Note on a potential contribution of entropy to the interaction parameter for dissimilar units in copolymers

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The intrinsic viscosity data reported in the literature for ethylene–butylene copolymers in several solvents are used to estimate the χ parameter characterizing the polymer–solvent interaction. The dependences of this parameter on the copolymer composition display unexpectedly pronounced minima which indicate a repulsive interaction of ethylene and butylene units. In view of their chemical similarity, which makes the enthalpy contribution to the interaction low, the behaviour is assigned to entropy-of-mixing effects.

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The interaction of chemically dissimilar monomer units is an important problem in the discussions of the dilute solution properties of copolymers[1,2]. The Flory–Huggins parameter χ_{AB} characterizing this interaction consists of an entropy and an enthalpy contribution:

$$\chi_{AB} = \chi_{AB}^{s} + \chi_{AB}^{h} \tag{1}$$

The entropic part χ_{AB}^{s} has usually been assumed to be small, and this assumption seemed to be supported by the finding that the χ_{AB} values for most copolymers investigated so far were close to the enthalpy term χ_{AB}^{h} computed from the solubility parameters, δ_i, of the copolymer constituents by means of the equation:

$$\chi_{AB}^{h} = (V_1/RT)(\delta_A - \delta_B)^2 \tag{2}$$

where V_1 is the mole volume of solvent[2], R is the gas constant and T is temperature.

By analysing the intrinsic viscosity data reported by Arnett and Stacy[3,4] for well defined copolymers of ethylene and butylene (EB copolymers), we obtained results which are at variance with the above concept.

Arnett and Stacy published the slope values J of the Burchard–Stockmayer–Fixman plots[5,6] ($[\eta]/M^{1/2}$ *versus* $M^{1/2}$) of the intrinsic viscosity data. The slope J is related to the polymer–solvent interaction parameter χ by the relation[7]:

$$J = 0.287\Phi_0(2/N)(\bar{v}^2/V_1)(\tfrac{1}{2} - \chi) \tag{3}$$

where $\bar{v}$ is the partial specific volume of polymer, Φ_0 is the Flory viscosity constant ($\Phi_0 = 2.5 \times 10^{21}\ \mathrm{mol}^{-1}$ if $[\eta]$ is expressed in dl g^{-1})[7], and N is the Avogadro number.

With copolymers the χ parameter consists of three components[1,2] ($\chi_A, \chi_B, \chi_{AB}$) corresponding to three types of interaction (AA, BB, AB):

$$\chi = \chi_A\varphi_A + \chi_B\varphi_B + \chi_{AB}\varphi_A\varphi_B \tag{4}$$

The symbol φ_i stands for the volume fraction of the ith copolymer component ($i = \mathrm{A, B}$).

The χ values for four EB copolymers in three solvents (α-chloronaphthalene, biphenyl, n-dodecanol) at 130°C are plotted against the volume fraction of butylene units, φ_B, in *Figure 1*. The volume fraction was evaluated from the respective weight fractions, using the values 1.266 and 1.246 cm^3 g^{-1} for the specific volumes of polyethylene and polybutylene, respectively. These were obtained by extrapolating to 130°C the specific volumes reported by Richardson *et al.*[8] and Zoller[9]. Since the specific volumes of homopolymers are very similar, we employed, for all copolymers, $\bar{v} = 1.26$ cm^3 g^{-1} obtained by extrapolating to 130°C the $\bar{v}$ values for polyethylene in α-chloronaphthalene[10]. We believe that the error thus introduced is not serious.

The χ parameters for $\varphi_B = 0.28$, 0.52 and 0.73 were computed from the J values at 130°C tabulated by Arnett and Stacy[3,4]. Those for $\varphi_B = 0.076$ in α-chloronaphthalene and biphenyl were obtained by linear interpolation.

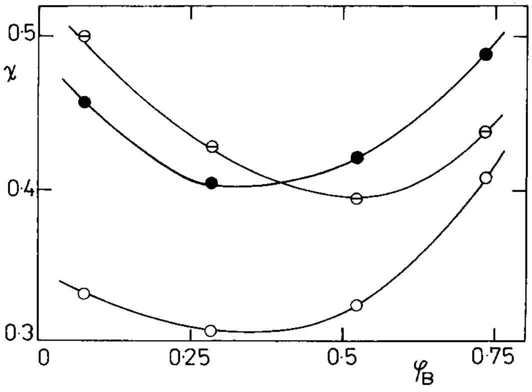

Figure 1 Dependence of the χ parameter on the copolymer composition. Data points from references 3 and 4: (○) α-chloronaphthalene; (●) biphenyl; (⊖) n-dodecanol. ϕ_B is the volume fraction of butylene units in the copolymers

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to 130°C of the plot of χ *versus* $1/T$ constructed from data for 125 and 140°C. The value for this sample in n-dodecanol corresponds to 125°C. It was not corrected because no data were available for other temperatures. It is somewhat overestimated.

