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Phase Behavior of Triglyceride Mixtures Involving Primarily Tristearin, 2-Oleyldistearin, and Triolein

E. S. LUTTON, Research and Development Department, The Procter and Gamble Company, Cincinnati, Ohio

THE phase behavior of triglyceride mixtures underlies the consistency phenomena of such plastic fats as shortenings and margarines. The knowledge of phase behavior moreover is potentially of aid in advancing the study of triglyceride composition of natural fats, one of the remaining great problems in fat research.

Bailey (1) has rather recently summarized the fundamental information on triglyceride solidification as revealed especially by melting point, solubility, dilatometry, and x-ray diffraction. Since then Craig (3) and Kerridge (7) have added to the picture.

The present paper covers some aspects of work on fat mixtures which has been carried out over a period of 10 years. Where it covers the same ground as the work of Craig *et al.* (3) and Kerridge (7), it is in large measure, although not entirely, confirmatory. In addition, it systematizes some of the information partly on the basis of the Hildebrand solubility law (5). It gives considerably more information on metastable forms than has hitherto been available for triglyceride mixtures and in some instances shows the effect of variability of treatment on stable forms and brings to bear the combined evidences of melting point, and of dilatometric and x-ray techniques.

It is necessary to refer to the previously published basis for classifying polymorphic forms (8a, b). The author believes there is no reason for altering his nomenclature or general views on glyceride polymorphism despite the discordant opinions of Malkin (9), who is universally acknowledged to be the pioneer in this field.

Experimental

In the present study the various triglycerides were the same as those of previous publications from this laboratory. These glycerides and mixtures thereof were studied by melting point, x-ray diffraction, and dilatometry.

In the preparation of mixtures care was taken to achieve homogeneity; weighed mixes were stirred 1 min. as dry powders (where possible) and 1 min. as melts.

Melting Point

Melting points were determined by methods previously described (8a). In the case of complete melting points of stable forms, low heating rates of 0.2°C. per minute were normally used to ensure close approach to equilibrium conditions. With metastable forms a thrust-in technique was necessary, and observations were made either of complete clarity or of definite softening. (The softening points are about a degree below corresponding points of complete clarity when the latter can be determined.)

X-ray Diffraction

X-ray diffraction was carried out by methods also previously described (8a). In general, samples were treated to produce the desired phase in thin-walled capillary tubes of Pyrex glass and were removed from their Pyrex sheath just prior to x-ray exposure in order to decrease exposure time and improve resolution of lines. Where possible, patterns were obtained with sample-to-film distance of 5 cm., which is sufficient to reveal short-spacing characteristics; but frequently longer distance (10 cm.) was necessary to reveal sufficient details in the long spacings, and, in a few instances, fine slits (0.005 in.) were employed in the collimating system to improve resolution.

When phase proportions were estimated, it was done by determining the relative intensities of characterizing lines. Where feasible, as for instance in the LLL-SSS system, mechanical mixtures of pure components were x-rayed for comparison with the treated melts.

Dilatometry

The essential features of the dilatometric technique have been reported (4). In the present studies, samples were generally melted, chilled, and stabilized for appropriate periods prior to measurement. Normally there was little evidence of vacuole formation, but, if serious, it was overcome by subjecting the whole dilatometer to a pressure of 3,500 lb. per square inch. This was accomplished by placing the whole dilatometer within a long bomb designed for high pressure hydrogenations. Pressure was built up, held at maximum, and released in three 15-min. periods. In the process mercury, the confining fluid, was forced into any existing vacuoles. The dilatometer data were used in two ways:

1. From raw dilatometer readings, phase proportions were estimated as indicated in Figure 6. Here:

$$\%\ \text{Solid} = \frac{BC}{AC} \times 100$$

From % solid values the solidus can be located in relation to the liquidus, which is obtained by melting point.

2. Actual specific volumes were calculated and % solid determined therefrom. As a first step, pycnometer liquid specific volumes at single reference temperatures were determined if not available (6), and linear interpolation was used to obtain values for mixes. With the aid of dilatometer readings, specific

volumes at other temperatures were obtained, for liquid, solid, and partially solid regions. Normal corrections for expansion of mercury and glass were applied. It was necessary also to make a stem correction for the exposed dilatometer capillary. This was done in this fashion:

$$R_c = R + \triangle R = R + 0.000152[L_o(T_o - T) + R(T - T_r)]$$

where

R_c = corrected dilatometer reading
R = experimental reading
$\triangle R$ = reading correction
L_o = total length of emergent dilatometer stem
T_o = reference temperature
T_r = room temperature (generally 25°C.)

