The 3-Dimensional Phase Diagram in Quaternary Systems of Polymers and Solvents

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Synopsis

A 3-dimensional phase diagram based on the equilateral tetrahedron has been developed to aid the visualization of the phase relations in a quaternary, multiphase system involving polymers and solvents. The technique developed is straightforward. It presents a clear picture of the "tie rods" and the "equilibrium surfaces" in a quaternary system as compared to the "tie lines" and "equilibrium curves" in a ternary system. With the aid of this 3-dimensional phase diagram, one can minimize the experimental effort in establishing the phase relations of a quaternary system.

INTRODUCTION

The exact calculation of the phase diagram of a ternary system involving at least one polymer component is extremely difficult[1,2] and the calculated equilibrium curve sometimes deviates significantly from the experimental values.[3] This is even more true with a quaternary system involving polymers. Therefore, in the polymer industry one generally relies on experimental data to study the phase relations of a ternary or a quaternary system. Data obtained for a ternary system can easily be presented in an equilateral triangular diagram[4] as shown in Figure 1. P is a polymer, S_1 a good solvent for the polymer, and S_2 a poor solvent for the polymer. Tie lines are established from data in the two-phase region to help visualize the relations of the two phases in equilibrium. Tie lines are used to indicate the two-phase regions in all the tenary phase diagrams in this paper. Other "empty" regions, or the regions without tie lines, in the ternary phase diagrams are single phase regions, or the region of complete miscibility, unless otherwise indicated.

It is much more difficult to present the data obtained for a quaternary system. Sometimes a series of many triangular diagrams with varying amounts of the fourth component has been used to present the data for a quaternary system.[5,6] In some cases 3-dimensional diagrams have been used to represent the compositions of a quaternary system, but no attempt was made to depict the phase relations such as the equilibrium curves and tie lines in a ternary system.[7–9] In order to visualize the phase behavior of a quaternary system involving polymers and solvents, a procedure has been established to construct the spatial equilibrium surfaces and tie rods in a 3-dimensional diagram.

THE EQUILATERAL TETRAHEDRON

The equilateral tetrahedron is used to represent the composition of a quaternary system. One of the properties of the equilateral tetrahedron is that the

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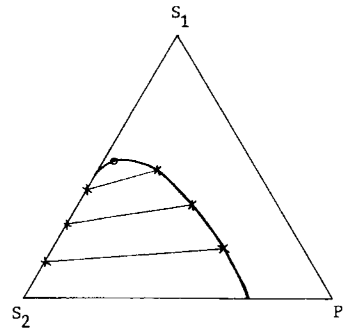

Fig. 1. Ternary phase diagram: (x) data points; (O) critical point.

sum of the distances from any interior point to the four surfaces always equals the height of the tetrahedron. Therefore, using an equilateral tetrahedron of unit height the distances from an interior point to the four surfaces can be used to represent the fractional composition of a quaternary system. The four equilateral triangular surfaces forming the tetrahedron are then diagrams for ternary systems with the fractional composition of the fourth component reduced to zero. Therefore, the 3-dimensional quaternary phase diagram is developed from four, 2-dimensional triangular ternary phase diagrams. The following systems will demonstrate the procedures.

One Polymer and Three Solvents—Case 1

The polymer (P) is completely soluble in two of the three solvents (S_1,S_2). The third solvent (S_3) only slightly swells the polymer. The first step in constructing a quaternary phase diagram is to construct four ternary phase diagrams each consisting of three of the four components involved ($P/S_1/S_2$, $P/S_2/S_3$, $P/S_3/S_1$, $S_1/S_2/S_3$). The ternary diagram for $P/S_2/S_3$ and $P/S_3/S_1$ are shown in Figure 2. These phase diagrams look very much like the ones presented by Tompa.[2] The two-phase region in (a) is larger than in (b), indicating that S_2 is a better solvent than S_1.

There is no two-phase region in the $P/S_1/S_2$ system since both S_1 and S_2 are

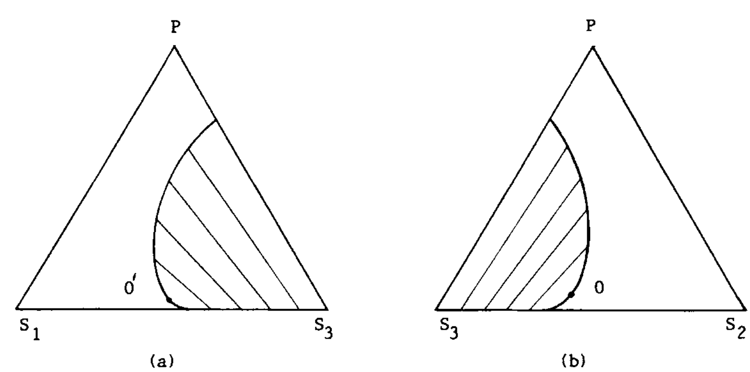

Fig. 2. Phase diagrams for the ternary systems with a polymer (P), a good solvent (S_1 or S_2), and a poor solvent S_3.