The dependences in *Figure 1* have pronounced minima indicating positive χ_{AB}. Similar plots were also obtained for 35°C but are not discussed here because they cover a rather narrow composition range. The data in *Figure 1* were further treated according to the equation:

$$(\chi_k - \chi_r)/(\varphi_{B,k} - \varphi_{B,r}) = (\chi_B - \chi_A) + [(\varphi_{B,k} + \varphi_{B,r}) - 1]\chi_{AB} \tag{5}$$

which is simply obtained from equation (4). The subscript r refers to a reference copolymer ($\varphi_{B,r} = 0.73$ in the present case) and k refers to other copolymers. From the intercept and slope of the plot based on equation (5) (*Figure 2*) we obtained the difference ($\chi_B - \chi_A$) of the interaction parameters for homopolymers and the χ_{AB} parameter, respectively (*Table 1*).

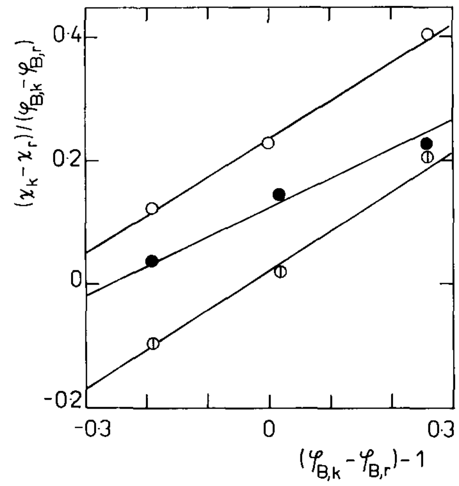

Figure 2 Plot according to equation (5). Symbols as in *Figure 1*

Table 1 Interaction parameters[a] for EB copolymers at 130°C

Solvent	α-Chloronaphthalene	n-Dodecanol	Biphenyl
$\chi_B - \chi_A$	0.23	0.02	0.17
χ_{AB}	0.61	0.64	0.47

[a] Computed with $V_1 = 160$, 245 and 162 cm^3 mol^{-1} for α-chloronaphthalene, n-dodecanol and biphenyl, respectively

The χ_{AB} values depend on the solvent but all of them are much higher than most values reported so far ($\chi_{AB} \leqslant 0.1$)[1,2]. The fact that the latter have been estimated from the intrinsic viscosity data by means of other equations can account only for a minor part of the difference.

High positive values of χ_{AB} indicate strong repulsive interaction (incompatibility) of ethylene and butylene units. If, assuming $\chi^s_{AB} = 0$, we calculate the difference of the solubility parameters (with $V_1 = 200\,\text{cm}^3\,\text{mol}^{-1}$ and $T = 403\,\text{K}$) according to equation (2), we obtain $\Delta\delta = 3.1\,\text{J}^{1/2}\,\text{cm}^{-3/2}$. That seems to be too high a value in view of the chemical similarity of the monomer units. The δ values for polyethylene, polypropylene and polyisobutylene are[11], respectively, 16.6, 17.8 and 16.4 $\text{J}^{1/2}\,\text{cm}^{-3/2}$. Their differences are smaller than that mentioned above.

These results suggest that, contrary to the current assumption, χ^s_{AB} is not zero. The assumption was founded on the lattice theory of polymer solutions showing that the mixing of chemically unlike polymers is associated with negligible combinatorial entropy. In the theory, the definition of the segment neglects potential differences in the shape and/or diameter of comonomers. As pointed out by Patterson[12], such a difference can play a role in the combinatorial entropy of mixing of polymer chains. We believe that it may be even more important in the excluded volume interaction of segments belonging to the same chain.

In the present system, sequences of ethylene units have a lower diameter than those of butylene units. The accommodation of units of the latter type in the neighbourhood of the former may be more difficult than the accommodation of similar units. This may make the χ^s_{AB} terms differ from zero.

References

1 Stockmayer, W. H., Moore, L. D., Fixman, M. and Epstein, B. N. *J. Polym. Sci.* 1955, **16**, 517
2 Fukuda, T. and Inagaki, H. *Pure Appl. Chem.* 1983, **55**, 154
3 Arnett, R. L. and Stacy, C. J. *J. Phys. Chem.* 1973, **77**, 1986
4 Stacy, C. J. and Arnett, R. L. *J. Phys. Chem.* 1973, **77**, 78
5 Burchard, W. *Makromol. Chem.* 1961, **50**, 20
6 Stockmayer, W. H. and Fixman, D. *J. Polym. Sci. C* 1963, **1**, 137
7 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper, New York, 1971
8 Richardson, M. J., Flory, P. J. and Jackson, J. B. *Polymer* 1963, **4**, 221
9 Zoller, P. *J. Appl. Polym. Sci.* 1979, **23**, 1057
10 Weston, N. E. and Billmeyer, F. W. *J. Phys. Chem.* 1963, **67**, 2728
11 Van Krevelen, D. W. and Hoftyzer, P. J. 'Properties of Polymers', Elsevier, Amsterdam, 1972, p. 85
12 Patterson, D. *Pure Appl. Chem.* 1972, **31**, 133