0.000152 is an empirical constant, depending mainly on the difference between density of Hg. at temperature of measurement and at room temperature. It was determined by noting the amount of rise in the Hg. column in a typical fat-filled dilatometer (placed in a normal manner in a bath set at a temperature well above room temperature) when the column was warmed to bath temperature. (The amount of rise is somewhat less than that calculated on the assumption that the whole capillary is at room temperature.)

Calculation of % Solid

A precise calculation of % solid is justified only when the solid phase is known and its specific volume measured. The procedure is indicated in Figure 7.

As a first approximation, at T_1

$$\% \, S_1 = \frac{BD}{AD} \times 100 = \frac{(V_{L_1})_{ex} - V_M}{(V_{L_1})_{ex} - V_{S_1}} \times 100$$

This quantity may be readily calculated. But a more nearly accurate value is

$$\% \, S_1 = \frac{BC}{AC} \times 100 = \frac{V_L - V_M}{V_L - V_{S_1}} \times 100, \quad (A)$$

where V_L is the actual specific volume of the liquid phase and is not, in general, linearly continuous with that of the melt.

A linear relation in liquid specific volume permits the assumption

$$(V_{L_1})_{ex} = \frac{(100 - \% \, S_1)V_L + \% \, S_1 \, (V_L)_{S_1}}{100}$$

where $(V_L)_{S_1}$ is the liquid specific volume of that material which, when 100% solid, has the specific volume V_{S_1}

$$V_L = \frac{100 \, (V_{L_1})_{ex} - \% \, S_1 \, (V_L)_{S_1}}{100 - \% \, S_1} \quad (B)$$

From equations (A) and (B) it is simplest to arrive at % S_1 by successive approximations.

By a similar but somewhat more involved process

$$\% \, S_2 = \frac{V_{M_1} - V_L}{V_{S_2} - V_L} \times (100 - P) \quad (C)$$

$$V_L = \frac{100 \, (V_{L_2})_{ex} - \% \, S_2 \, (V_L)_{S_2}}{100 - \% \, S_2} \quad (D)$$

P = % solid at $T_{1,2}$ and is assumed to remain constant below that temperature.

$$V_{M_1} = \frac{100}{100 - P}\left(V_M - \frac{P}{100} V_{S_1}\right) =$$

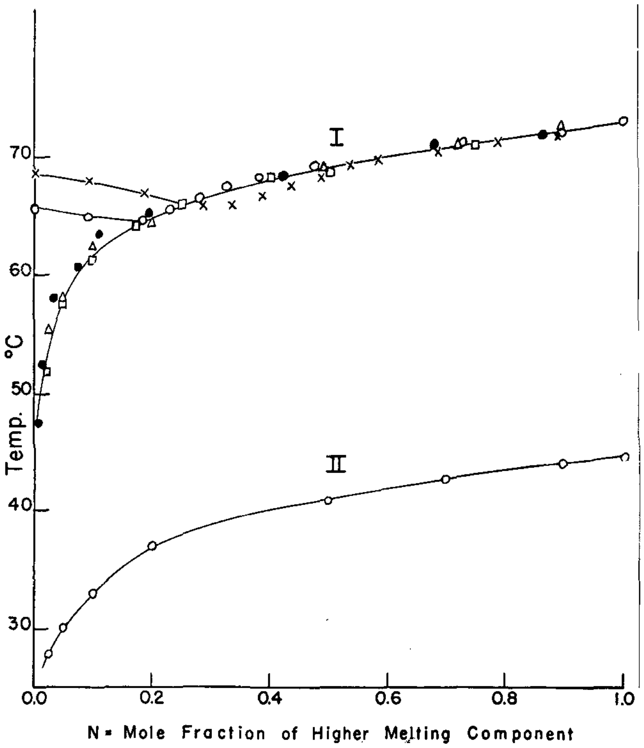

FIG. 1. M.p.s. of binary systems: I, SSS as higher melting component; lower melting components are O-PPP, ●-LLL, □-SOS, △-OOO, X-PSP; II, SOS as higher melting component with OOO. The solid lines drawn from the melting points of the higher melting components are calculated from the Hildebrand Solubility Law with the assumption that heat of fusion in cal./g. is 50 for SSS and 45 for SOS.

sp. vol. of the remaining (100-P) % of the system. Equations C and D can also be solved by successive approximations.