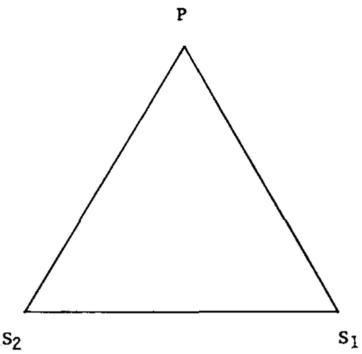

Fig. 3. Ternary phase diagram of a polymer and two good solvents consists of one homogeneous phase.

good solvents for the polymer. Therefore, the phase diagram for $P/S_1/S_2$ is simply an "empty" triangle, as shown in Figure 3. This "empty" triangle is presented here for illustrative purpose. It is later used in Figure 5 as one of the four elements for the construction of the quaternary phase diagram. The three solvents are assumed to be mutually miscible. Therefore, the phase diagram of $S_1/S_2/S_3$ would also be an empty triangle. However, it can be seen from Figures 2(a) and 2(b) that if a small amount of the polymer is dissolved in a certain mixture of the good solvents S_1 and S_2 and then titrated with the poor solvent S_3, the point of precipitation can be found. Starting with different ratios of S_1/S_2, the points of precipitation for each will establish a line of precipitation for the polymer P in the solvent system of $S_1/S_2/S_3$, as shown in Figure 4.

Now the three-phase diagrams in Figures 2 and 3 and the precipitation diagram in Figure 4 can be arranged as shown in Figure 5. The three lateral triangles are then folded upwards so that the three P apexes meet to form a tetrahedron as shown in Figure 6. By connecting the two equilibrium curves on the two triangular surfaces ($P/S_2/S_3$ and $P/S_3/S_1$), a curved equilibrium surface is formed, as shown in Figure 6. Connecting the two critical points on each critical curve, a critical line is formed which divides the equilibrium surface into two portions. Any quaternary system with composition corresponding to a point (M) within the envelope of the equilibrium surface will form two phases with compositions

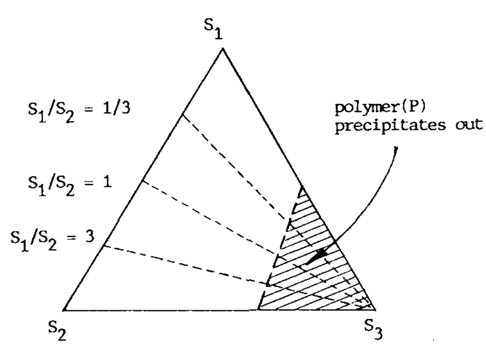

Fig. 4. Precipitation diagram of a small amount of the polymer (P) in the ternary solvent system $S_1/S_2/S_3$.

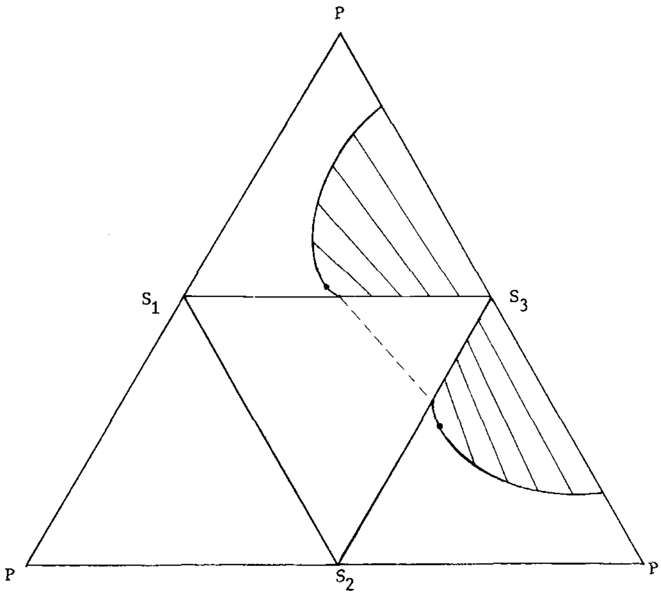

Fig. 5. The four diagrams in Figures 2–4 are placed together so that the common sides are combined.

