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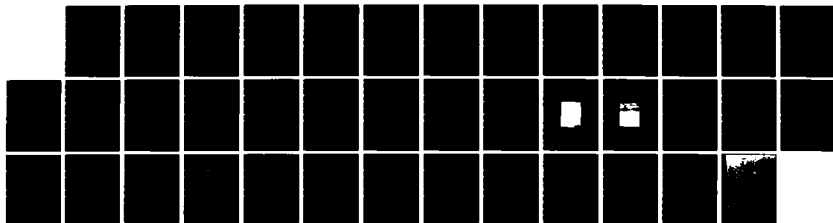
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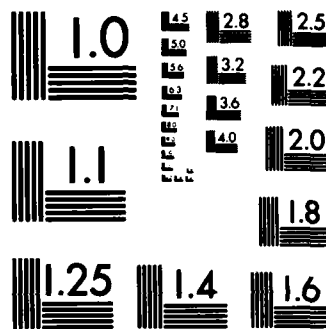
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Homogenizing Properties of Diblock
Polymers in Blends of Corresponding Homopolymers

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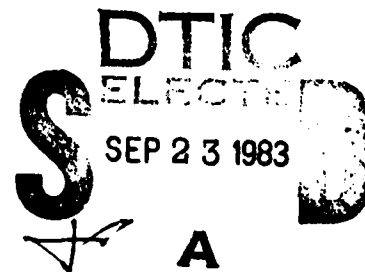
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August 22, 1983

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enabling an experimental phase diagram to be determined. These findings are compared with current theories of phase behavior for blends of diblock copolymers and homopolymers. ✓

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Homogenizing Properties of Diblock Polymers in Blends with Corresponding Homopolymers

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Introduction

Diblock copolymers and homopolymer blends are generally heterogeneous materials due to unfavorable interactions between unlike chain segments.^{1,2} Addition of diblock copolymers to homopolymer blends usually produces an emulsifying effect, which reduces the heterogeneities to a microscopic scale. In a few polymer systems, the inclusion of diblock copolymers in homopolymer blends produces a single phase morphology in an otherwise phase separated homopolymer blend. This homogenizing capability has been observed for polystyrene-*b*-poly α -methyl styrene^{3,4} and polyisoprene-*b*-polybutadiene diblock^{5,6,7} copolymers when blended with the corresponding homopolymers. Previous work in this laboratory has also shown that diblock copolymers of 1,2-polybutadiene-*b*-1,4-polybutadiene can exhibit a similar solubilizing effect.⁸

The homogenizing capability of these copolymers has been shown to vary with the diblock copolymer composition and molecular weight.³⁻⁸ The need to develop a more quantitative understanding of this homogenization phenomenon prompted the work reported here, which considers the 1,2- and 1,4-polybutadiene system. The results are considered in the framework of recent thermodynamic theories in a later section. The choice of a rubber polymer system as opposed to the glassy polystyrene/poly α -methyl styrene system allows a closer approach to equilibrium morphologies and minimizes variations which might arise from sample processing history. In addition, the 1,2- and 1,4-polybutadiene system affords the opportunity to study a system with a uniform chemical composition.⁹

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Experimental Section

Materials

In order to facilitate the eventual development of a phase diagram, well characterized, nearly monodisperse samples were used. Some of the polymers used in this work have been described in previous work from this laboratory.⁹ These polymers were synthesized anionically using n-butyllithium as an initiator in hexane and 1,2 dipiperidino ethane (DPE) as a polar modifier during polymerization of 1,2 polybutadiene homopolymers and block segments. The use of DPE as a polar modifier, first reported by Halasa, et al.^{10,11} leads to an atactic microstructure of nearly 100% 1,2 repeat units.

Polymers synthesized for inclusion in the present study were prepared in benzene using n-butyllithium as an initiator. The initiator concentration was determined by titration according to the method of Eppley and Dixon.¹² Reagent grade benzene was distilled under an argon atmosphere to remove water and then redistilled after the addition of butyllithium. A middle fraction from the second distillation was collected and further purified according to a living gels technique.¹³ Butadiene gas was deinhibited and then condensed over calcium hydride and stirred for 2 hours. After degassing, the butadiene was vacuum distilled onto a sodium mirror and successively distilled onto a fresh mirror every 12-24 hours. Generally five or six mirrors were required for purification, evidenced by a thin film of polymer on the flask wall. DPE purification was accomplished via a modified living gels technique.

Characterization of the polymers is summarized in Table 1. NMR spectra were run on a Varian T-60 spectrometer to determine relative amounts of 1,2

and 1,4 repeat units. In addition, a C^{13} NMR spectrum of a 1,2 homopolymer (26K, 1,2; Table 1) verified the purity of the 1,2 microstructure as nearly 100%. Molecular weight determinations were made via size exclusion chromatography. DuPont Zorbax bimodal columns were used with THF as the mobile phase. Diblock copolymer molecular weights were determined using a weighted average method¹⁴ and the method of Ho-Duc and Prudhomme.¹⁵ The molecular weights calculated by these two methods were almost identical, and both were in good agreement with the value determined by first block analysis and NMR composition data. The presence of a small amount of a high molecular weight impurity due to coupling during termination was observed in the polymers synthesized prior to this work, as previously documented.⁹ However, the polymers synthesized here show no evidence of coupling. This is clearly shown in Figure 1 which compares GPC traces for the two diblocks used in this work.

Experimental Methods

Polymer blends were prepared by dissolving appropriate amounts of the homopolymers and diblock copolymers in cyclohexane and then spin casting¹⁶ a uniform film. Cyclohexane was chosen as a solvent since it has a solubility parameter intermediate to those predicted for 1,2 and 1,4 polybutadiene; this choice of solvent should minimize any preferential solvation effects.⁹ Films prepared by spin casting were vacuum dried to remove residual solvent and were then lightly crosslinked to facilitate handling. Crosslinking was accomplished by irradiating the films with high energy electrons; specimens which were subsequently stained and examined by electron microscopy received a total dose of 40 Mrad, while 10 Mrad was sufficient for specimens subjected to dynamic mechanical testing.

The various polymer blends were determined by both dynamic mechanical analysis and by transmission electron microscopy. Mechanical spectra were

obtained on a Toyo Baldwin model DDV-II-C Rheovibron operated at 3.5 Hz between -100 and 20°C. Samples were cut and end-buttet with epoxy to aluminum tabs, minimizing grip effects.¹⁷ The appropriate instrument compliance factors were determined separately and used in data analysis.^{18,19} Samples examined by electron microscopy were first stained by the 'ebonite' method, developed by Smith and Andries.²⁰ This staining method has been used in this laboratory for several years⁶⁻⁹ and provides adequate contrast for viewing blends of different diene materials. The staining procedure also hardens the samples, which may then be placed directly in an ultramicrotome and cut into thin sections.

Results

The morphology inferred from dynamic mechanical testing agreed in all cases with that observed in the electron microscope. In the case of homogeneous materials, the observed glass transition is shifted to a temperature intermediate to that of the homopolymer transitions. A plot of the transition temperature vs. blend composition in Figure 2 shows that the single transition temperature of the homogeneous compositions roughly approximates a weighted average of the homopolymer glass transition temperatures.

Representative electron micrographs are shown in Figure 3. While the contrast obtained is not as good as can be obtained with osmium tetroxide in a saturated/unsaturated polymer blend, there is a sufficient mass density difference to observe a heterogeneous phase separation when present.

A summary of all the blends prepared and their resulting state of morphology is given in Table 2. The overall blend composition, number average molecular weight, and proportion of diblock copolymer in the blend are also shown for each sample. The molecular weight is normalized by the

critical molecular weight for a symmetric diblock of 1,4 and 1,2 polybutadiene, estimated as 7.8×10^4 by Cohen and Wilfong.⁹

Discussion

In a previous paper²¹ an empirical framework was developed for describing the behavior of blends of diblock copolymers and homopolymers. A three dimensional diagram was developed with two axes representing the blend molecular weight and composition, while the third axis represented the proportion of diblock polymer in the blend. The two end planes of such a three-dimensional representation depict the phase diagrams for homopolymer blends and for pure diblock copolymers as shown in Figure 4. In this earlier treatment,²¹ the homopolymer behavior was predicted from the Flory-Huggins spinodal curve, while the diblock copolymer behavior was estimated by setting Helfand's equations²² for the free energy of a diblock copolymer equal to zero. Although this procedure does not represent a strictly valid thermodynamic determination of the homogeneous-to-heterogeneous phase transition, it has none-the-less proven useful in correlating a vast array of data on diblock copolymer behavior.^{8,9,21}

Once the two ends of the diagram have been fixed, the phase transition boundary for a blend of homopolymers and diblocks can be estimated by a linear interpolation²¹ of the two diagrams, which implies the system exhibits ideal solution behavior. Such an interpolation is depicted in Figure 4 for blends with 50% diblock weight fraction. The curves representing the homopolymer and the diblock copolymer phase diagrams are not identical, so the shape varies slightly with different diblock fractions, most noticeably at

the extreme compositions. The major difference between the curves, however, is the location of the critical molecular weights. For homopolymers of 1,2 polybutadiene and 1,4 polybutadiene the critical molecular weight is 1.4×10^4 , a factor of 5.6 lower than the diblock value. Thus, in the three dimensional space enclosed by the phase diagram, the heterogeneous region is a concave-upward trough-shaped volume element which slopes downward towards the region of lower proportions of diblock.

The compositions for the samples prepared in this work were chosen so that the blends would be very near the point of phase separation predicted by the ideal solution behavior. Once the phase nature of a given sample was determined, a new blend was prepared with the same diblock copolymer proportion, nearly the same molecular weight, and a composition which would place it closer to the actual point of phase separation. By finding two samples with nearly the same composition which were homogeneous and heterogeneous, a point on the phase boundary could be experimentally located and compared with the ideal solution assumption mentioned above.