For the calculations in the present paper the values for specific volume in Table I were used. These were determined from a combination of available liquid specific volumes (6), experimental pycnometer values, and experimental dilatometric values.

TABLE I

Specific Volume Values for Calculation of % Solid

Composition	Specific Volume[a]
SSS, (V_{S_1})	0.9698 + 0.00034 T
SOS, (V_{S_1})	0.9808 + 0.000425 T
SSS, $(V_L)_{S_1}$	1.0902 + 0.00087 T
SOS, $(V_L)_{S_1}$	1.0890 + 0.00085 T
20% SSS + 80% 000, $(V_{L_1})_{ex}$	1.1407 + 0.00082 (T-70)
20% SOS + 80% 000, $(V_{L_1})_{ex}$	1.1147 + 0.00082 (T-70)

[a] Average values for coefficient of expansion are given.

Location of the Solidus

From the amount of solid (determined in either of the aforementioned two ways) and the position of the liquidus it is possible to locate a solidus point. From each dilatometer, solidus values at several different temperatures can, in general, be obtained.

$$\text{Since } \% \text{ solid} = \frac{C - L_T}{S_T - L_T} \times 100$$

where C = composition of sample in %

L_T = composition of liquidus at that temperature in %
S_T = composition of solidus at that temperature in %

then $$S_T - L_T = \frac{C - L_T}{\%\ \text{solid}},$$

hence $$S_T = L_T + \frac{C - L_T}{\%\ \text{solid}}$$

Discussion

It appears definite from Figure 1 for the group of binary triglyceride systems here discussed that the Hildebrand solubility relation (5) holds, and that melting points for mixes with SSS as the higher melting component are given by the following relation down to a temperature where the second component begins to appear

$$\log \text{mole } \% = 2 + \frac{50 \times 891}{4.575} (1/T_o - 1/T)$$

where 50 = heat of fusion of SSS in cal/g
891 = M.W. of SSS
T_o = m.p. of SSS
T = m.p. of mix

Likewise the following relation holds for the system OOO-SOS

$$\log \text{mole } \% = 2 + \frac{45 \times 889}{4.575} (1/T_o - 1/T)$$

A heat of fusion of 50 cal/g. for SSS is in reasonable agreement with the value of 54.6 given by Charbonnet and Singleton (2) (a value which may be somewhat high due to the method of extrapolation used). A value of 45 cal/g. for SOS is in line with the observation that lower melting glycerides have lower heats of fusion (2).

There is a rather large departure by data for PSP-SSS from the other data on the side of lower melting, and this seems chargeable to a particular incompatibility of beta prime-stable PSP with beta-stable SSS.

The data for the binary system PPP-SSS in Figure 2 show the nearly linear relationship for alpha melting points *versus* composition, which is common with glycerides that are close in melting level. The intermediate beta prime level is hard to characterize with precision but appears to show a very substantial departure from linearity. In the case of the stable beta form there is a clearly defined eutectic at about 16% (by wt.) SSS and 63.5°C. The solidus for beta as deduced from a combination of x-ray and dilatometric results falls close to the position suggested by Kerridge (7). It is believed however that the stearic-rich phase at the eutectic composition is somewhat lower in stearic content than indicated by Kerridge. This is deduced from the x-ray data of Table II.

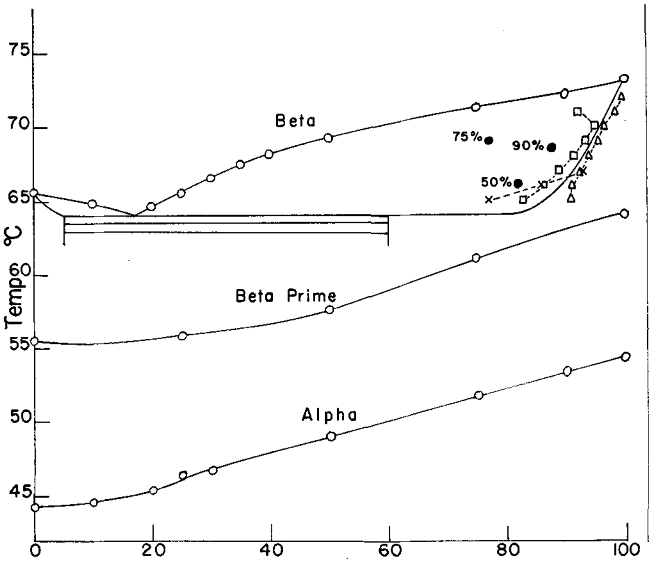

FIG. 2. Binary system PPP-SSS; O—m.p., ●—solidus points from x-ray data, X—solidus points from dilatometer with 50% SSS, □—with 75% SSS; △—with 90% SSS.