corresponding to M_1 and M_2 on opposite portions of the equilibrium surface. The line connecting M_1,M,M_2 is called a "tie rod" in the space of the quaternary system, which corresponds to the tie line on the plane of a ternary system. The relative quantities of the two phases M_1/M_2 is inversely proportional to the two distances MM_1/MM_2, as in the case with conventional ternary diagrams. A few tie rods can be determined experimentally, and tie rods for other compositions can then be interpolated from the known tie rods. From this model it can be seen that the equilibrium surface tangents over the $S_1S_2S_3$ surface instead of intersecting the $S_1S_2S_3$ surface. Therefore, there is no two-phase region on the $S_1S_2S_3$ surface. However, a small amount of the polymer added to the ternary solvent mixture in the region covered by the equilibrium surface would bring the point within the envelope of the equilibrium surface, and precipitation would take place along the tie rod. One can also visualize the phase relations of any composition in the tetrahedral quaternary phase diagram. An example of such a quaternary system illustrated in Figure 6 is isoprene/ethylbenzene/hexane/methyl ethyl ketone.

Two Polymers and Two Solvents—Case 2A

The two polymers (P_1,P_2) are incompatible with each other. S_1 is a good solvent for both polymers, and S_2 is a poor solvent for both polymers. The four ternary phase diagrams, each consisting of three out of the four components, are presented in Figure 7. The four ternary phase diagrams are combined to form the quaternary phase diagram shown in Figure 8. In Figure 8 the wedged space $BEFS_1$ outside the shaded equilibrium surface is the one-phase region of a homogeneous, dilute solution of the polymers P_1 and P_2 in the solvent mixture of

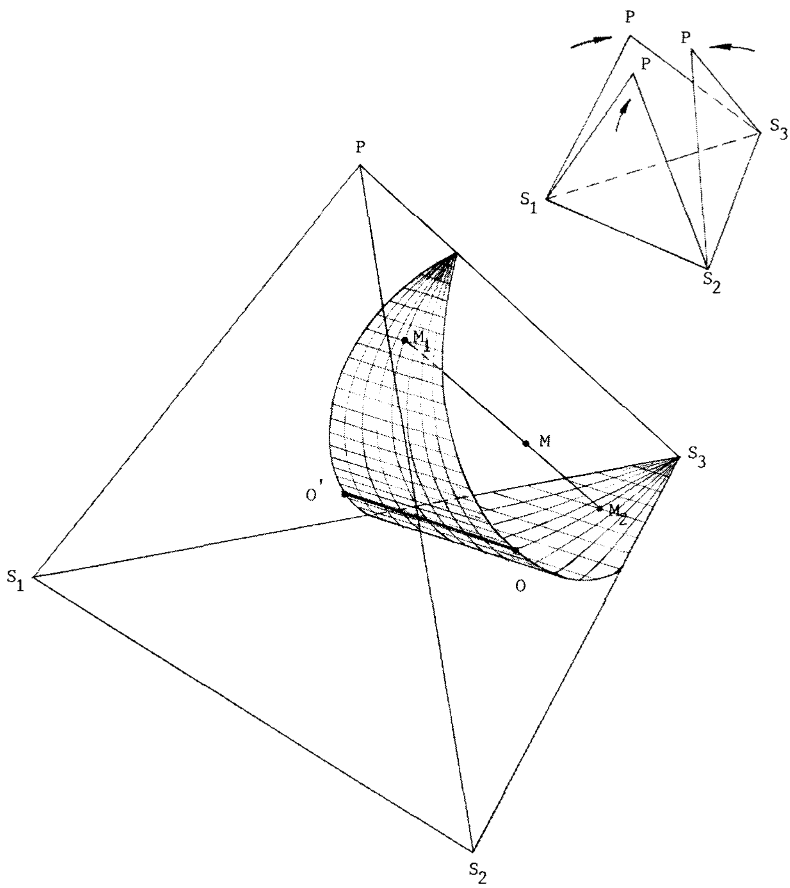

Fig. 6. The formation of a tetrahedron as a quaternary phase diagram.

