LOWER CRITICAL SOLUTION TEMPERATURES FOR POLYDIMETHYLSILOXANE

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By

George Earl Vogel

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ABSTRACT

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Lower critical solution temperatures, T_{CL}, were determined for five well characterized fractions of polydimethylsiloxane in n-pentane, n-butane, propane, neopentane, tetramethylsilane, dimethyl ether, and methyl chloride.

Linear relationships were found for $1/T_{CL}$ vs $1/x^{1/2}$, where x is the polymer size function. These relationships show that the L.C.S.T. data can be treated in a manner similar to upper critical solution temperature data, as given in the Flory-Huggins treatment, even though the L.C.S.T. phenomena are not predicted by this theory. Entropy of dilution parameters, ψ_1, and θ_L temperatures were calculated for each solvent. It was found that the θ_L temperatures correlated reasonably well with the solvent critical temperatures. It was also found that linear relationships exist for T_{CL} vs $1/x^{1/2}$. This is in accordance with a more recent theoretical treatment of Patterson, Delmas, and Somcynsky[5]. More and different types of data are needed before any distinctions between the two treatments can be made.

The effect of pressure on the L.C.S.T. data is discussed. Pressure corrections could alter considerably the quantitative nature of the data; however, the qualitative nature would remain essentially unchanged.

ACKNOWLEDGMENTS

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INTRODUCTION

Although it now appears that the existence of lower critical solution temperatures (L.C.S.T.) may be universal in polymer-solvent systems, this phenomenon was first observed in pure hydrocarbon mixtures only in very recent years. A great deal of attention is being directed toward this subject because of the thermodynamic implications of the L.C.S.T.'s, and the classical conventional polymer solution theories will require some drastic revisions to provide a theoretical framework for the phenomena.

Freeman and Rowlinson[1] first observed the L.C.S.T. phenomena for hydrocarbon solutions of hydrocarbon polymers. Nearly all the systems they investigated exhibited L.C.S.T.'s, all of which were between the normal boiling point and the gas-liquid critical point of the pure solvent. The existence of L.C.S.T.'s in solutions of certain pairs of polar liquids and even in aqueous solutions of certain polymers had been recognized for some time, but never had they been observed in completely nonpolar systems. In the former, the observed L.C.S.T.'s were attributed to an entropy increase upon breaking hydrogen bonds between solvent and solute. However in the latter case (the completely nonpolar systems), the L.C.S.T.'s obviously result from forces of an entirely different nature. The authors of this initial report attributed this phenomenon to the decreasing configurational energy and increasing molar volume of the solvent which result in the solvent becoming thermodynamically poorer at higher temperatures.

In conjunction with the above work, Rowlinson and Freeman[2] reported their findings of a study of the miscibility of a series of pure hydrocarbons containing between 24 and 37 carbon atoms with ethane and propane. No liquid-liquid phase separations were observed in the propane systems up to the critical endpoint of the solutions. However, L.C.S.T.'s ranging from 3.7° to 27.7°C were observed for all the ethane solutions. These findings are an indication of the importance of the molecular size and energy of interaction differences between the solvent and solute.

Davenport and Rowlinson[3] have subsequently studied the miscibility of liquid methane with a large number of hydrocarbons having from four to eight carbon atoms. Some hydrocarbons containing five carbon atoms and nearly all those containing more than five carbon atoms were incompletely miscible with methane, with many of the systems exhibiting L.C.S.T.'s. In general the miscibility decreased with increasing numbers of carbon atoms in the solute. However, other factors were also found to affect the miscibility: branched isomers were more miscible than straight chain isomers, olefins were less miscible than paraffins, diolefins and acetylenes were less miscible than olefins, cyclics were less miscible than non-cyclics, and aromatic compounds were found to be very insoluble. The authors suggest that a L.C.S.T. occurs whenever the solute is a molecularly dense liquid of strong intermolecular forces and the solvent a liquid of low molecular density and weak intermolecular forces. A solvent that is approaching its gas-liquid critical point fulfills this last condition well.

