BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1554—1556 (1973)

Interaction Parameters of Poly(*o*-chlorostyrene)-Solvent Systems

Kunihiko Gekko and Kimiyoshi Matsumura*

Department of Food Science and Technology, Faculty of Agriculture, Nagoya University, Nagoya 464

** Department of Chemistry, Aichi Kyoiku University, Kariya 448*

(Received August 14, 1972)

The thermodynamic properties of a polymer-solvent mixture have generally been analysed using the equation introduced by Flory and Huggins:[1,2]

$$\ln a_1 = \ln(1-v_2) + v_2 + \chi v_2^2 \tag{1}$$

where a_1, v_2, and χ represent the activity of the solvent, the volume fraction of the polymer, and the interaction parameter between the polymer and the solvent respectively. It has been indicated, on the basis of both experimental and theoretical studies,[3-7] that the χ value depends on the polymer concentration. However, we do not have enough systematic investigations[8-10] to be able to understand the characteristic behavior of χ in relation to such physical quantities of the polymer and the solvent as the dipole moment. In this paper, we will discuss the effects of the concentration and the dipole moment on the interaction parameters of poly(*o*-chlorostyrene)-solvent systems by means of isopiestic vapor-pressure measurements.

Experimental

Materials. Atactic poly(*o*-chlorostyrene)(PoCS) was prepared and fractionated following the method reported in the previous paper.[11] The average molecular weight of the polymer used in this experiment was determined to be 60.7 × 10^4 by measuring the intrinsic viscosity of toluene solutions at 25°C.[12] The density of this material was 1.268 and 1.255 g/ml at 25 and 40°C respectively. To clarify the dipole-moment effect of the solvent on χ, we used benzene and methyl ethyl ketone (MEK) as solvents; they have almost identical molar volumes and cohesive energy densities. These solvents were purified by the conventional purification method.

Methods. The apparatus and procedures for measuring the equilibrium vapor sorption were similar to those used in a previous paper.[6] The volume fraction of the polymer at equilibrium was calculated from the experimentally-determined weight fraction by assuming that the solvent volume and the polymer volume are additive on mixing. The activity, a_1, of the solvent was obtained from $a_1 = P_1/P_1^0$, where P_1^0 and P_1 are the vapor pressure of the pure solvent and of the solvent on the polymer solution respectively at a given temperature.

Results and Discussion

The sorption isotherms of benzene and MEK for PoCS are shown in Fig. 1, in which the data for polystyrene(PS)–benzene[13] and PS–MEK[14] systems are also shown as references. It is clear that benzene more easily comes into contact with both polymers, PoCS and PS, than MEK does. This is consistent with the fact that MEK becomes a theta solvent for PoCS at 25 °C, though benzene is a good solvent.[12] From the values of v_2 and P_1/P_1^0, we calculated the Flory-Huggins interaction parameter, χ, using Eq. (1). The values thus obtained are listed in Table 1 and are plotted against v_2 in Fig. 2. In general, the concentration dependence of χ has been expressed by a series of v_2 by Huggins:[7]

$$\chi = A + Bv_2 + Cv_2^2 + \cdots\cdots \tag{2}$$

where *A*, *B*, *C*, *etc.* are constant values independent

---

1) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

2) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

3) W. R. Krigbaum and D. O. Geymer, *J. Amer. Chem. Soc.*, **81**, 1859 (1959).

4) C. H. Baker, W. B. Brown, G. Gee, J. S. Rowlisnos, D. Stubley, and R. E. Yeadon, *Polymer*, **3**, 215 (1962).

5) C. Booth, G. Gee, G. Holden, and G. R. Williamson, *Polymer*, **5**, 343 (1964).

6) H. Ochiai, K. Gekko, and H. Yamamura, *J. Polym. Sci.*, **9**, 1629 (1971).

7) M. L. Huggins, *J. Amer. Chem. Soc.*, **86**, 3535 (1964).

8) H. Yamakawa, S. A. Rice, R. Corneliussen, and L. Kotin, *J. Chem. Phys.*, **38**, 1759 (1963).

9) R. Corneliussen, S. A. Rice, and H. Yamakawa, *ibid.*, **38**, 1768 (1963).

10) H. Daoust and A. Hade, *Polymer*, **9**, 47 (1968).

11) K. Matsumura, *Makromol. Chem.*, **124**, 204 (1969).

12) K. Matsumura, *Polym. J.*, **1**, 322 (1970).

13) E. C. Baughan, *Trans. Faraday Soc.*, **44**, 495 (1948).

14) C. E. H. Bawn, R. F. J. Freeman, and A. R. Kamaliddin, *ibid.*, **46**, 677 (1950).

Table 1. The variation of P_1/P_1^0 and χ with v_2 for PoCS–benzene and PoCS–MEK systems

Benzene						MEK		
25 °C			40 °C			25 °C		
P_1/P_1^0	v_2	χ	P_1/P_1^0	v_2	χ	P_1/P_1^0	v_2	χ
0.9747	0.414	0.55	0.8419	0.660	0.57	0.8899	0.711	0.82
0.6928	0.784	0.62	0.7880	0.730	0.64	0.8222	0.768	0.84
0.5830	0.830	0.58	0.6384	0.801	0.57	0.6745	0.845	0.88
0.3566	0.915	0.62	0.4714	0.883	0.65	0.4646	0.916	0.95
0.2400	0.947	0.63	0.1159	0.978	0.69	0.4631	0.925	1.04
0.1607	0.965	0.60				0.2415	0.968	1.13

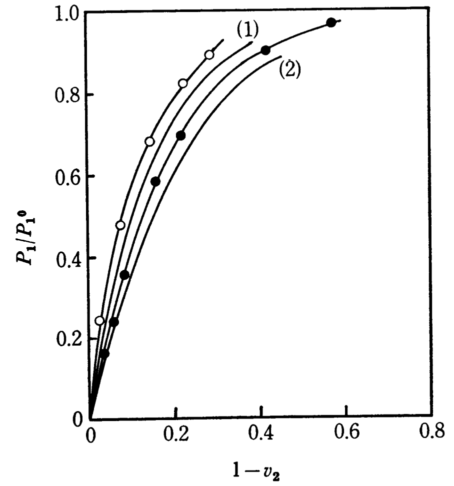

Fig. 1. The sorption isotherms of benzene (-●-) and MEK (-○-) for PoCS at 25 °C. The line (1) and (2) represent the data for PS-MEK system at 25 °C14) and PS-benzene system at 20 °C13), respectively.