S_1 and S_2. The space enclosed by the equilibrium surface and the curved surface $AM_1'BM_2'C$ is the two-phase region. Any quaternary system with a composition corresponding to a point (M) within this region will separate into two phases following a tie rod, with compositions corresponding to M_1 and M_2 located on the opposite portions of the equilibrium surface divided by the critical line BO. The space inside $ABCS_2$ is the three-phase region. Any quaternary system with a composition corresponding to a point Q within the region will separate into three phases, a solvent phase of the mixture S_1 and S_2 and two swelled polymer phases with compositions corresponding to M_1' and M_2' on the edge of the shaded equilibrium surface. A number of tie rods may be experimentally determined in the two-phase region so that other tie rods can be interpolated from them. An example of such a quaternary system shown in Figure 8 is Parlon® P-10 [chlorinated poly(propylene), Hercules Inc.]/isoprene/ethylbenzene/methanol

Two Polymers and Two Solvents—Case 2B

The two polymers (P_1,P_2) are incompatible with each other. S_1 is a good solvent for P_1 but a poor solvent for P_2. S_2 is a good solvent for P_2 but a poor

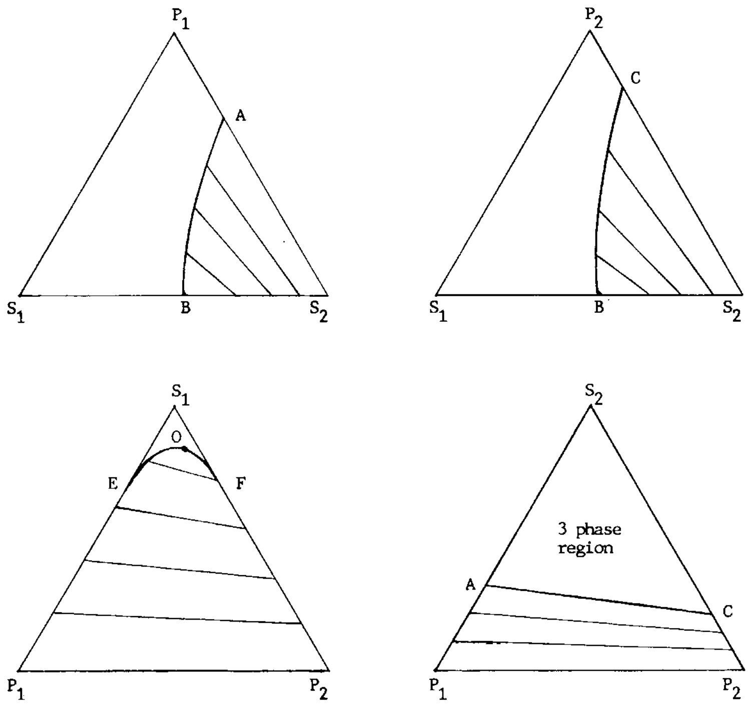

Fig. 7. Ternary phase diagrams each consisting of three out of the four components in Case 2A.

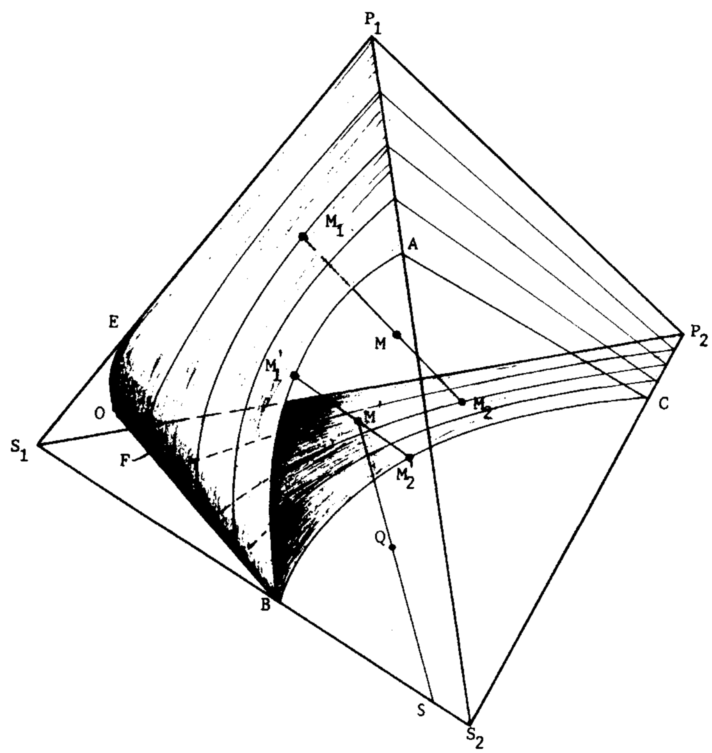

Fig. 8. Quaternary phase diagram of a system of two polymers and two solvents—Case 2A.