TABLE II

Long Spacings (Å) from High Resolution Patterns of PPP-SSS

% SSS	Beta Form		
	Stabilized 44°C.[a]	Stabilized 49°C.[b]	Stabilized 60°C.[c]
20	41.1	40.4, 42.5	40.6, 42.9
50	43.3	40.4, 42.9	41.0, 42.9
80	45.0	45.1	44.6

[a] 3 weeks 38°, 6 weeks 44°C.
[b] 3 weeks 38°, 6 weeks 44°, 3 days 49°C.
[c] 3 weeks 38°, 6 weeks 44°, 3 days 49°, 1 week 60°C.

Thus it is actually possible to obtain a continuous series of beta solid solutions by "stabilizing" chilled mixes no higher than 44°C. With higher temperature storage the solid solution breaks up to give a SSS-rich phase which, from its long spacing, contains considerable PPP. The method used by Kerridge (7) for thaw-point determination seems likely to lead to low values for SSS content in the SSS-rich phase as may be more evident from analogy with the SOS-SSS system.

Both dilatometric and x-ray studies were performed on mixes of PSP and SSS and yielded results in line with those for PPP-SSS. Thus the metastable alpha forms show continuous solid solution formation, as do the beta prime forms, but fully stabilized mixes break into two phases, beta prime for PSP-rich and beta for SSS-rich composition. (See Table III.)

Dilatometer evidence suggests solidus lines closely corresponding to those for PPP-SSS.

The beta prime data reveal the variation in melting level possible with unstabilized phases. Thus for PSP a softening point of 64.0° compares with a com-

TABLE III

Long Spacing Data (Å) for the System PSP-SSS

Alpha (melt, chill)

% SSS	S.P. °C.	L. S.
0	46.5	46.8
20	47.2	48.6
50	50.6	49.3
80	53.1	50.7
100	54.2	50.6

Beta Prime (melt, solidify 30 min. at alpha s.p.)

% SSS	S.P. °C.	L. S.
0	64.0	42.9
20	61.8	43.7
50	62.8	44.6
80	63.7	45.7
100	64.0	46.8

Stable Forms (melt, chill, 30 days 58°C.)

	M.P. °C.	I	II
0	68.7	42.95	
30	66.0	43.0	45.2
50	68.6	43.0	45.0
60	69.9	43.1	44.9
80	71.4		45.15
100	72.9		

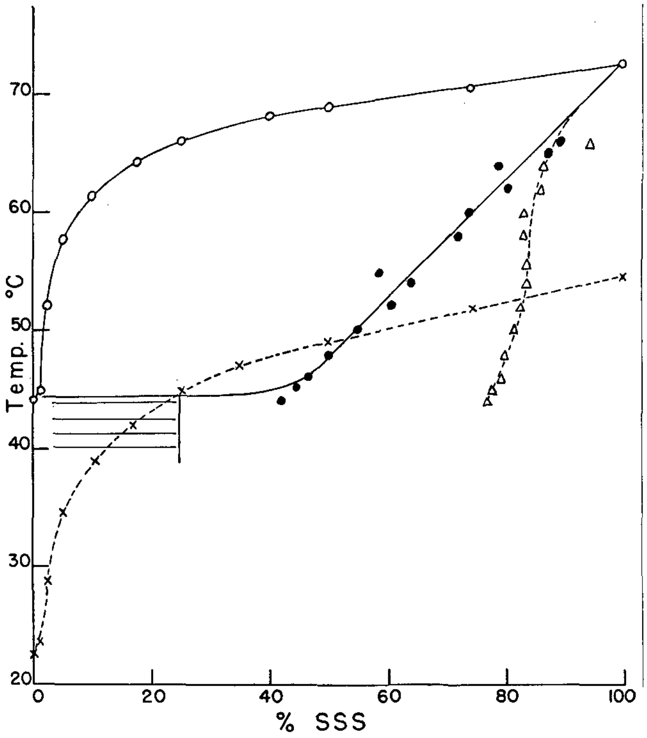

Fig. 3. Binary system SOS-SSS: O—m.p.s. of stable form, X—melting points of alpha form, ●—solidus points for 38°C. storage, △—pseudo-solidus points for 60°C. storage.