Baker and co-workers[4] have studied the phase equilibria of solutions of polyisobutene of various molecular weights in n-pentane, and also measured the thermodynamic properties of these solutions. They found that polymer solutions which are approaching a L.C.S.T. are incompatible with the Flory-Huggins equation since they exhibit negative heats and entropies of dilution. These, indeed, are thermodynamic requirements of any binary solution whose miscibility is decreasing with increasing temperature, i.e., approaching a L.C.S.T. This also implies that the Flory free energy of interaction parameter, χ , should be increasing with temperature near a L.C.S.T. The authors show that this is indeed the case for the system n-pentane-polyisobutene. Since, in the lower temperature regions where the Flory-Huggins equation is valid, $\frac{\partial \chi}{\partial T}$ is negative, χ passes through a minimum at some temperature.

Using solubility parameter theory and the molecular theory of polymer solutions developed by Prigogine and co-workers, Delmas, Patterson, and Somcynsky[5] have developed an expression for the free energy of interaction parameter, χ :

$$R\chi = A(r_1/T) + B(T/r_1) \qquad (1)$$

where r_1 is the number of segments in the solvent molecule, and A and B are constants depending on the solvent-polymer pair. The authors measured calorimetrically the heats of mixing for polyisobutylene (unfractionated) in the n-alkane solvents. Using values for A and B calculated from these data and from other published data, they used equation (1) to predict the L.C.S.T. for these systems. Their predicted values are in fair agreement with those found experimentally by Freeman and Rowlinson[1].

Kinsinger and Ballard[6,7], as a result of a study of the phase equilibria in solutions of well characterized fractions of polyoctene-1 in n-pentane, have shown quantitatively the dependence of the L.C.S.T. on the molecular weight of the solute. A linear relationship was observed when $1/T_{CL}$ was plotted against $1/x^{1/2}$, where x is the polymer size function defined in the Flory-Huggins theory as:

$$x = v_p M_p / V_1 . \tag{2}$$

Here, v_p is the specific volume of the polymer at the precipitation temperature, M_p is the weight-average molecular weight of the polymer, and V_1 is the molar volume of the solvent at T_{CL}. In this respect, the L.C.S.T. phenomena correspond to the familiar upper critical solution temperatures (U.C.S.T.) where such plots are common, and are used to calculate the entropy of dilution parameter, ψ_1, and the Flory temperature, θ. The authors, therefore, re-designate this Flory temperature as θ_U, and define a corresponding temperature, θ_L, which is obtained from plots of the above type, for systems exhibiting a L.C.S.T., by extrapolating to infinite molecular weight ($1/x^{1/2} \longrightarrow 0$).

Tetreault[8] determined the L.C.S.T.'s for characterized fractions of a number of poly-α-olefins in n-pentane and n-butane. He likewise observed a linear relationship between $1/T_{CL}$ and $1/M^{1/2}$. The author also reports, for the first time, L.C.S.T.'s of a three component system (two solvents and one polymer). The L.C.S.T. behavior in this system is quite similar to that in binary systems.

The dependence of a L.C.S.T. on pressure has been demonstrated recently by Allen and Baker[9]. They investigated the L.C.S.T. of the polyisobutene-isopentane system as a function of pressure up to 400 p.s.i., and found the fairly large pressure coefficients, dT_c/dP, of 0.46 and 0.40 deg. atm.$^{-1}$ for two different fractions of polyisobutene. Ehrlich and co-workers[10,11,12], on the other hand, have observed that at very high pressures (hundreds of atmospheres) some systems exhibit negative pressure coefficients. They have in fact determined critical solution pressures for polyethylene in hydrocarbon solvents. However, these are of an entirely different nature than the L.C.S.T.'s under discussion. Since the temperatures required were well above the solvent critical temperatures, their work involved gas-liquid instead of liquid-liquid equilibria.

