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# On the Intramolecular Repulsion Effect in Random Copolymer Solubility

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The purpose of this Note is to clarify the nature of the effect mentioned in the title. This effect seems to be misunderstood or overinterpreted by a number of workers in the field of polymer solubility and miscibility.

The equation for the Flory interaction parameter of a binary random copolymer with a solvent, $\chi_{CS}$, was written by Stockmayer et al.[1] in terms of the interaction parameters of the corresponding homopolymers with the solvent and with each other as follows:

$$\chi_{CS} = \chi_{AS}\phi_A + \chi_{BS}\phi_B - \chi_{AB}\phi_A\phi_B \qquad (1)$$

where $\phi_A$ and $\phi_B$ are the volume fractions of monomers of types A and B in the copolymer, respectively, $\chi_{AS}$ and $\chi_{BS}$ are the interaction parameters of homopolymers A and B with the solvent, S, respectively, and $\chi_{AB}$ is the interaction parameter between homopolymers A and B. The same equation, using different notation, was first shown in a footnote in a paper by Simha and Branson.[2] Equation 1 was generalized by Krause et al.[3] for random copolymers containing an arbitrary number of different monomer units and for mixtures containing more than one random copolymer:

$$\chi_{CD} = \sum_I\sum_J \chi_{IJ}\phi_I{}^C\phi_J{}^D - (1/2)\left[\sum_I\sum_J \chi_{IJ}\phi_I{}^C\phi_J{}^C + \sum_I\sum_J \chi_{IJ}\phi_I{}^D\phi_J{}^D\right] \qquad (2)$$

where $\chi_{CD}$ is the interaction parameter between two random copolymers C and D; C or D could as easily be a homopolymer or a solvent, in which case it contains only one type of repeat unit. The homopolymer–homopolymer or homopolymer–solvent interaction parameters are the $\chi_{IJ}$, and $\phi_I{}^C$ refers to the volume fraction of monomer I in copolymer C, with similar definitions for the similar terms. Since terms of the type $\chi_{II}$ are identically zero, eq 2 is not as complicated as it looks. At any rate, eq 2 contains terms that are positive in the interaction parameters between different monomer units in different types of molecules, C and D, and negative terms in the interaction parameters between different monomer units in the same molecule, either C *or* D. These negative terms in the intramolecular interaction parameters lead to the conclusion that a positive interaction parameter between two monomers in the same random copolymer molecule enhances miscibility of this copolymer with other molecules. This is evident in the simplest case, eq 1, where, for given values of the parameters $\chi_{AS}$ and $\chi_{BS}$, a positive $\chi_{AB}$ decreases the value of $\chi_{CS}$.

These considerations are not, however, evidence for intramolecular repulsions in the random copolymer since the actual interaction energies, $\epsilon_{IJ}$, between neighboring pairs of segments or solvent molecules are invariably negative as referred to infinite separation. That is, all interaction forces are *attractive*. For example, in simple lattice models,[4] the interaction parameter $\chi_{AB}$ is proportional to the difference $(2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB})$. Each of the $\epsilon$'s is negative, but the difference is positive in the majority of cases in which specific interactions such as hydrogen bonding do not occur. Thus, it is best to regard all $\chi$ parameters, including those for unlike segments within random copolymers, as measures of the relative strengths of the various *attractive* interactions.

A revealing case of the above assertion obtains if the Hildebrand[5] solubility parameters are used to calculate the interaction parameters between all pairs. In this case

$$\chi_{IJ} = \frac{V_r}{RT}(\delta_I - \delta_J)^2 \qquad (3)$$

where $\delta_I$ and $\delta_J$ are the solubility parameters of the homopolymers corresponding to the polymer segments I or J or to solvents I or J, $R$ is the gas constant, and $T$ is the absolute temperature. If either I or J is a solvent, $V_r$ is usually the molar volume of the solvent; if I and J are both polymer segments, then $V_r$ is a reference volume, often taken as 100 cm$^3$ mol$^{-1}$. (If we are calculating interaction parameters for a particular mixture, the same value of $V_r$ must be used in all calculations.) If we set $\delta_C$ as the solubility parameter of a random copolymer and if we use eqs 2 and 3 together, we always find that[6]

$$\delta_C = \sum_I \delta_I\phi_I{}^C \qquad (4)$$

Equation 4 shows that the solubility parameter of a random copolymer is just the weighted average, using volume fractions, of the solubility parameters of the homopolymers corresponding to its segments. Thus, no intramolecular repulsion effect appears as such when solubility parameters are used in calculations of random copolymer solubility. In this special case, the apparent intramolecular repulsion effect, noted when interaction parameters are used, may be regarded as an artifact connected with the quadratic nature of eq 3.

Equations 2 and 4 were rederived later by Paul and Barlow,[7] who discussed their consequences at length, mostly when eq 3 does not hold. Although eq 3 holds remarkably well for mixtures involving random copolymers, especially if these mixtures involve only high polymers in which no specific interactions occur, in most cases the solubility parameter treatment is no longer to be regarded as anything but a convenient and far from trustworthy approximation for the interaction energies since there can be large noncombinatorial contributions to the free energy of solution which affect $\chi$. Nevertheless, in spite of this, it seems preferable in all cases to think of the strength of the attractive interactions between the repeat groups, both intermolecular and intramolecular, as contributing to the terms in eqs 1 and 2 rather than in terms of an intramolecular repulsion effect.

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## References and Notes

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