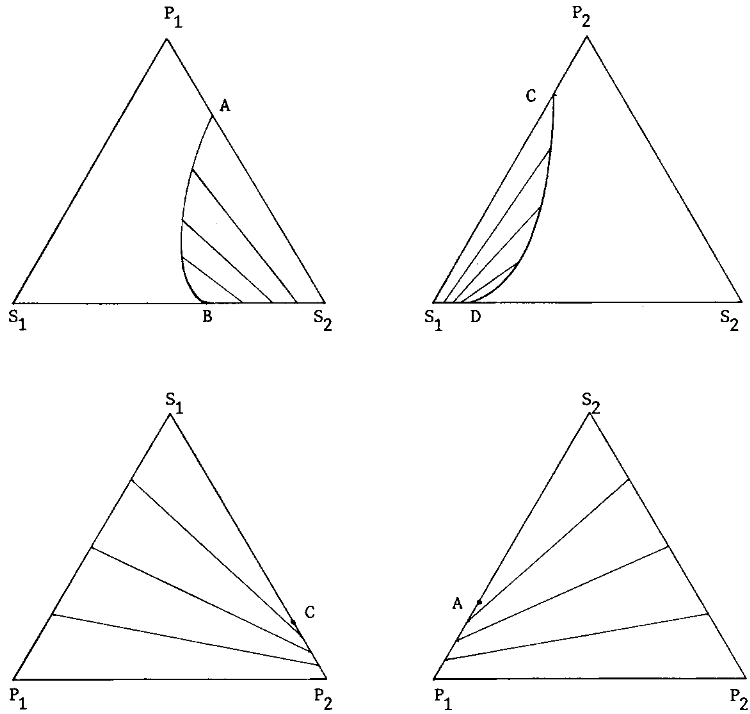

Fig. 9. Ternary phase diagrams each consisting of three out of the four components in Case 2B.

solvent for P_1. The four ternary phase diagrams each consisting of three out of four components, are presented in Figure 9. The four ternary phase diagrams are combined to form the quaternary phase diagram shown in Figure 10. In Figure 10 the wedged space between the shaded equilibrium surface and a portion of the edge BD is the one-phase region of a homogeneous, dilute solution of the polymers P_1 and P_2 in the solvent mixture of S_1 and S_2. Anywhere else in the tetrahedron is a two-phase region. Any quaternary system with a composition corresponding to a point (M) within this region will separate into two phases, following a tie rod, with compositions corresponding to M_1 and M_2 located on the opposite portions of the equilibrium surface divided by the critical line BED. As one end of the tie rod M_1 moves to the upper portion of the equilibrium curve ABS_2 on the $S_1S_2P_1$ plane, the other end of the tie rod M_2 moves to the lower portion of this equilibrium curve as shown by $M_1'M_2'$. Consequently, the tie rods in the 3-dimensional space become the tie lines in the 2-dimensional plane in these extreme cases. M_2 moves to the apex point S_2 when M_1 moves to point A. As M_1 moves to the left portion of the equilibrium curve S_1DC, the equilibrium composition M_2 moves to the right portion of the equilibrium curve on the $S_1S_2P_2$ plane as shown by $M_1''M_2''$. M_2 moves to point C when M_1 moves to the apex point S_1. As M_1 moves from the apex point S_1 to the apex point P_1, M_2 moves from point C to the apex point P_2. As M_1 moves from the apex point P_1 to A, M_2 moves from the apex point P_2 to the apex point S_2. An example of such a quaternary system as shown in Figure 10 is isoprene/poly(methyl methacrylate)/ethyl benzene/methyl ethyl ketone.