Virtually all the L.C.S.T. investigations made to date have involved polymers with carbon-carbon or carbon-oxygen chains and hydrocarbon solvents. The lone exception to this is a brief mention by Freeman and Rowlinson[1] of a silicone, erroneously reported as polydimethylsiloxane, exhibiting a L.C.S.T. of -1°C with ethane. It was the intent of the author, therefore, to investigate thoroughly the L.C.S.T. phenomena for a polymer system other than the above mentioned organic types, in hopes that the results of such a study would be of some value to those attempting to interpret these phenomena on a theoretical basis. The polymer system thus chosen was that of polydimethylsiloxane in carefully prepared and well characterized fractions.

THEORY

When two unlike liquids are mixed, many types of behavior can occur, depending on the nature of the pair. The liquids may be completely miscible at all temperatures and concentrations, they may exhibit complete miscibility over only limited temperature and concentration ranges, or they may be incompletely miscible for all temperatures over certain concentration ranges. Those systems exhibiting incomplete miscibility are characterized by having either an upper critical solution temperature (U.C.S.T.), above which the two components are miscible in all proportions, or a lower critical solution temperature (L.C.S.T.), below which the two components are miscible in all proportions, or both. Examples of each of these general situations are illustrated as phase diagrams in Figures 1 through 4.

The stability of a binary liquid system can be characterized through the chemical potential, μ_i, of each component. For a binary system whose components are in equilibrium, it can be shown from first principles of thermodynamics[13] that

$$\frac{\partial \mu 1}{\partial n_2} = \frac{\partial \mu 2}{\partial n_1} < 0, \qquad (3)$$

where n_i is the number of moles of component i. Using the Gibbs-Duhem relation, it can be further shown that

$$\frac{\partial \mu 1}{\partial n_2} = \frac{x_1}{n}\left(\frac{\partial \mu 1}{\partial x_2}\right) \text{ and } \frac{\partial \mu 2}{\partial n_1} = \frac{x_2}{n}\left(\frac{\partial \mu 2}{\partial x_1}\right) \qquad (4)$$

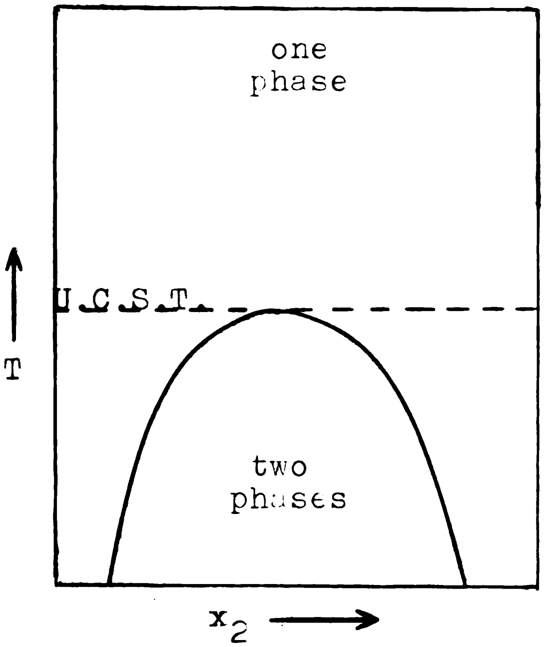


Figure 1. System exhibiting a U.C.S.T.

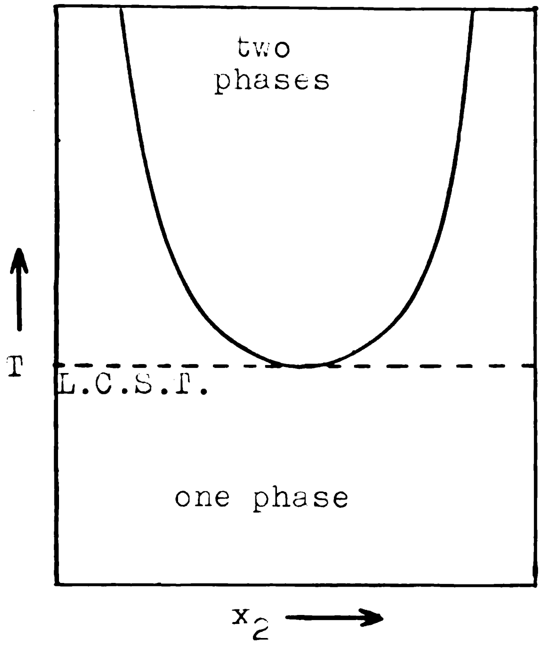


Figure 2. System exhibiting a L.C.S.T.