The results obtained at diblock copolymer compositions of 75%, 50%, and 25% are compared with the predicted phase behavior in Figure 5. In the first two instances, there are homogeneous samples in the predicted heterogeneous region. This suggests that the critical molecular weight predicted by the ideal solution assumption at these diblock copolymer fractions is too low; that is, a positive deviation from the linear interpolation is found. For the blends with 25% diblock copolymer weight fraction there is a heterogeneous sample in the homogeneous region, and a negative deviation is found.

Shifting the phase diagram up or down to fit the data yields a range for the critical molecular weight at each proportion of copolymer. This

procedure of minimum and maximum critical molecular weights is demonstrated in Figure 6 for the plane of 50% diblock copolymer. A similar analysis was done for all of the phase diagrams with different proportions of diblock copolymer. In shifting the diagram, the interpolated shape of the curve was held constant and only the location (critical molecular weight) was changed.

For blends with 25% diblock copolymer fraction there is no appropriate shift which will fit all of the data. If the curve is shifted downwards, for example, so that all the heterogeneous samples lie in the interior of the phase diagram, data points for homogeneous samples will fall in the heterogeneous region as well. At this proportion of diblock copolymer, the range of critical molecular weights was adjusted to fit the results using only those samples prepared with the 27/33 diblock copolymer which does not contain any high molecular weight coupled polymer (see Fig. 1). In this case, only one of the samples prepared at this diblock copolymer fraction cannot be fit into the scheme. At some proportions of diblock polymer, only a minimum critical molecular weight could be determined, since only homogeneous samples were prepared.

When the experimentally determined range of critical molecular weight is plotted against diblock copolymer fraction, as shown in Figure 7, the locus is seen to be somewhat sigmoidal rather than linear. Thus it appears that the addition of small amounts of a diblock polymer does not have as great an effect on raising the critical molecular weight as predicted by the linear interpolation. At around 40% diblock fraction, the experimental results and the ideal solution predictions are in good agreement while at higher content of diblock polymer, the homogenizing capabilities observed are greater than that predicted by the linear interpolation. Also shown in Figure 7 is a locus

of critical molecular weights determined from a theory of phase behavior proposed by Leibler.²³ This theory is strictly valid only for the symmetric case of a diblock copolymer of equal sized blocks in the presence of homopolymers of equal degree of polymerization as the overall diblock. Nevertheless we compare this theory with the experimental results in greater detail in the following paragraphs; the important observation here is that a sigmoidal locus is predicted, although it is perhaps not as pronounced as the curvature observed in the experimental results.

The disagreement of the experimental results with the ideal solution interpolation is more evident when viewed in the form of a ternary diagram. As demonstrated by Bates,²⁴ a planar ternary mapping of the data may be derived from the three-dimensional diagram. The three different polymers used in any given blend are the vertices of a uniquely specified triangular phase diagram, as shown in Figures 8a and b. All of the blends which may be prepared from the three selected polymers lie on the plane defined by these points, and each plane so-defined intersects the trough-shaped heterogeneous region in a unique way. The final planar ternary diagram is obtained by projecting onto the base of the three dimensional diagram.

Examples of projected diagrams of this type, as well as the corresponding experimental results, are shown in Figure 9. The heterogeneous region is defined by the straight-line interpolation discussed above. Several homogeneous samples are observed in the heterogeneous region at high diblock proportions in Figure 9b. If the heterogeneous region is defined according to the experimental sigmoidal locus (Figure 7) much better agreement is observed, as shown in Figure 10.

By comparing the ternary diagrams for blends with the different diblock copolymers (Figures 9a and 10) it becomes apparent that the 27/33 diblock copolymer is a much better homogenizing agent than the 33/100 diblock. Although both diblock copolymers are homogeneous, the molecular weight of

the 33/100 diblock is greater than the critical molecular weight and is homogeneous only by virtue of its composition which places it outside the heterogeneous region.⁹ The high molecular weight of this copolymer, however, means that planes representing the composition of blends prepared from the 33/100 diblock copolymer will always have a significant amount of intersection with the trough-shaped heterogeneous region; thus most of the blends which may be prepared from this copolymer must be heterogeneous. In the case of the 27/33 diblock copolymer, which is well below the critical molecular weight, there is a much larger range available for homogeneous compositions. For this case, there is also a critical diblock copolymer content above which all blends are homogeneous, regardless of composition. For blends with 30,000 molecular weight homopolymers, this is determined experimentally to be 54%, while the linear interpolation predicts the value to be 65%.

Leibler^{23,25,26} has developed a thermodynamic treatment for blends of homopolymers with a copolymer which allows a ternary diagram to be drawn for the case where the copolymer is symmetric and has the same molecular weight as the homopolymers. His treatment may also be extended to include copolymers of differing molecular weights, and thus the blends prepared from the 27/33 diblock copolymer may be examined in this framework.

In order to make use of this theory, the segmental interaction parameter, χ , must be estimated. The critical molecular weight for a diblock copolymer is predicted^{25,26} to be $N\chi = 10.5$. Because the 27/33 diblock is homogeneous, $N\chi$ for this polymer is necessarily below 10.5. In addition, previous work in this laboratory⁹ has shown that a 30/50 1,2/1,4 polybutadiene diblock copolymer is heterogeneous, indicating that $N\chi$ for this polymer is greater than 10.5. From these two limiting cases, one can determine a range for χ : $.0069 \leq \chi \leq .0093$.

Using the value of 7.8×10^4 estimated by Cohen and Wilfong⁹ as the critical molecular weight, χ is equal to .0074 for the 1,2/1,4 polybutadiene system. It is worth noting that this range for χ may be expressed as a range of solubility parameters as well.⁹ If the solubility parameter for 1,2 polybutadiene is taken as the only reported value, $\delta = 8.10^{26}$, then the range of values for χ translates to a range of 8.37 to 8.41 for the solubility parameter of 1,4 polybutadiene, which is narrower than that found in the literature.²⁷

The binodal and spinodal curves calculated for the 1,2/1,4 polybutadiene system are plotted in Figure 11. Excellent agreement with the experimental results is observed.

Summary

Comparing Figures 10 and 11, we see that projections from the three dimensional representation lead to ternary diagrams which more closely resembles the spinodal curve than the binodal. This is expected, since the Flory-Huggins spinodal curve was used to locate the heterogeneous region at the homopolymer end to the three dimensional diagram.

A combination of the theoretical work of Leibler^{23,25,26} and the empirical approach of constructing a three dimensional representation serves to explain the experimental results reported here. The empirical approach using an ideal solution approximation can be improved upon by incorporating the sigmoidal curvature of the locus of critical points predicted by Leibler. Nevertheless, the empirical treatment represents a useful first order estimation of the morphological behavior from only a few simple parameters.

Acknowledgements

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Table 1: Characterization Results

<u>Polymer</u>	<u>$\bar{M}_n^a$</u>	<u>$\bar{M}_w/\bar{M}_n^a$</u>	<u>% 1,2 content^b</u>
30K 1,4	29,600	1.10	13%
26K, 1,2	26,400	1.06	99.5% [†]
27/33 Diblock:			
First Block	33,100	1.08	10.5%
Total Polymer:			
By method of ref. 14	60,300	1.11	51.5%
By method of ref. 15	59,100		
By NMR and First Block	61,000		
100K 1,4 ^c	97,000	1.12	13.2%*
30K 1,2 ^c	29,600	1.07	95%*
33/100 Diblock: ^c			
First Block	100,000	1.08	11.3%*
Total Polymer:	133,000	1.08	35.0%*
45K 1,4 ^d	44,000	1.04	13.0%

a. As determined by GPC analysis

b. As determined by proton NMR analysis

c. Synthesized at Firestone Laboratories (9)

d. Synthesized by Bates (24)

