

Polymer Miscibility in Mixed Organic Liquids Having Acid-Base Interaction—A Modified Two-Dimensional Approach

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Synopsis

A mixture of two organic liquids, each of which is a solvent for a given polymer, may become a nonsolvent mixture, if there is strong acid-base interaction between the two solvents. Experimental results of such cases are presented for five polymers. These results are then correlated with the proposed modified form of the two-dimensional approach. In the modification, an additional term for taking into account the acid-base interaction is added to the expression for the hydrogen-bonding solubility parameter of the liquid mixture; the dispersion forces and polar interactions are assumed to be undisturbed by the occurrence of the acid-base interaction.

INTRODUCTION

In the case of polymer miscibility in mixed organic liquids, it has been shown that, for a given polymer, the solvent power of a liquid (solvent or nonsolvent) can be improved by adding a properly selected solvent or nonsolvent.¹⁻⁹ However, studies of the case of mixing two solvents to form a nonsolvent are rare. Experimentally, Gee¹ found that "cellulose acetate can dissolve in aniline and glacial acetic acid but not in a mixture of these two solvents." Theoretically, Chen⁸ proposed a criterion for selecting such a solvent pair. He showed that the Scatchard interaction parameter between such two solvents, based on the lattice theory of solution, must be negative, indicating a domination of the acid-base interaction over all other types of interaction.

This paper presents some experimental results on the miscibility of five polymers in binary liquid mixtures composed of a proton donor solvent and a proton acceptor solvent. These results include cases of solubility, swelling and insolubility. It was found that these results can be correlated with the proposed modified form of the two-dimensional (2D) approach. The original 2D approach^{6,7} was found to be inapplicable to these results.

EXPERIMENTAL

The polymers studied are poly(vinyl acetate), pure phenolic resin, epoxy resin (Epikote 1001 from Shell Chemical Co.), poly(vinyl butyral), and cellulose acetate.

According to Chen,⁸ to make a mixed nonsolvent out of two original solvents requires that one solvent must contain proton donors (acid) and the other proton acceptors (base). The solvents containing proton donor used in this work are acetic acid (65), formic acid (66), butyric acid (67A), and chloroform (49); and the solvents containing proton acceptors are aniline (42), diethylamine (47),

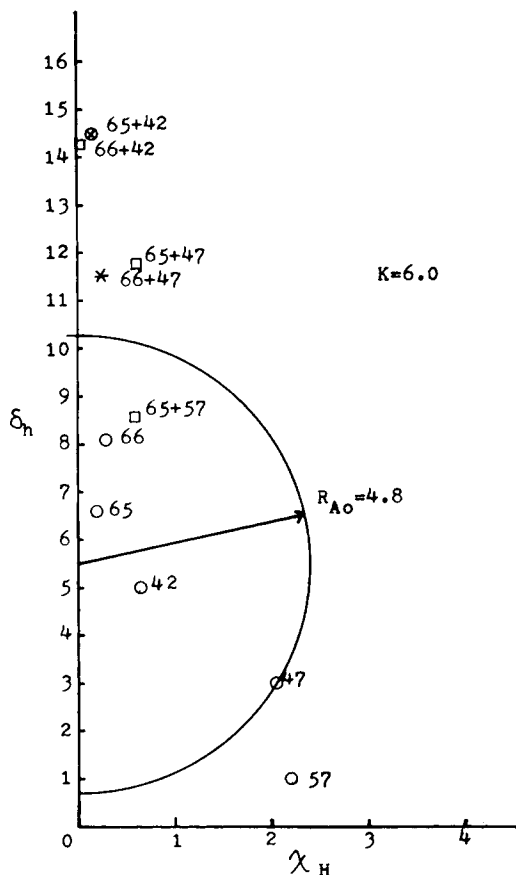


Fig. 2. Solubility of poly(vinyl butyral) in mixed organic liquids. Symbols same as in Figure 1.

saturated with formic acid. Benzene and formic acid are not completely miscible, 5 ml of benzene can only tolerate a few drops of formic acid without causing phase separation. This datum is not included in the following correlation.