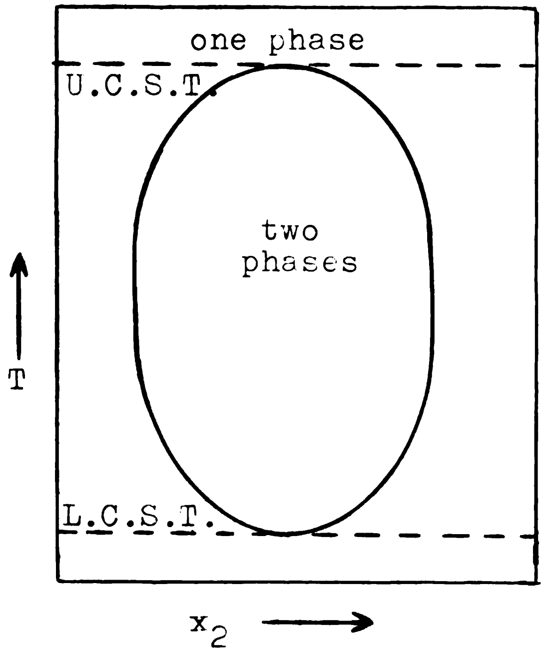


Figure 3. System exhibiting both U.C.S.T. & L.C.S.T; with U.C.S.T.> L.C.S.T.

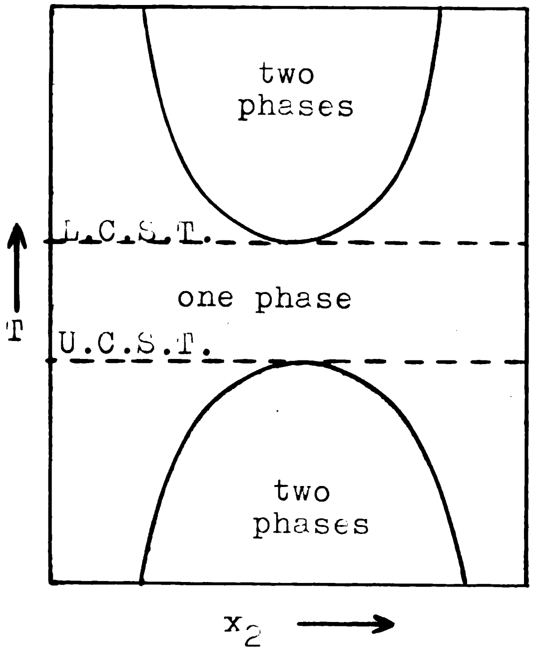


Figure 4. System exhibiting both U.C.S.T. & L.C.S.T: with U.C.S.T.< L.C.S.T.

where x_i = mole fraction of component i, and $n = n_1 + n_2$. Therefore, equation (4) is equivalent to

$$\frac{\partial \mu 1}{\partial x_2} < 0 \quad \text{and} \quad \frac{\partial \mu 2}{\partial x_1} < 0. \tag{5}$$

A graphical representation of this behavior is shown in Figure 5. In curve 1, representing a temperature below the lower critical temperature, T_{CL}, a single phase exists and the conditions of equation (5) are always satisfied. On the other hand, curve 3, which represents a temperature above the critical temperature, consists of three parts: one corresponding to the solvent-rich phase, one for the solute-rich phase, and the horizontal line joining the two representing the simultaneous presence of two phases. At T_{CL} (curve 2), this horizontal portion reduces to a single point of inflection, C, which is mathematically characterized by the condition

$$\frac{\partial \mu 1}{\partial x_2} = \frac{\partial^2 \mu 1}{\partial x_2^2} = 0. \tag{6}$$