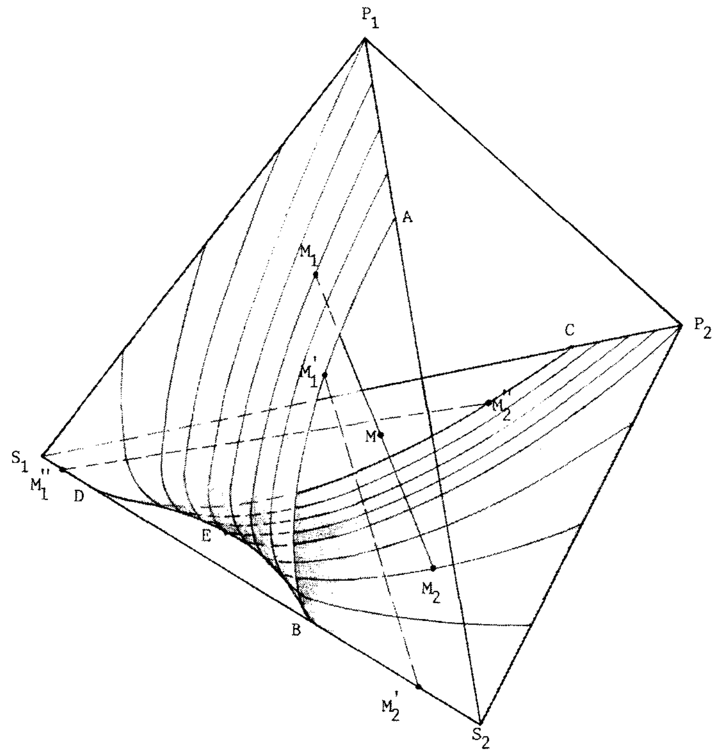

Fig. 10. Quaternary phase diagram of a system of two polymers and two solvents—Case 2B.

Four Polymers—Case 3A

The three polymers P_1,P_2,P_3 are mutually compatible in all proportions. The fourth polymer P_4 is compatible with P_3 in all proportions and is compatible with P_1 and P_2 in very limited domains of composition. The four ternary phase diagrams, each consisting of three out of the four components, are presented in Figure 11. The four ternary phase diagrams are combined to form the quaternary phase diagram shown in Figure 12. In Figure 12 the space inside the tetrahedron and enclosed by the curved equilibrium surface AOBDO′C is the two-phase region. Only surface tie lines are shown. The trend of the internal tie rods can be visualized from the surface tie lines. The rest of the space inside the tetrahedron is the one-phase region. A mixture of the three polymers P_1,P_2, and P_4 with a composition corresponding to the point M in Figure 12 is not homogeneous and has a tendency to separate into two phases with compositions corresponding to M_1 and M_2. However, if the polymer P_3 is added to the mixture, it will move the composition of the overall mixture from M towards P_3, as indicated by the dashed line from M to P_3. If enough P_3 is added, the point representing the composition of the quaternary mixture will move through the equilibrium surface and into the one-phase region. The mixture then becomes homogeneous. With the help of such a 3-dimensional phase diagram, one can minimize the experimental points needed to gain a clearer picture of a complicated polymer blend system.

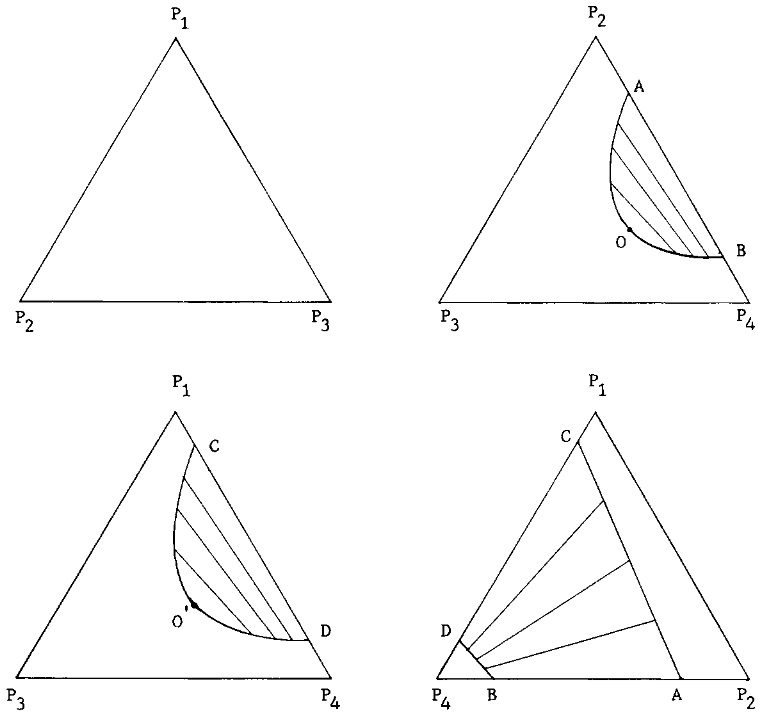

Fig. 11. Ternary phase diagrams each consisting of three out of the four components in Case 3A.