† As determined by Carbon-13 NMR at Bell Laboratories

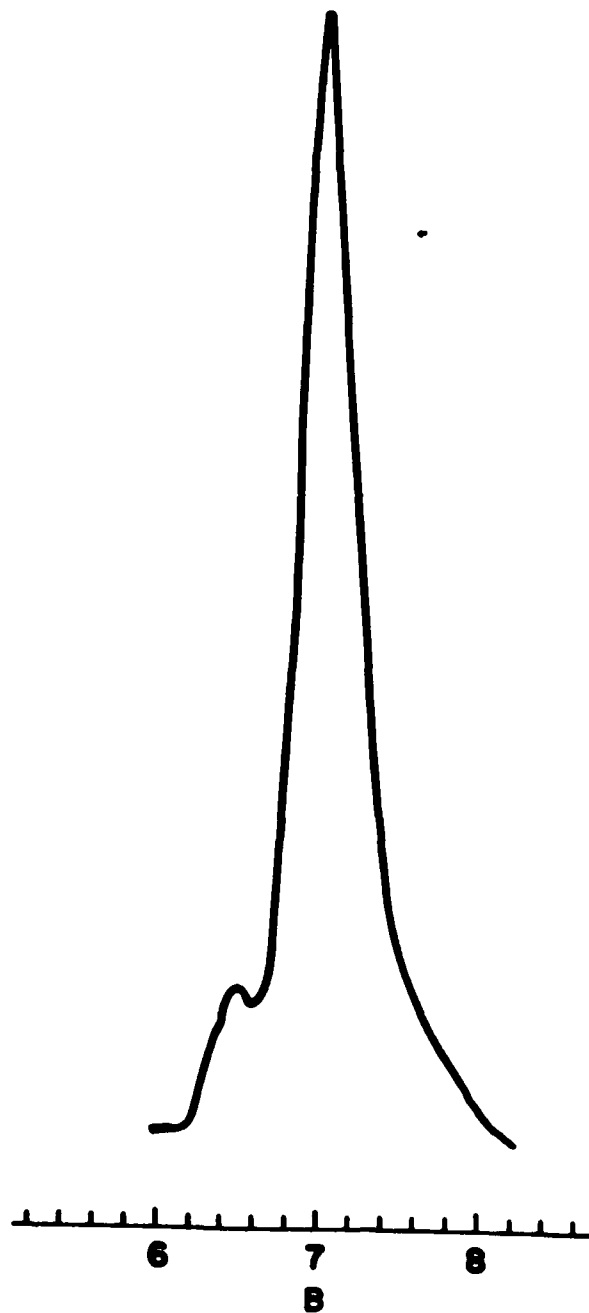
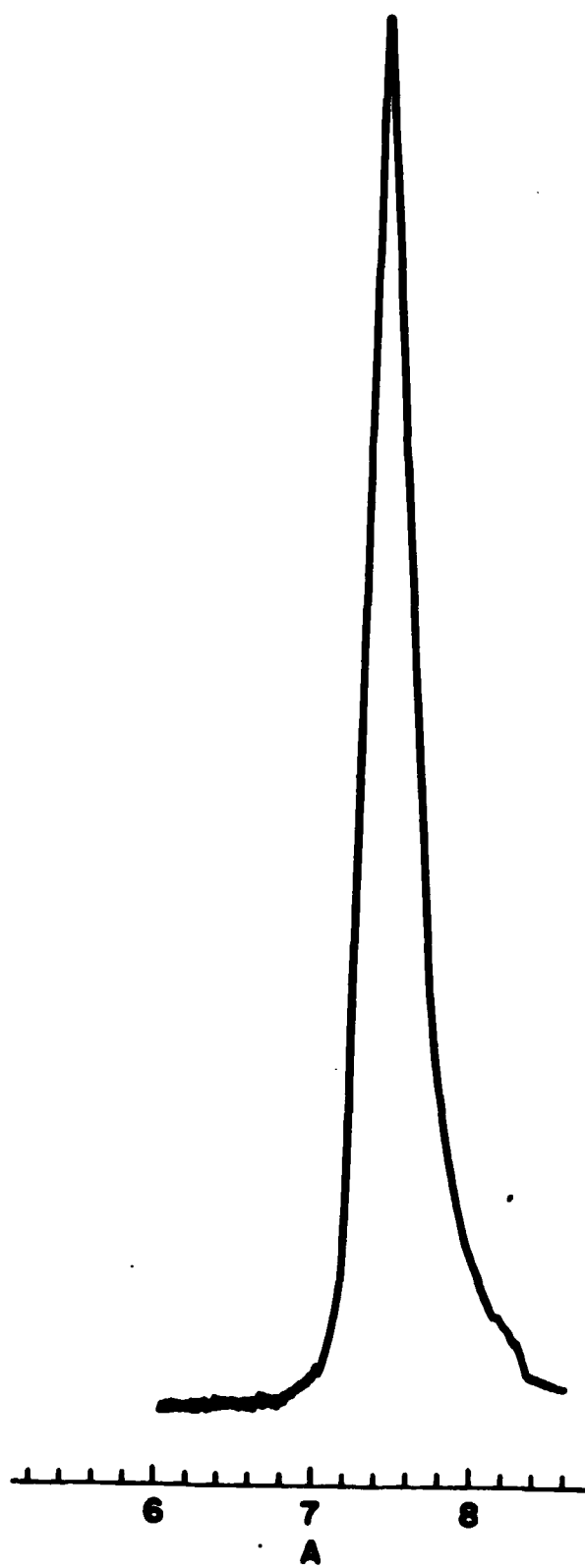
* As determined by IR analysis at Firestone Laboratories (9)

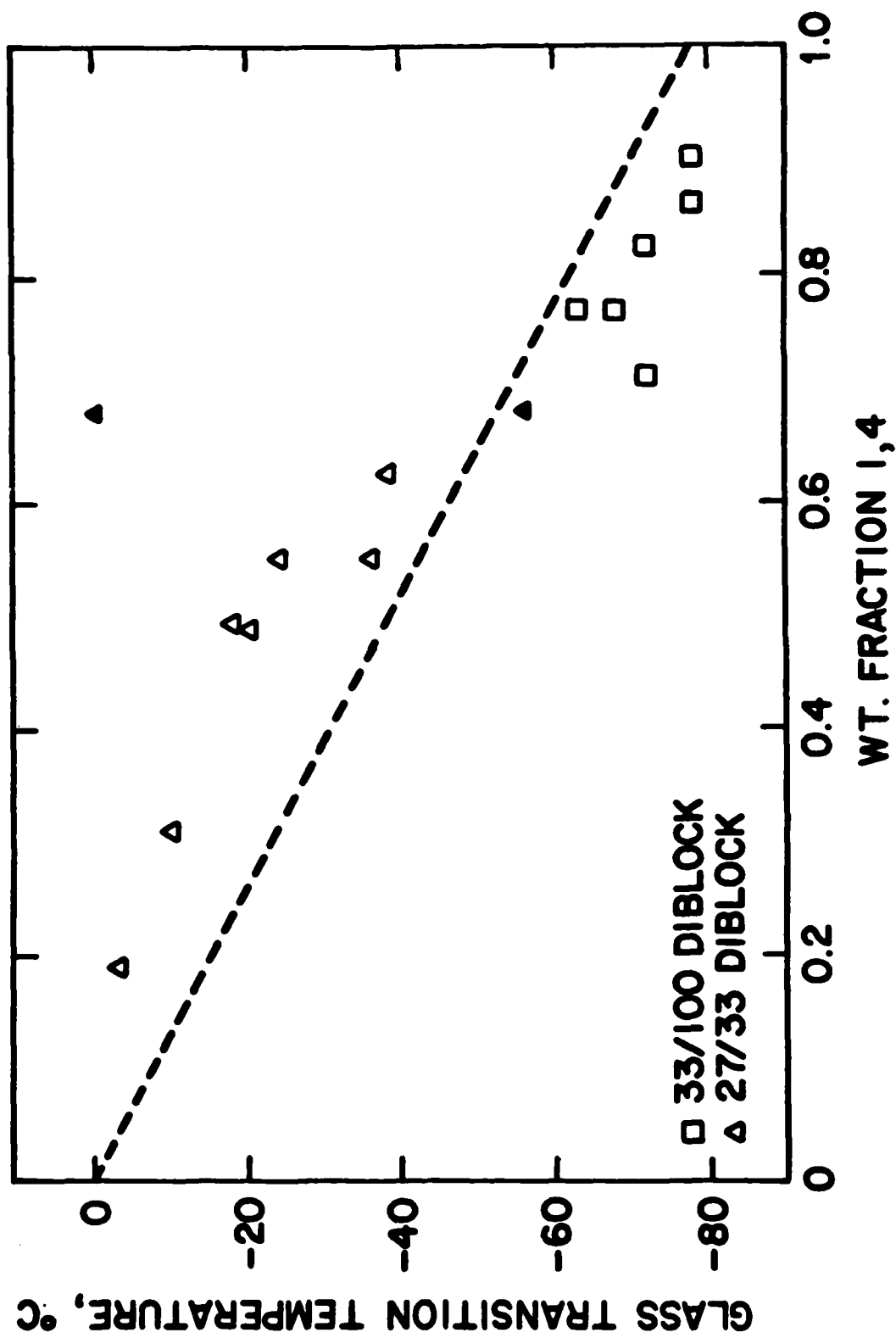
Table 2: Summary of Blends Prepared

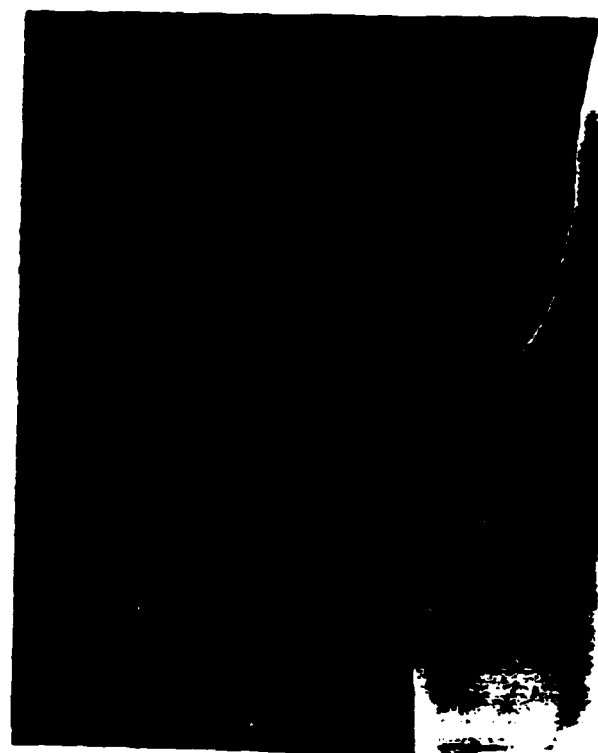
<u>Diblock:</u>	<u>Homopolymers:</u>	<u>Wt. % 1,4:</u>	<u>Log M/M_{crit}</u>	<u>Morphology:</u>
100% 27/33		.55	-.1064	Homogeneous
65% 27/33	22% 26K 1,2 13% 30K 1,4	.488	-.2577	Homogeneous
55% 27/33	26% 26K 1,2 19% 30K 1,4	.493	-.2911	Homogeneous
50% 27/33	15% 26K 1,2 35% 30K 1,4	.625	-.2977	Homogeneous
50% 27/33	22% 26K 1,2 28% 30K 1,4	.55	-.3030	Homogeneous
40% 27/33	11% 30K 1,2 49% 30K 1,4	.71	-.3155	Homogeneous
40% 27/33	51% 30K 1,2 9% 30K 1,4	.31	-.3155	Homogeneous
25% 27/33	21% 26K 1,2 54% 30K 1,4	.68	-.3680	Heterogeneous
25% 27/33	69% 30K 1,2 6% 30K 1,4	.19	-.3961	Homogeneous
90% 33/100	10% 45K 1,4	.793	.1585	Homogeneous
75% 33/100	6% 26K 1,4 19% 96K 1,4	.768	.1200	Homogeneous
50% 33/100	44% 97K 1,4 6% 26K 1,2	.825	.0903	Homogeneous
50% 33/100	32% 45K 1,4 18% 26K 1,2	.710	-.1358	Homogeneous
50% 33/100	50% 45K 1,4	.885	-.0649	Homogeneous
25% 33/100	8% 30K 1,2 67% 97K 1,4	.8625	.0418	Homogeneous
25% 33/100	4% 26K 1,2 71% 97K 1,4	.9025	.0845	Homogeneous

