20 | 0.099 | 30 | 0.066 | 0.028 | −0.065 |
| 20 | 0.125 | 40 | 0.063 | 0.077 | −0.075 |
| 10 | 0.157 | 20 | 0.079 | 0.053 | −0.065 |
| 20 | 0.087 | 30 | 0.058 | 0.021 | −0.065 |
| 10 | 0.231 | 20 | 0.116 | 0.148 | −0.085 |
| 20 | 0.116 | 30 | 0.077 | 0.044 | −0.075 |
| 30 | 0.085 | 40 | 0.064 | 0.025 | −0.070 |
| 10 | 0.210 | 30 | 0.070 | 0.151 | −0.079 |
| 10 | 0.198 | 30 | 0.066 | 0.116 | −0.069 |
| 10 | 0.231 | 30 | 0.077 | 0.192 | −0.083 |
| $\overline{P}=2450$ | | | | | |
| 10 | 0.156 | 20 | 0.078 | 0.046 | −0.058 |
| 10 | 0.115 | 20 | 0.058 | 0.024 | −0.055 |
| 10 | 0.186 | 20 | 0.093 | 0.066 | −0.069 |
| 20 | 0.093 | 30 | 0.062 | 0.023 | −0.060 |
| 20 | 0.075 | 30 | 0.050 | 0.014 | −0.059 |
| 10 | 0.135 | 20 | 0.068 | 0.030 | −0.050 |
| 30 | 0.084 | 40 | 0.063 | 0.020 | −0.059 |
| 40 | 0.069 | 50 | 0.055 | 0.012 | −0.049 |
| 10 | 0.109 | 20 | 0.055 | 0.023 | −0.060 |
| 50 | 0.082 | 60 | 0.068 | 0.020 | −0.055 |

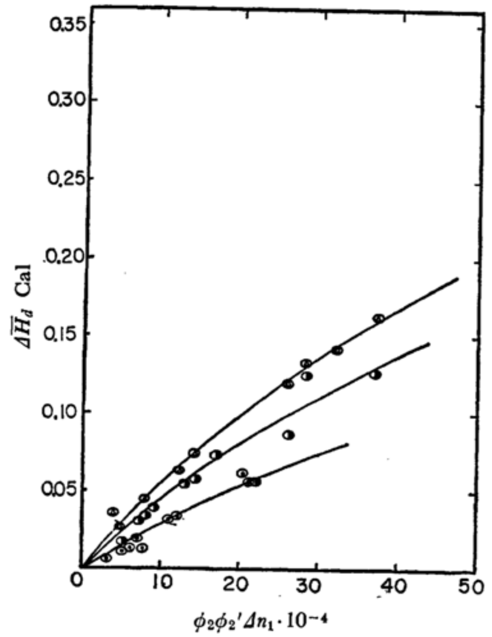

Fig. 1(a). The plot of the heat of dilution, $\Delta\overline{H}_d$, against $\phi_2\phi_2'\Delta n_1$.

Mn
$4\cdot10^4$ ◬
$15\cdot10^4$ ◑
$20\cdot10^4$ ⊙
P.V.Ac.—Benzene

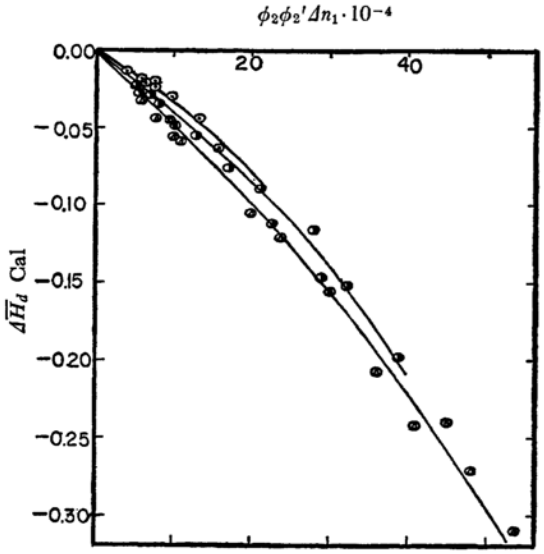

Fig. 1(b). The plot of the heat of dilution, $\Delta\overline{H}_d$, against $\phi_2\phi_2'\Delta n_1$.

Mn
$4\cdot10^{-4}$ ◬
$15\cdot10^{-4}$ ◑
$20\cdot10^{-4}$ ⊙
P.V.Ac.—M.E.K.

Table 2. Dependence of the interaction heat parameter on the concentration: $\chi_H=\chi_1+\chi_2\phi_2$

| | $\chi_1$ | $\chi_2$ |
|---|---|---|
| PVAc-Benzene | | |
| $\overline{P}=1$ | 0.230 | |
| $\overline{P}=480$ | 0.095 | −0.096 |
| $\overline{P}=1850$ | 0.071 | −0.047 |
| $\overline{P}=2450$ | 0.046 | −0.011 |
| PVAc-MEK | | |
| $\overline{P}=1$ | −0.140 | |
| $\overline{P}=480$ | −0.088 | −0.10 |
| $\overline{P}=1850$ | −0.059 | −0.12 |
| $\overline{P}=2450$ | −0.048 | −0.11 |
| $\overline{P}=3500$[7] | −0.038 | −0.17 |

* $\overline{P}$: degree of polymerization.

also according to the Huggins[6] theory. The Huggins theory, however, includes various factors characteristic of polymer solutions, so our results can not be quantitatively compared with those of this theory because of the lack of information concerning the chain configuration of the polymer molecules in the solution.

Further, the value of $\chi_1$, which is the interaction heat parameter in the dilute solution, decreases in absolute value as the molecular weight increases, as is shown in the first column in Table 2.

Such a dependence of the $\chi_1$ parameter on the molecular weight has been found for other polymer solutions in previous papers.[3–4]

The dependence of the $\chi_1$ parameter on the molecular weight has been theoretically derived by Huggins, who also explained it by using the dilute solution theory of polymers. For example, according to the theory the second virial coefficient can generally be given by the following equation:

$$A_2=(\bar{u}_2{}^2/V_1)\phi_1(1-\theta/T)F(X)$$

where $F(X)$ is the complicated function of the molecular weight and the excluded volume ($\beta$); it decreases as the molecular weight increases.

The approximate treatment of the second virial coefficient gives the apparent interaction parameter, $\chi_1$, as:

$$\chi_1=(\phi_1\theta/T)F(X)$$

which is written as:

$$\chi_1=\chi_1(X=0)F(X)$$

Since $F(X)$ decreases with an increase in the molecular weight, the apparent interaction parameter, $\chi_1$, decreases with an increase in the molecular weight of the polymer.

Our results seem to be qualitatively in good agreement with the dilute solution theory of Flory.

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[6] M. L. Huggins, *J. Am. Chem. Soc.*, **86**, 3535 (1964).

[7] J. D. Ferry, *J. Chem. Phys.*, **17** 1107 (1949).