Four Polymers—Case 3B

Polymers P_1 and P_2 are compatible in all proportions. P_3 and P_4 are also compatible in all proportions. However, P_1 is not compatible with P_3 or P_4. P_2 is not compatible with P_3 or P_4 either. The four ternary phase diagrams are shown in Figure 13. The combined quaternary phase diagram is shown in Figure 14. From Figure 14 it can be seen that any mixture of the four components will have a tendency to separate into two phases, one with P_1 and P_2 only and the other with P_3 and P_4 only. One phase would have a composition corresponding to a point on line P_1P_2 and the other on line P_3P_4. Because P_1P_2 and P_3P_4 are perpendicular to each other in space, there is only one way to draw a straight line through any given interior point M and intersect both P_1F_2 and P_3P_4. This line is M_1MM_2. With the interior point M fixed, moving M_1 either way along line P_1P_2 will tilt the point M_2 off the line P_3P_4. Therefore, these four polymers will not form a homogeneous solution no matter what composition is used.

DISCUSSION

The tetrahedral phase diagram can also be used to study the phase behavior of a system with two polymers and a third polymer with varying molecular weight or a third copolymer with varying composition. In this case, a point between P_1 and P_2 apexes would indicate a component with molecular weight between

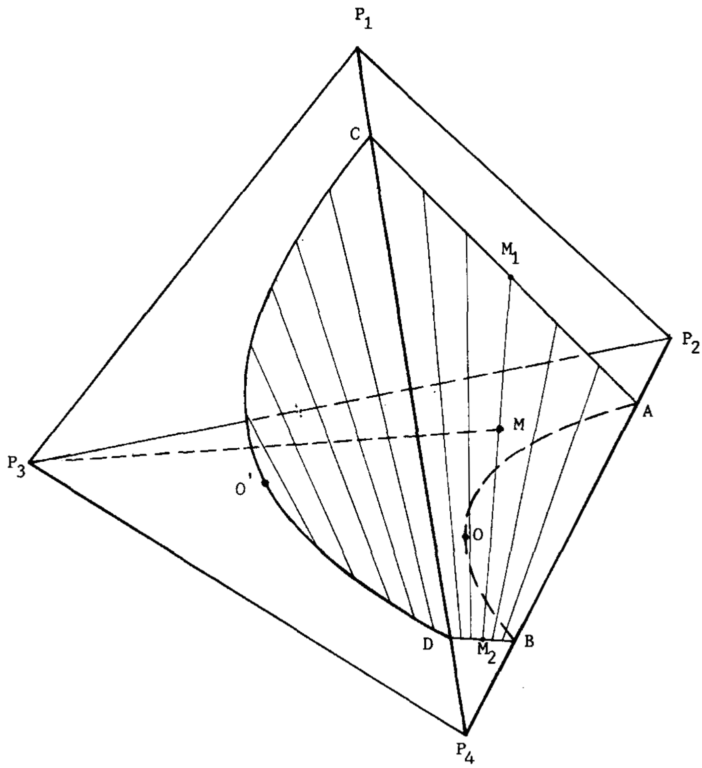

Fig. 12. Quaternary phase diagram of a system of four polymers—Case 3A.

P_1 and P_2 or a copolymer with composition between P_1 and P_2 instead of a mixture of the two polymers P_1 and P_2. In the same sense, the tetrahedral phase diagram can also be used to study the system of two copolymers each with varying composition.

There are three ways to present the 3-dimensional quaternary phase diagram. The simplest way is to draw diagrams as shown in this article. However, it takes some imagination to visualize a 3-dimensional model sketched on 2-dimensional paper. To minimize the need of imagination, a 3-dimensional tetrahedron can be made with clear plastic sheets or plates with phase equilibrium surfaces and a few experimentally determined tie rods built into it. This approach requires more effort. However, once the model is built, the quaternary system can be more readily visualized. A third approach is to use computer graphics. A computer program can be developed to accept and store phase equilibrium data and use the techniques described in this article to create a 3-dimensional tetrahedral quaternary phase diagram and display it on the CRT screen so that the user can rotate the tetrahedron and look at it from all directions. The program can also be written so that it will accept an input composition and display its corresponding location in the tetrahedron. If this composition is located in the two-phase region, the computer program will calculate and display the tie rod involved using values interpolated from experimental data. The program can also be written so that the numerical values of the compositions and amounts of the two phases in equilibrium will be displayed simultaneously with the 3-