Figure Legends

- Figure 1. HPSEC traces for the (a) 27/33 and (b) 33/100 diblock copolymers used in the blends. Note that the 27/33 copolymer does not exhibit any high molecular weight (coupled) polymer, estimated as 11% of the 33/100 copolymer.
- Figure 2. Transition temperature, determined by Rheovibron, plotted as a function of overall blend composition.
- Figure 3. Electron micrographs for the (a) 27/33 diblock copolymer (homogeneous); (b) Blend of the 25% 27/33 diblock, 21% 26K 1,2 homopolymer, 54% 30K 1,4 homopolymer (heterogeneous).
- Figure 4. Three dimensional phase diagram. Curve at 0% diblock copolymer fraction is spinodal curve for homopolymers. Curve at 100% diblock is solution to $\Delta G = 0$ for Helfand's equations. Curve at 50% diblock fraction is linear interpolation of the end diagrams.
- Figure 5. Experimental results for blends containing: (a) 75% diblock copolymer; (b) 50% diblock copolymer, and (c) 25% diblock copolymer, respectively.
- Figure 6. Minimum and maximum shifts in critical molecular weight for samples with 50% diblock copolymer composition.
- Figure 7. Critical molecular weight as a function of diblock copolymer content in blend. (a) ideal solution interpolation (_____); (b) determined from Leibler's theory (-----). Experimental results are the triangles.
- Figure 8. Three dimensional phase diagrams for homopolymer and 30K 1,2. (a) blends with 33/100 diblock copolymer, 45K 1,4 homopolymer (b) blends with 27/33 diblock copolymer with 30K homopolymers. Points A, B and C in each diagram represent the 1,2-PBD homopolymer, 1,4-PBD homopolymer, and diblock polymer respectively.
- Figure 9. Ternary diagrams for the (a) 33/100 blend system and (b) 27/33 blend systems shown in Figure 8.
- Figure 10. Ternary diagram reflecting experimental locus.
- Figure 11. Ternary diagram showing binodal curve (-----) and spinodal curve (.....) calculated from Leibler's theory for blends with the 27/33 diblock polymer.