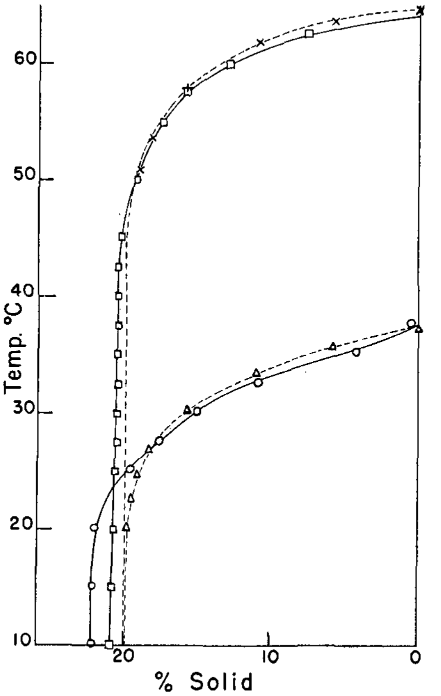

Fig. 4. Comparison of experimental and calculated % solid. X—calculated % solid for 20%SSS—80% OOO, □—experimental % solid; O—calculated % solid for 20% SOS—80% OOO, △—experimental % solid.

plete melting point of 68.7°C. although x-ray evidence indicates the same polymorph corresponds to both melting levels. Then the continuous series of solid solutions for PSP and SSS in the beta prime form is a feature of interest which further justifies regarding the stable beta prime form of PSP and the metastable beta prime form of SSS as related polymorphs.

The SOS-SSS system is particularly interesting because of the large departure shown for non-equilibrium cases from the equilibrium cases. In the equilibrium case SSS takes considerable SOS into solid solution although very little SSS is taken in by SOS. This appears in Figure 5 as well as Figure 3. In Figure 5 it is shown how a stabilized sample melts considerably at about 45°C. to leave a phase which contains a very large proportion of SOS. With an increase in temperature SOS is gradually melted out. But on further chilling and stabilizing, this SOS is for the most part incapable of crystallizing with the high-melting solid and must form an almost exclusively SOS phase. This effect causes an apparent shift in solidus as indicated in Figure 3. The true solidus is thought to be the solid line although it is theoretically possible for a solid solution to hold more than the equilibrium proportion of a lower melting component if the outer crystal layers "shield" the inner layers from the action of solvent.

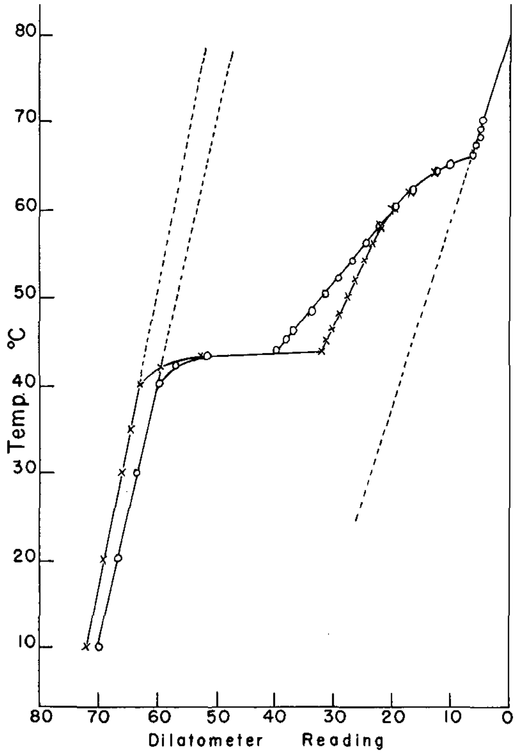

Fig. 5. Dilatometer curves for the composition 75% SOS—25% SSS; O—after 38°C. storage, X—after 60°C. storage.

Two simple comparisons of experimental and calculated % solid are shown in Figure 4. These involve the systems OOO-SSS and OOO-SOS. The agreement is about as good as one could expect, considering the various assumptions and the errors of experiment. The results on 80% OOO-20% SSS excellently confirm the findings of Craig *et al.* (3) on a 66.5%-33.5% mixture, namely that over the range 10°-50°C. the solid content is nearly identical with the tristearin percentage, which simply bespeaks a low SSS solubility in OOO and a negligible degree of OOO-SSS solid solution formation.