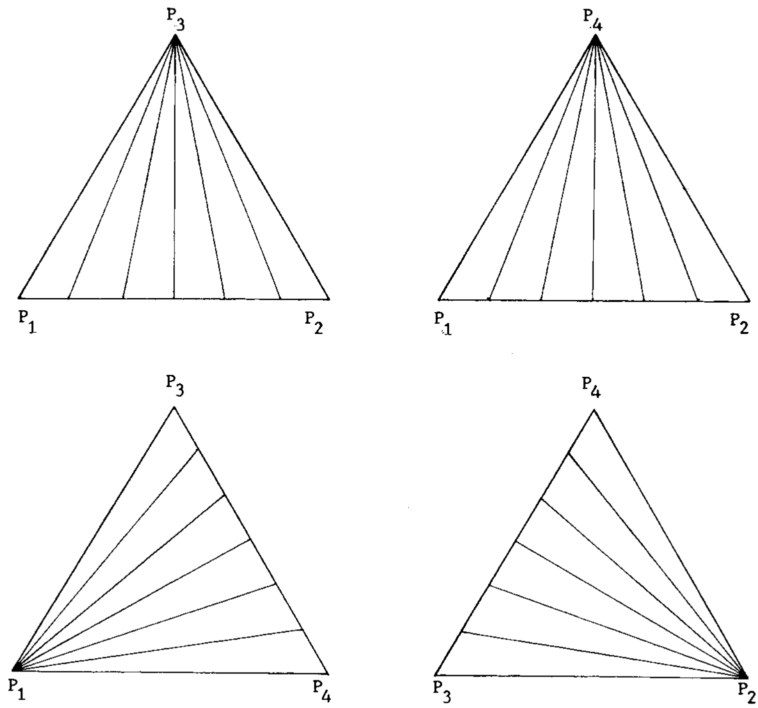

Fig. 13. Ternary phase diagrams each consisting of three out of the four components in Case 3B.

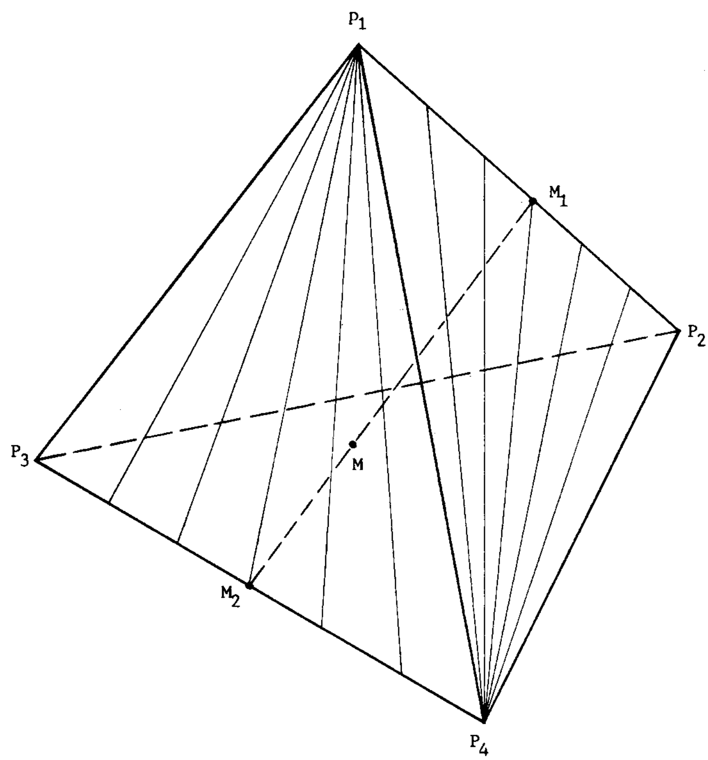

Fig. 14. Quaternary phase diagram of a system of four polymers—Case 3B.

dimensional quaternary phase diagram rotating on the CRT screen. Such a computer graphics program can greatly help one understand quaternary systems of polymers and solvents or of polymer blends.

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References

1. R. L. Scott, *J. Chem. Phys.*, **17**, 268 (1949).
2. H. Tompa, *Trans. Faraday Soc.*, **45**, 1142 (1949).
3. A. R. Shultz and P. J. Flory, *J. Am. Chem. Soc.*, **74**, 4760 (1952).
4. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca/London, 1953, Chap. 5.
5. S. Friberg and I. Burasczenska, *Prog. Colloid Polym. Sci.*, **63**, 1 (1978).
6. A. M. Bellocq, D. Bourbon, and B. Lemanceau, *J. Colloid Interfacial Sci.*, **79**, 419 (1981).
7. A. M. Bellocq et al., *J. Colloid Interfacial Sci.*, **74**, 311 (1980).
8. A. M. Bellocq et al., *J. Dispersion Sci. Technol.*, **2**, 27 (1981).
9. J. Biais et al., *J. Dispersion Sci. Technol.*, **2**, 67 (1981).

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