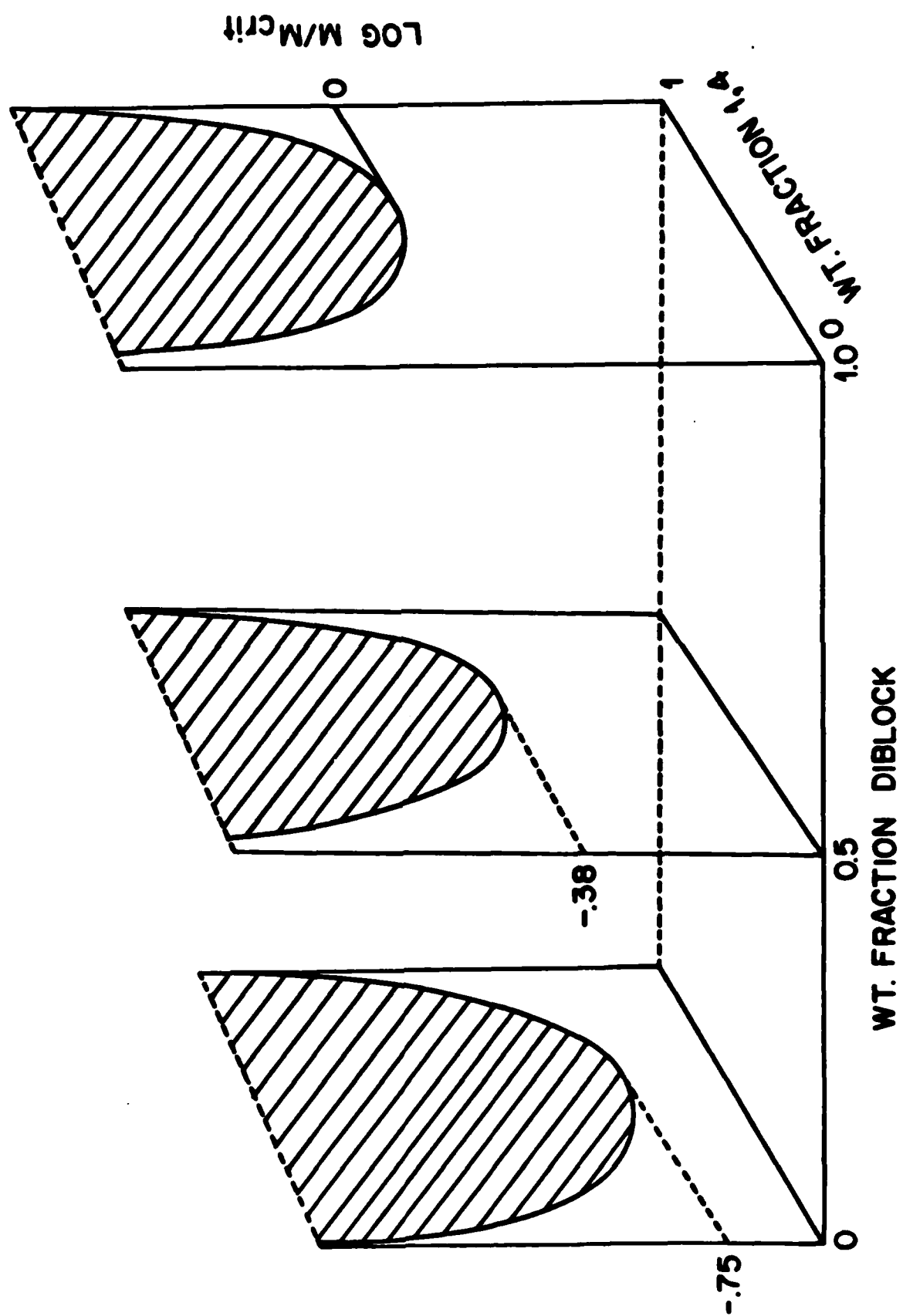


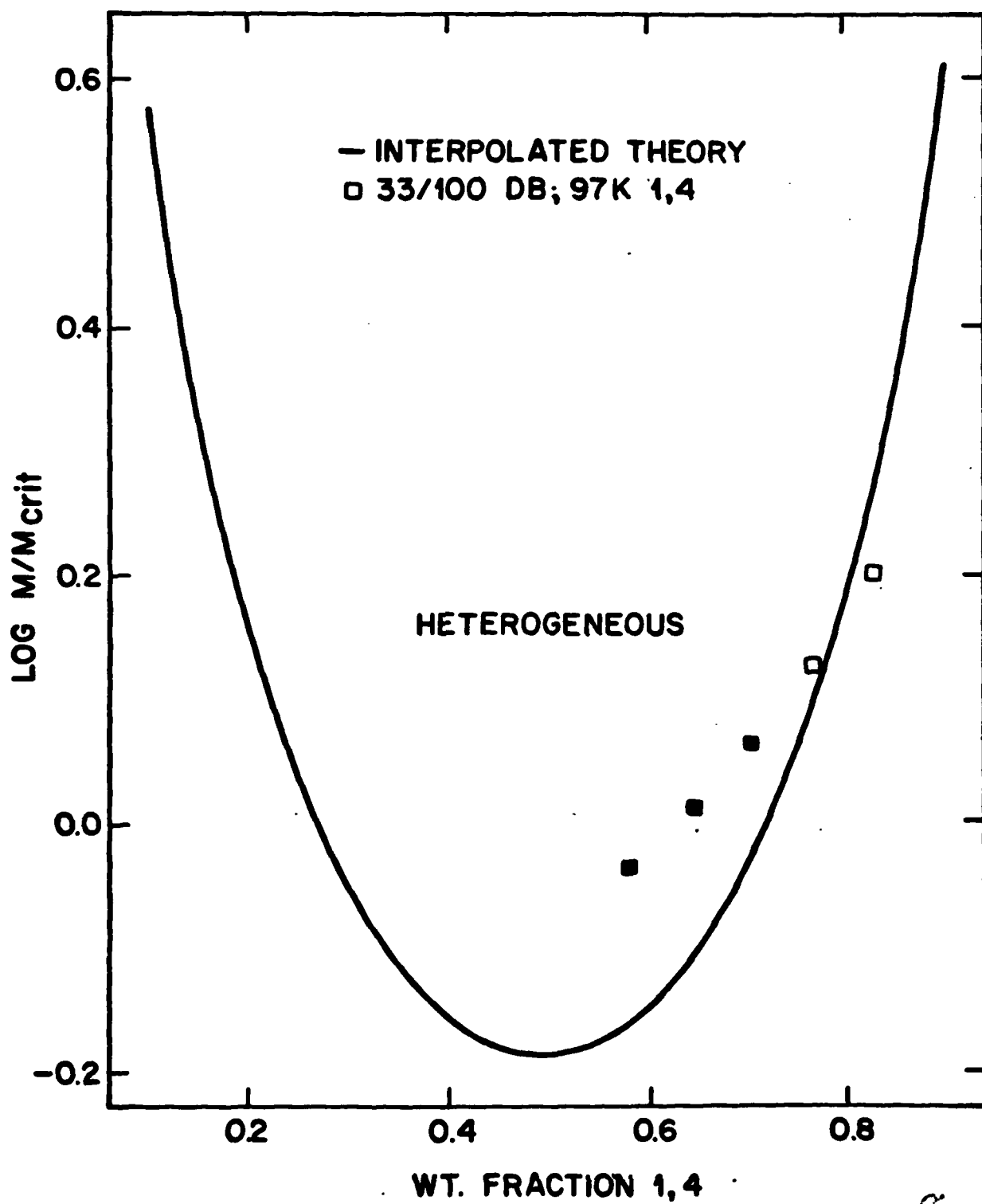


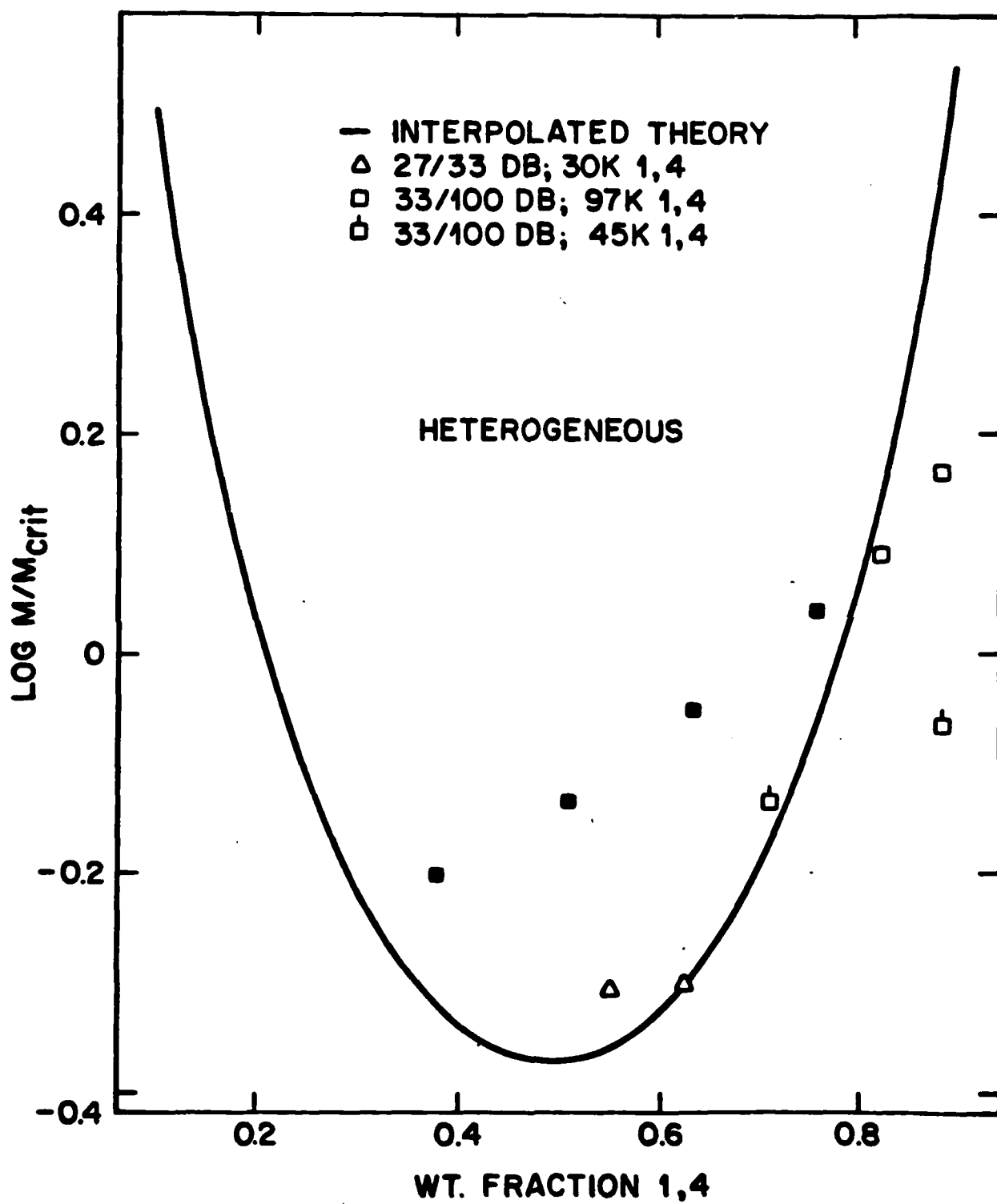
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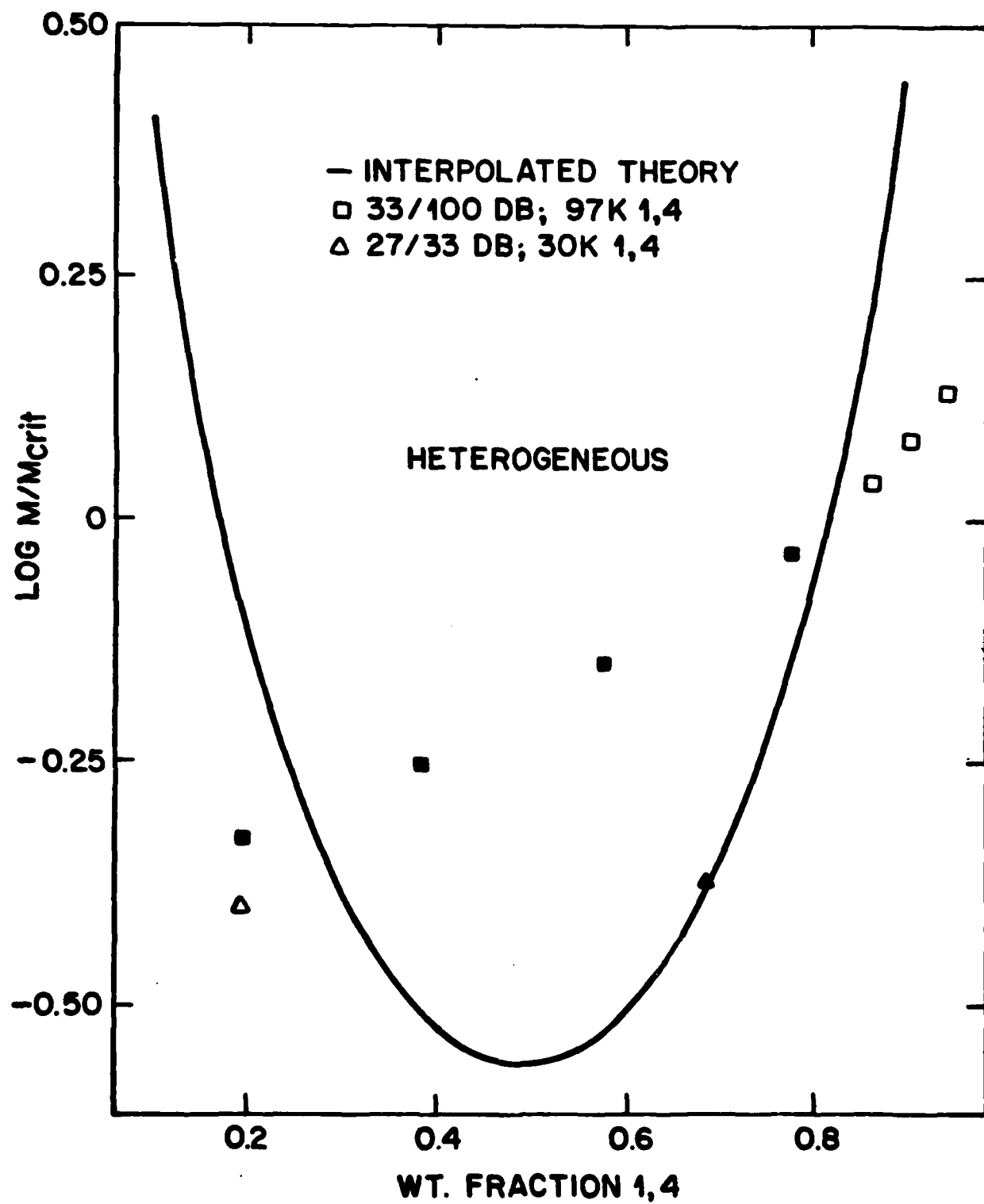


