

# Applicability of the Two-Dimensional Approach to Polymer Miscibility in Pure and Mixed Organic Liquids

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## Synopsis

Previously it was proposed that the solvent power of a pure or mixed organic liquid for a given polymer can be characterized by two parameters  $\delta_h$  and  $\chi_H$ . Using these two parameters, a two-dimensional (2D) solubility diagram can be constructed to predict solubility or insolubility. In the investigation only the polymers, poly(methyl methacrylate), polystyrene, and poly(vinyl acetate), were used to demonstrate the applicability of the 2D method. In this note, applicability of the 2D method to the 33 polymers investigated in Hansen's works is presented.

## CALCULATIONS AND CONCLUSIONS

The calculation procedures for the two- and three-dimensional (2D and 3D) approaches are identical to those shown in refs. 1-4. The values of  $\delta_d$ ,  $\delta_p$ ,  $\delta_h$ , and polymer miscibility data were taken from Hansen's works.<sup>3,4</sup> In this paper, the number assigned for each liquid and the alphabet assigned for each polymer are the same as in Hansen's works for ease of comparison.

### Polymer-Pure-Liquid Systems

All the polymer-liquid systems in Hansen's works were investigated. Deviations of the correlation for a specific polymer were taken as the number of solvents which should locate inside the solubility circle and sphere according to these two approaches but locate outside, and as the number of nonsolvents which should locate outside these regions but actually locate inside. For instance, for polymer C (epoxy resin) there are 48 solvents and five nonsolvents out of 87 liquids used. Using the 2D approach, 15 out of the 48 solvents locate outside the circle and one out of the five nonsolvents locates inside the circle. Using the 3D approach, 14 out of the 48 solvents locate outside the sphere and one out of five nonsolvents locates inside the sphere. For this polymer the deviation of correlation of the former approach is slightly larger than that of the latter approach for the solvent and is the same for nonsolvent. It was found that the 2D approach is particularly poorer for polymers A [poly(ethyl methacrylate)] and S (polyester) in the solvent case and for polymers  $\bar{F}$  [poly(vinyl chloride)] and  $\bar{L}$  (lignin) in the nonsolvent case.

For calculation of the deviation of correlation for solvents, the sum of the numbers of solvents which do not locate in the soluble regions for each polymer was divided by the sum of the numbers of solvents used for each polymer. The

TABLE I  
Systems of Polymer Solubility in Mixed Liquids Deviating from the 2D and 3D Correlation

| Polymer                     | 2D    | 3D    |
|-----------------------------|-------|-------|
| C (epoxy resin)             | 6-48  | 6-48  |
| I (urea formaldehyde resin) | —     | 40-61 |
| J (1/2 sec. nitrocellulose) | 3-46  | —     |
|                             | 24-46 | 24-46 |
| Q (blocked isocyanate)      | 1-44  | 1-44  |
|                             | —     | 6-44  |
|                             | —     | 40-47 |
| S (polyester)               | 46-52 | 46-52 |

deviations for the 2D approach is 15% (219/1476) and for the 3D approach is 14% (209/1476). Thus these approaches work about equally well for the solvent.

Similar calculations for nonsolvents gave deviations of 10% (72/720) for the 2D approach and 4% (28/720) for the 3D approach. Therefore, the former is somewhat poorer than the latter.

For the over all deviation (solvent case plus nonsolvent case) there are 13% [(219 + 72)/(1476 + 720)] for the 2D approach and 11% [(209 + 28)/(1476 + 720)] for the 3D approach.

In the development of the 3D approach, Hansen has adjusted the values of  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  of liquids and polymers so that for a given polymer there is a solubility sphere in the  $\delta_d$ - $\delta_p$ - $\delta_h$  diagram. Thus if these values are readjusted for the solubility circles, in  $\delta_h$ - $\chi_H$  diagram, the accuracy of the 2D approach will probably be improved.

For the systems investigated, liquids whose solvent powers failed to be predicted are found to be spread over various kinds of liquid rather than distributed in some specific kind, such as alcohols, ethers, ketones, etc.

### Polymer-Mixed-Liquid Systems

All of the data of polymer-mixed-liquid systems in Hansen's work were calculated using the 2D approach except those for which the concentration of mixed liquid was not specified. The liquid mixtures were composed of two equal volumes of nonsolvents or poor solvents and should locate inside the solubility regions according to both approaches. However, for the 2D approach five out of 65 systems deviate from the correlation and for the 3D approach seven out of 65 systems. Systems which fail to be correlated with the 2D method also fail to be correlated with the 3D method except one. Systems which deviate from the correlations are listed in Table I.

### References

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