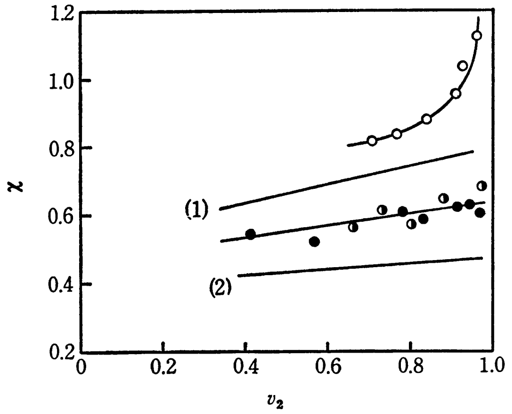

Fig. 2. The concentration dependence of χ for PoCS-benzene (-●-, 25 °C; -◐-, 40 °C) and PoCS-MEK (-○-, 25 °C) systems. The lines (1) and (2) represent the data for PS-MEK system at 25 °C14) and for PS-benzene system at 20 °C13), respectively.

of the concentration. In the system of PoCS–benzene, there exists a linear relation with a small positive slope between v_2 and χ, similar to the case in the PS–benzene solution. The effect of the temperature on χ for this system could not be ascertained in this experiment, which may suggest that there is almost no heat of mixing. On the other hand, in the PoCS–MEK system there is remarkable concentration dependence of χ, requiring the third and the higher terms on the right-hand side of Eq. (2), and the χ values are considerably larger than those of the PoCS–benzene system.

Now, it is considered that χ depends on the enthalpy factors, such as the cohesive energy and the interaction energy due to the dipole moment or the hydrogen bonding between the solvent and polymer molecules, and also on the entropy factors, such as the size and shape of the polymer and solvent molecules. The molar volume of MEK is 89.6 ml/mol, which is close to that of benzene, 89.3 ml/mol at 25°C. Further the solubility parameters of benzene and MEK are 9.15 and 9.22 (cal/ml)$^{1/2}$ respectively. Judging from these data, there seems to be almost no difference in the solvent power between the two solvents. Accordingly, the characteristic difference in χ between the systems of PoCS–benzene and PoCS–MEK is probably due to such factors as the molecular shapes, the hydrogen-bonding abilities, and the dipole moments of the solvents; the dipole moment of benzene is zero, and that of MEK is 2.75 Debye (D). We may consider that the effect of the hydrogen bond is not so predominant for this characteristic behavior of PoCS–MEK system, by analogy with the results for the vapor-pressure behavior of the polypropylene–MEK and natural rubber–MEK systems.5)

According to Yamakawa *et al.*,8) the thermodynamic interaction parameter, χ, is the sum of the χ^* which arises from the non-polar interaction and the χ_p which arises from the polar interaction; that is, $\chi=\chi^*+\chi_p$. For the concentration dependence of χ_p, the following conclusion was also obtained by them:

(a) χ_p increases with an increase in the concentration when the dipole moment of the solvent (μ_1) is greater than that of the polymer segment(μ_2)

(b) $\chi_p=0$ when $\mu_1=\mu_2$

(c) χ_p decreases with an increase in the concentration when $\mu_1<\mu_2$. It was also found that the polarizabilities of the solvent and the polymer segment affect χ_p to a smaller extent than the dipole moments do.8) Furthermore, χ^* may usually be considered as a slowly decreasing function of the concentration from both the theoretical and experimental points of view.8,15,16) In analyzing the results we obtained on the basis of the above theoretical conclusion, we take

---

15) M. Fixman, *J. Chem. Phys.*, **35**, 889 (1961).

16) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York (1953), p. 515,

0.36D for the μ_2 of PS[17] and assume that the μ_2 of PoCS is the same as the dipole moment of *o*-chlorotoluene, 1.43D, since no value has been reported for the μ_2 of PoCS.

The remarkable increase in χ with the polymer concentration for the PoCS–MEK system where $\mu_1>\mu_2$ suggests that, for this system, the contribution of χ_p to the total χ is significant in comparison with that of χ^*, as much as in the PS–MEK system. That is, the continuum model of concentrated solutions by Yamakawa *et al.*[8] is considered to be valid for the PoCS–MEK system also. On the other hand, the χ values for the systems of PoCS–benzene and PS–benzene increased slowly with the concentration, as is shown in Fig. 2, though they should decrease with the concentration judging from the fact that $\mu_1<\mu_2$, if the continuum model is valid for these systems. This discrepancy of the continuum model for the PoCS–benzene system may be due to the orientation of the benzene rings of the polymer and the solvent, since such an orientation has been found in the case of the PS-benzene system.[18]

---

17) W. R. Krigbaum and A. Roig, *J. Chem. Phys.*, **31**, 544 (1959).

18) H. Tompa, *J. Polym. Sci.*, **8**, 51 (1952); K. Sato and A. Nishioka, *J. Polym, Sci.*, *A-2* **10**, 489 (1972).