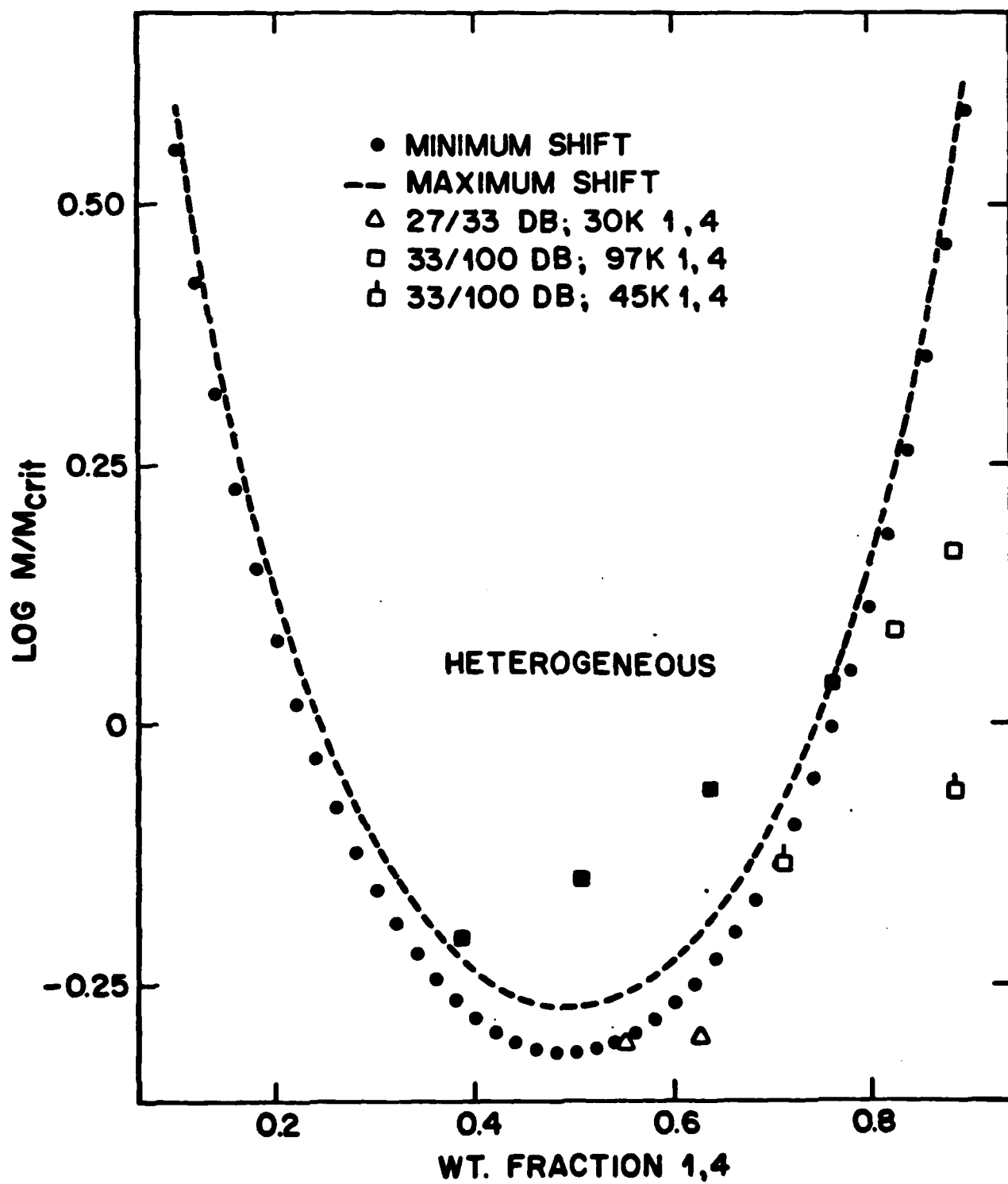
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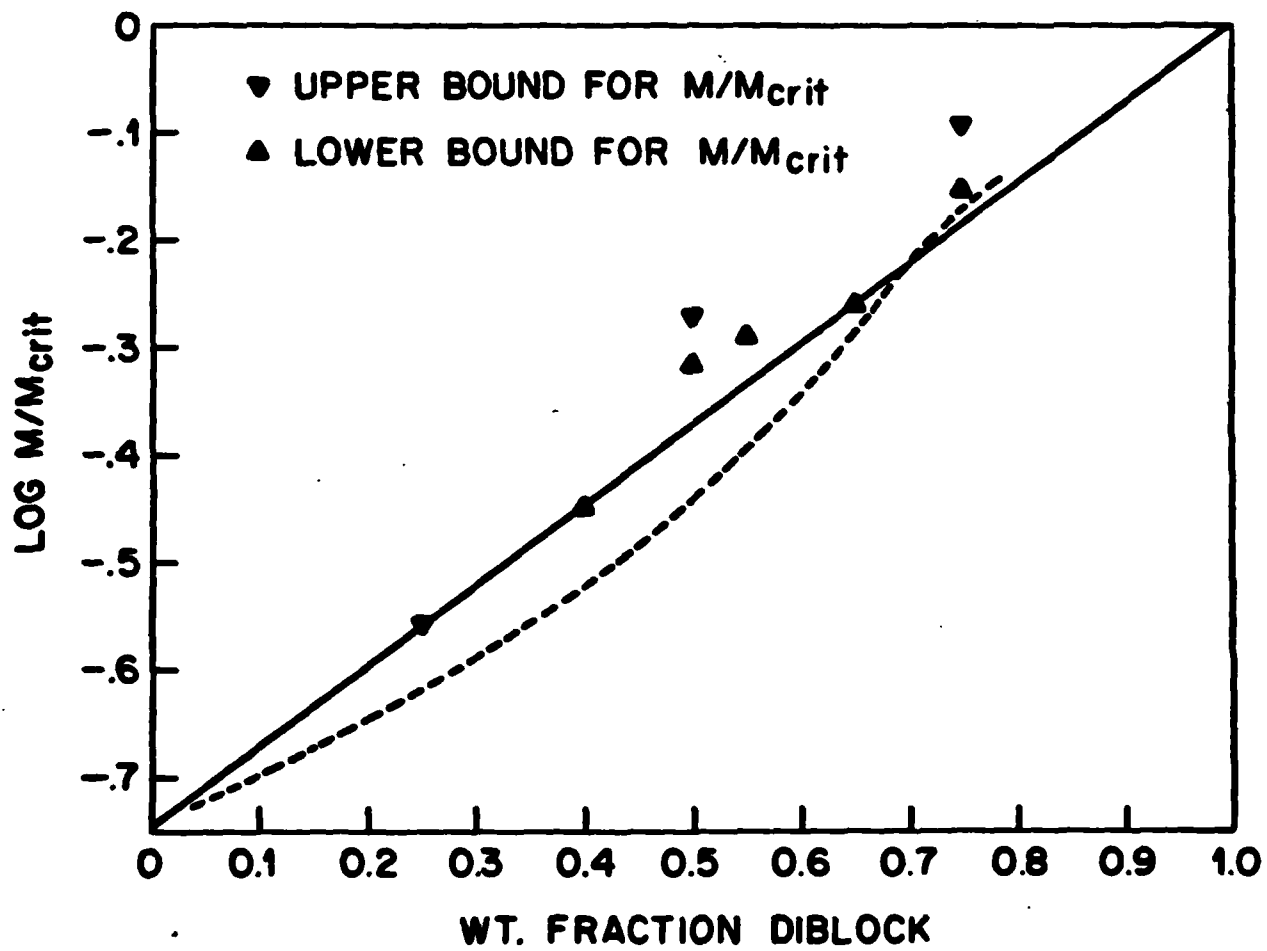