THE MODIFIED TWO-DIMENSIONAL APPROACH

In the prediction of polymer miscibility in pure and mixed organic liquids using the 2D approach^{6,7} the solvent power of a liquid for a given polymer was characterized by the two parameters $\delta_{h,L}$ and $\chi_{H,PL}$, where $\delta_{h,L}$ is the hydrogen-bonding solubility parameter of the liquid, and $\chi_{H,PL}$ is a term taking account of the dispersion and polar interactions between the liquid and the polymer and of effects due to temperature and molecular size of the liquid and can be calculated from properties of the pure liquid and polymer. For the mixed liquid case, values of these two parameters can be calculated from those of pure liquid case using the proposed mixing rules.⁷

For a given polymer, the liquid mixture composed of two solvents, is always a solvent according to the 2D approach. However, the experimental results in Figures 1–5 have shown that a mixture of two solvents may become a nonsolvent if there is strong acid-base interaction in the mixture. The 2D approach is thus inapplicable to this case.

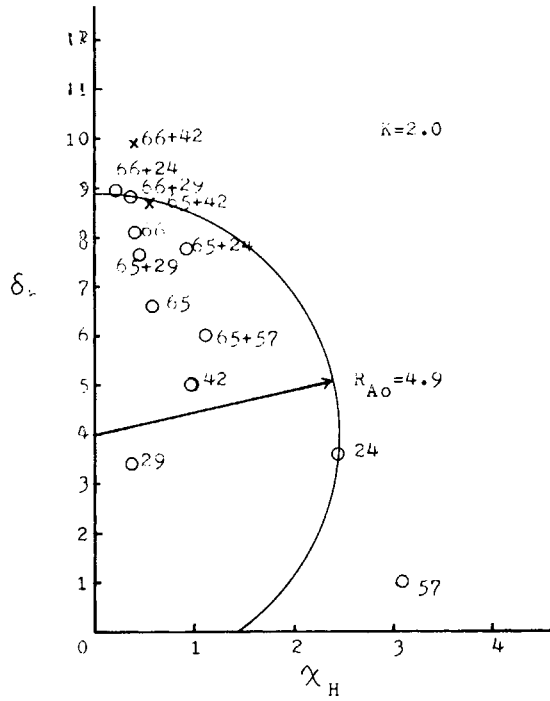


Fig. 3. Solubility of poly(vinyl acetate) in mixed organic liquids. Symbols same as in Figure 1.

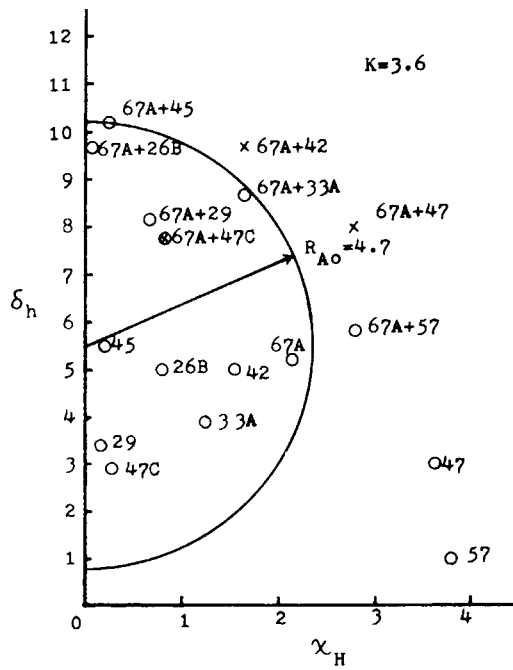


Fig. 4. Solubility of epoxy resin in mixed organic liquids. Symbols same as in Figure 1.