With regard to the system LLL-SSS, not depicted here in detail, it is believed that Kerridge's (7) so-

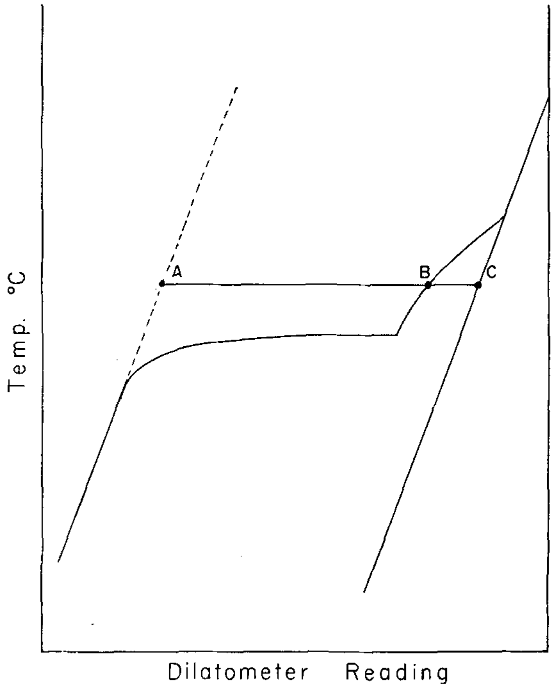

FIG. 6. Schematic dilatometer curve to indicate determination of % solid directly from raw dilatometer readings.

lidus running down from SSS indicates too much LLL content since dilatometer curves for as little as 10% LLL show a sharp break, due to LLL melting very near the LLL melting point; and x-ray patterns of 25-75 and 75-25 mixes of LLL-SSS show two sets of long spacings whose magnitudes and whose intensities are closely comparable to those of mechanical mixtures.

It was indicated that solid solution will occur in fats when there is sufficient similarity in chain length and melting point. With the chain length differences which exist between LLL and SSS and the melting point differences between OOO and SOS or SSS, solid solution appears to be negligible.

Acknowledgment

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Summary

A study of binary systems involving SSS with PPP, PSP, LLL, SOS, or OOO, also SOS with OOO shows, for these triglycerides, agreement of liquidus position with the Hildebrand solubility law. Solid solution is essentially absent in LLL-SSS and OOO-SSS and OOO-SOS but definitely occurs with PPP-SSS, PSP-SOS, and SOS-SSS, where it is clearly shown by x-ray and dilatometric evidence. Solid solutions are particularly evident with metastable forms. Possibility of wide departure from equilibrium behavior is shown for "stabilized" samples in the SOS-SSS case; low melting components melted out of solid solution below the system's complete melting point are able to reenter the solid solution phase only to a limited extent.

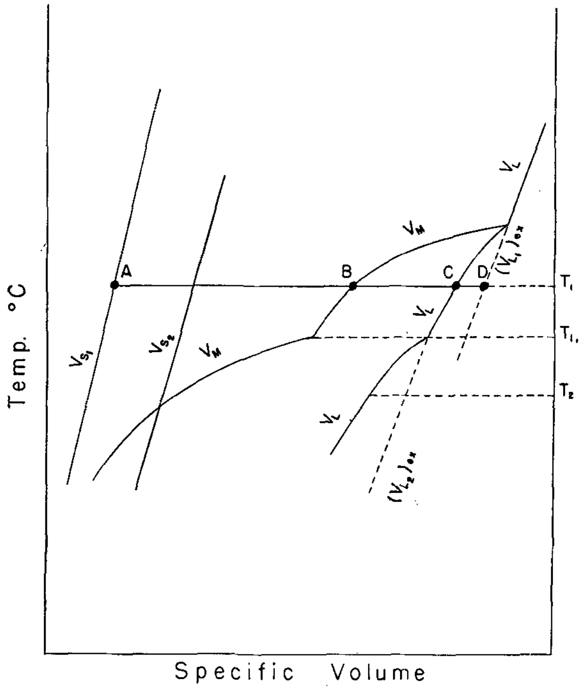

Fig. 7. Schematic dilatometer curve for precise determination of % solid; V_L is the sp. vol. of the liquid phase; $(V_{L_1})_{ex}$ is the sp. vol. extrapolated from that of the melt; V_{S_1} is the sp. vol. of the only solid phase which exists from $T_{1,2}$ to the complete m.p.; V_{S_2} is the sp. vol. of the solid phase which begins to come out at $T_{1,2}$; V_M is the sp. vol. of the partially solidified mix; $(V_{L_2})_{ex}$ is the sp. vol. of the liquid phase drawn parallel to $(V_{L_1})_{ex}$ from the actual value of V_L at $T_{1,2}$.

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