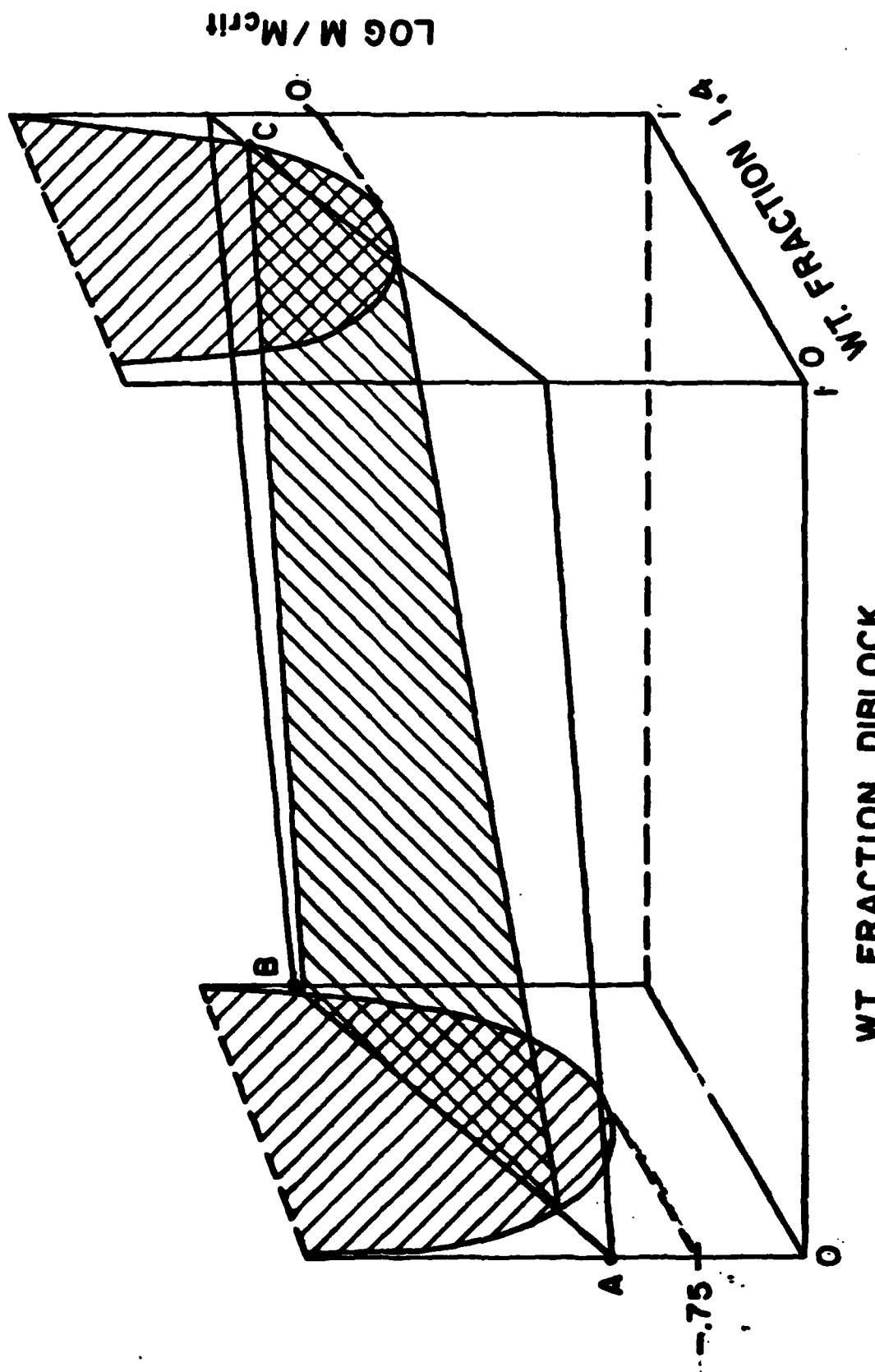


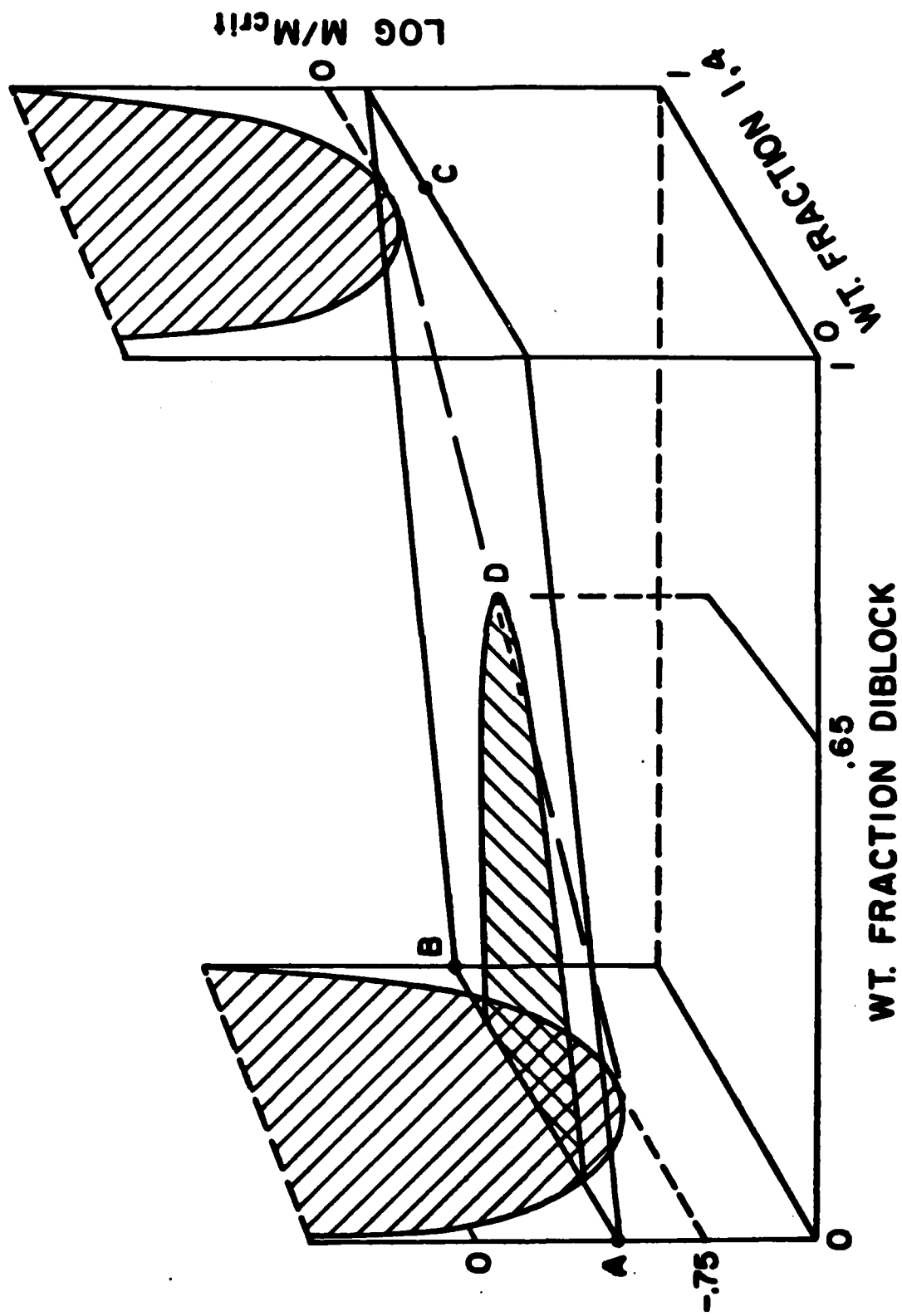




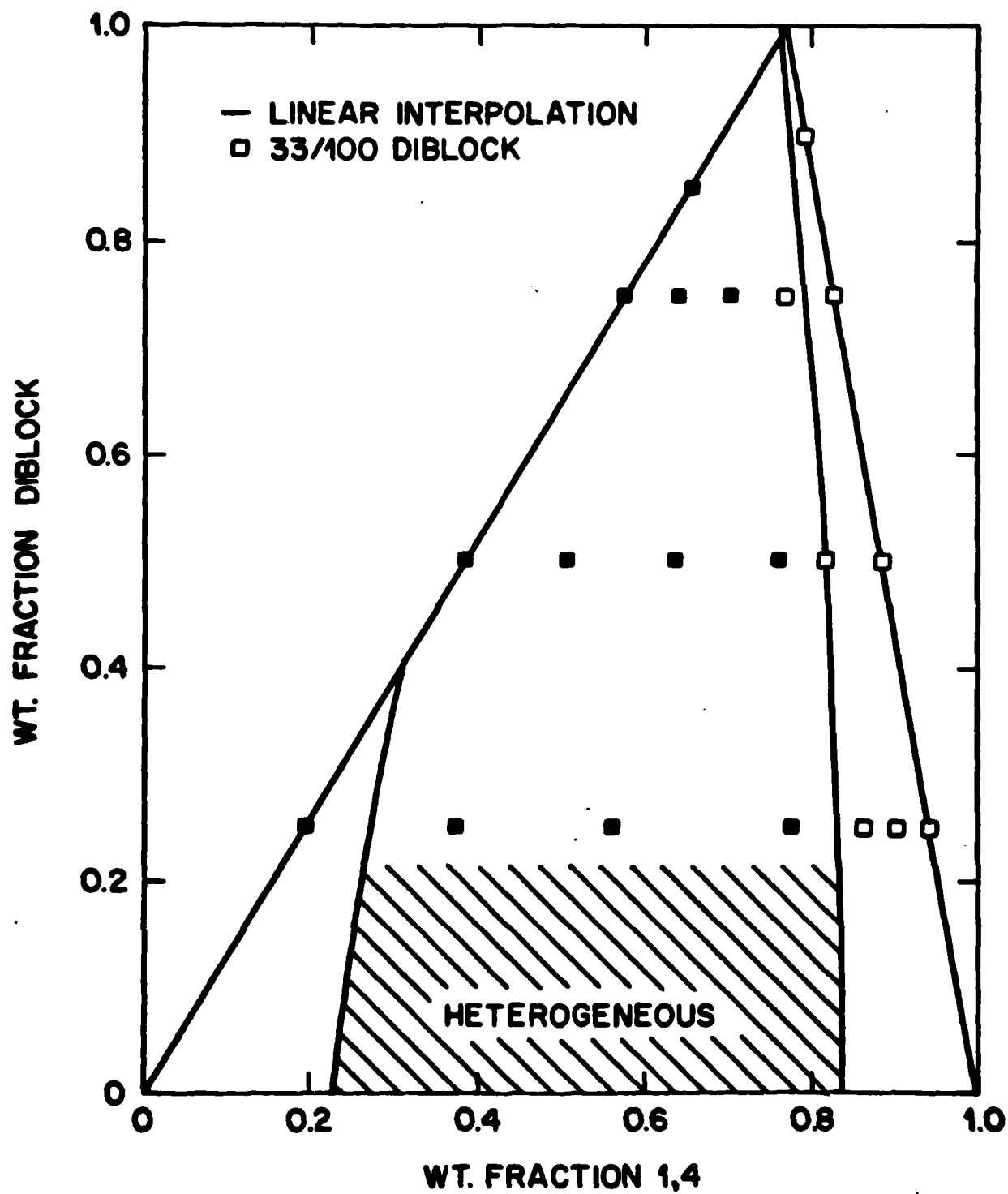


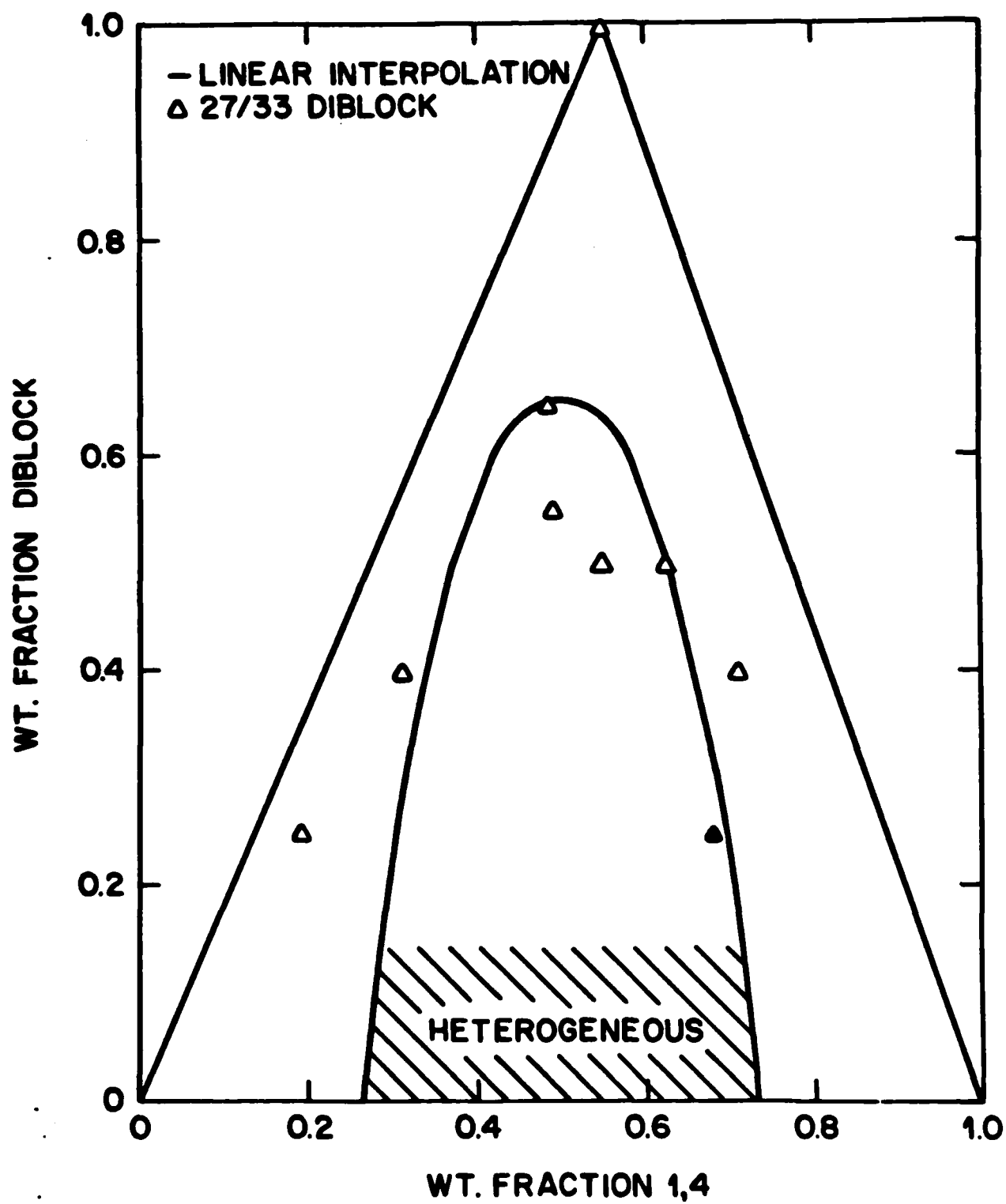