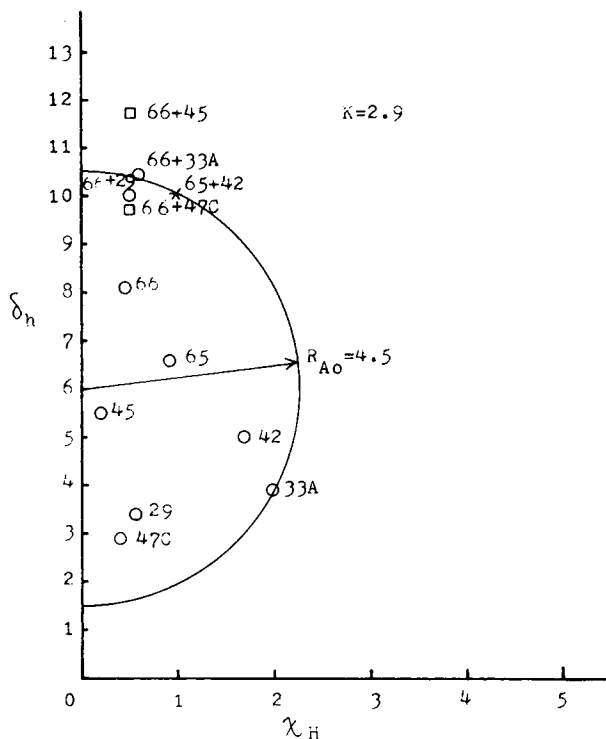


Fig. 5. Solubility of cellulose acetate in mixed organic liquids. Symbols same as in Figure 1.

In liquid mixtures involving acid-base interaction, the molecules of a base and those of an acid may associate to form a complex through hydrogen bonding. To dissociate this complex requires energy to break the hydrogen-bonding bridges in addition to the dispersion and polar interactions. Therefore, in calculating δ_h of the mixture, an additional term [the last term in eq. (1)] for taking this energy into account should be considered. Thus, the 2D approach should be modified in such a way that the expression for χ_H for mixed liquid systems remains unchanged; but that for $\delta_{h,L}$ should be expressed as

$$\delta_{h,L} = (\phi_1^0 \delta_{h,1}^2 + \phi_2^0 \delta_{h,2}^2)^{1/2} + K \phi_1^0 \phi_2^0 (\delta_{h,1} \delta_{h,2})^{1/2} \quad (1)$$

where K is a constant and can be determined empirically. This modified form was used to correlate the data as shown in the next section.

CORRELATIONS

In locating a liquid mixture, which involves acid-base interactions in the 2D diagram, δ_h of the mixture was calculated using eq. (1), and χ_H of the polymer-mixed-liquid system as in the original 2D approach.⁷ The values of δ_d , δ_p , and δ_h of polymers and solvents used were taken from Hansen's work.⁵ Correlations of the experimental data with the modified 2D approach are shown in Figures 1-5. For a given polymer, the value of the constant K was determined in such a way so that the number of mixed solvents lying outside the circle is minimum and the number of mixed nonsolvents lying outside the circle is maximum. The values of K for the polymers investigated are listed in the figures.

The correlations for pure phenolic resin, poly(vinyl butyral) and poly(vinyl

acetate) are good, while for epoxy resin, three out of eight systems and for cellulose acetate, three out of five systems deviate from the correlations. The value of K increases with increasing radius of the solubility circle except for poly(vinyl acetate).

DISCUSSION

1) The reduction in solvent power of an acid solvent by adding a selected base solvent, or vice versa, can be attributed to the formation of complexes through hydrogen bonding between these two solvents. This complex formation can result in (a) a reduction in the entropy of mixing of the polymer solution in comparison to those without complex formation and (b) a reduction in the number of active sites in the acid solvent which is capable of forming hydrogen bonding with the polymer molecules.

2) It is believed that the present modification can also be applied to modify the Hansen's three-dimensional (3D) approach by adding the last term in eq. (1) to his expression for δ_h of mixed liquids, since the 3D and 2D approaches are essentially the same and have the same applicability.^{6,7,9}

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