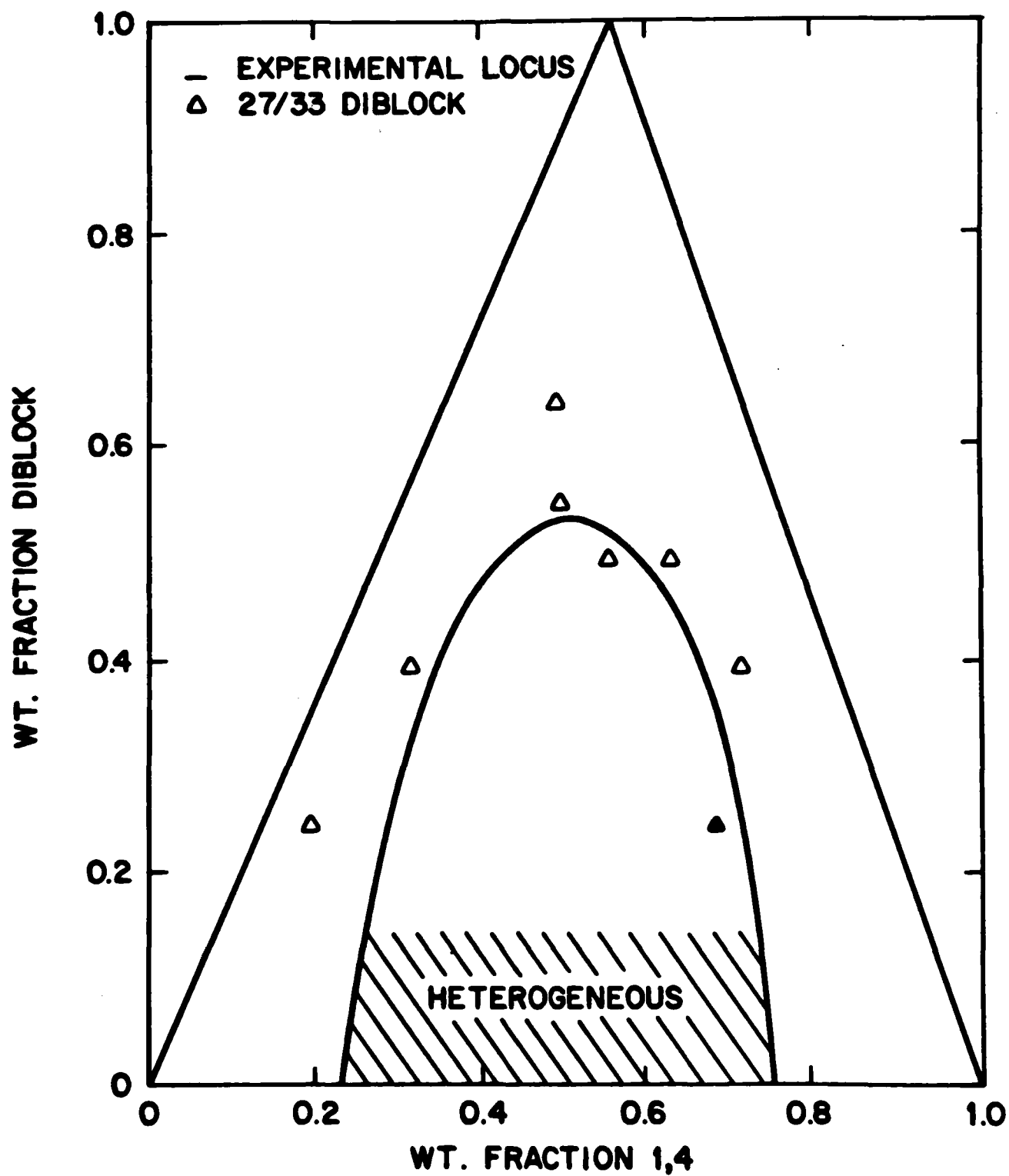


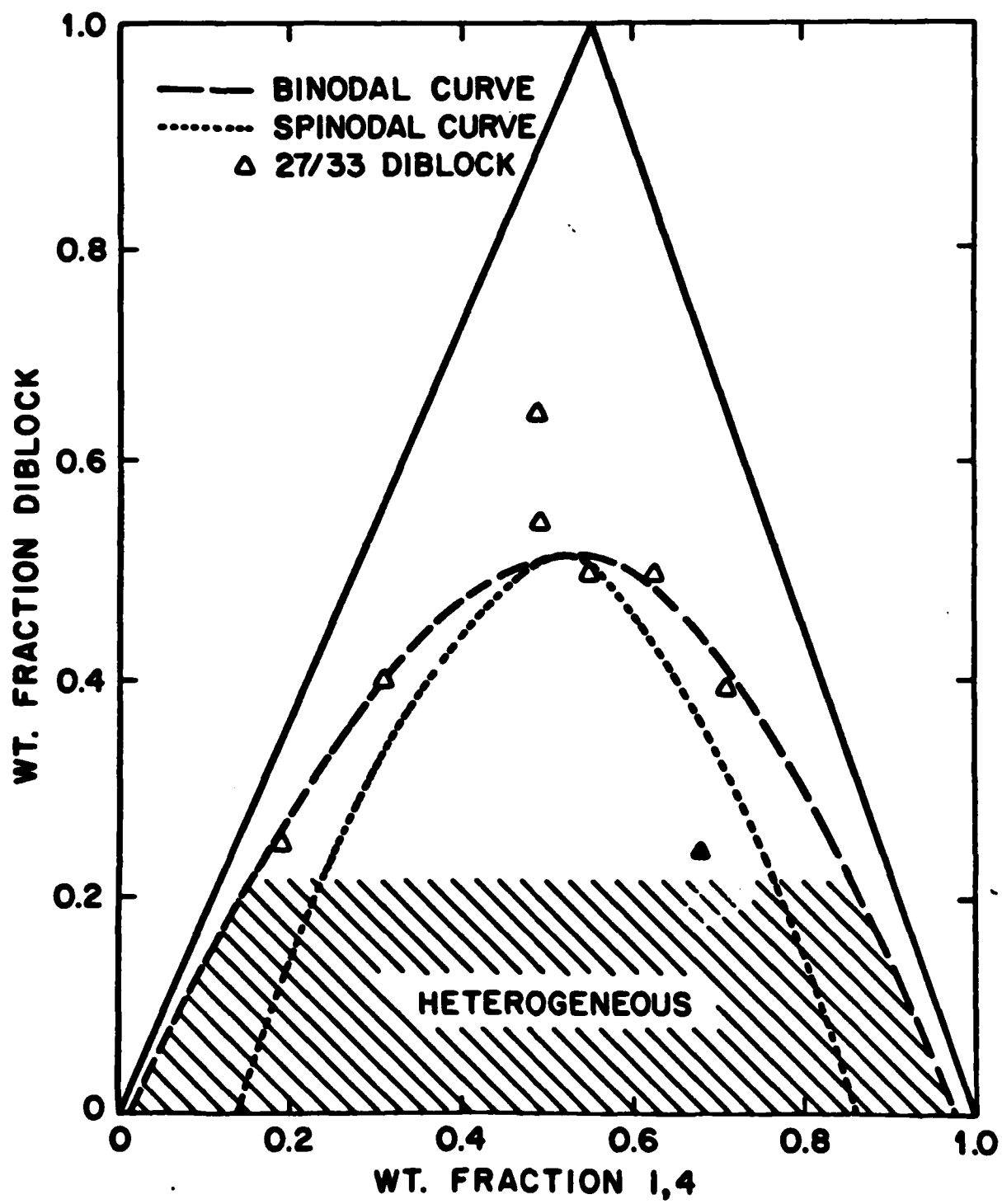


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