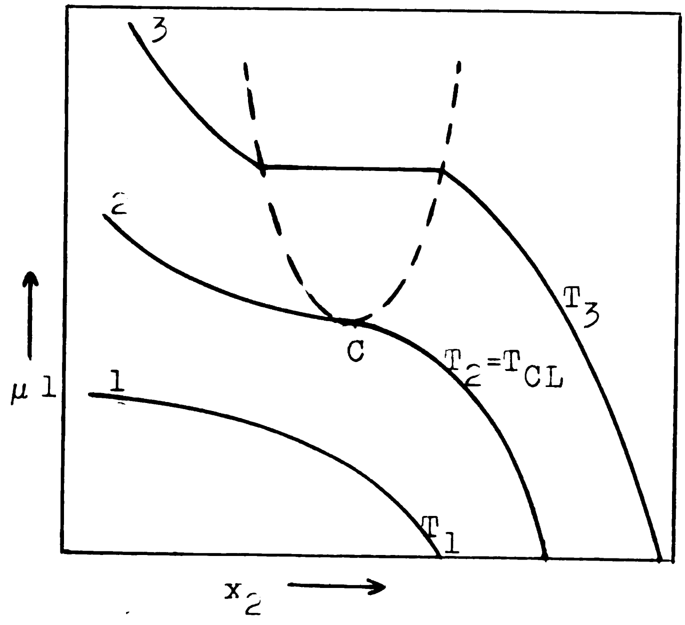


Figure 5.

Variation of chemical potential with composition

The conditions for stability (5) can also be expressed in terms of the molar free energy of the mixture, since it can be shown that

$$\left(\frac{\partial \mu 1}{\partial x_2}\right)_{T,P} = -x_2 \left(\frac{\partial^2 \bar{F}}{\partial x_2^2}\right)_{T,P}. \qquad (7)$$

Therefore, the condition for stability is

$$\frac{\partial^2 \bar{F}}{\partial x_2^2} > 0, \qquad (8)$$

and at the critical point

$$\left(\frac{\partial^2 \bar{F}}{\partial x_2^2}\right)_C = 0. \qquad (9)$$

The shape of the coexistence curve for a two component system, i.e., whether the system exhibits a lower or an upper critical solution temperature, depends upon the mean molar enthalpy of the mixture in the following way:[13a]

At a L.C.S.T., $$\left(\frac{\partial^2 \bar{H}}{\partial x_2^2}\right)_C > 0 \qquad (10)$$

and at a U.C.S.T., $$\left(\frac{\partial^2 \bar{H}}{\partial x_2^2}\right)_C < 0. \qquad (11)$$

These conditions require that the heat of mixing, ΔH_M, is decreasing with temperature for systems near their L.C.S.T., and increasing with temperature for systems near a U.C.S.T.

The above conditions can also be expressed in terms of the molar entropy of the system by considering the relation

$$\bar{F} = \bar{H} - T\bar{S}. \qquad (12)$$

From equation (9) it follows that

$$\left(\frac{\partial^2\bar{H}}{\partial x_2^2}\right)_C = T\left(\frac{\partial^2\bar{S}}{\partial x_2^2}\right)_C. \qquad (13)$$

The curvature of the molar entropy is therefore the same as that for the molar enthalpy, and from equations (10), (11), and (13), we have the additional critical conditions:

$$\left(\frac{\partial^2\bar{S}}{\partial x_2^2}\right)_C > 0 \quad \text{for a L.C.S.T.} \qquad (14)$$

and

$$\left(\frac{\partial^2\bar{S}}{\partial x_2^2}\right)_C < 0 \quad \text{for a U.C.S.T.} \qquad (15)$$

The pressure dependence of solution critical temperatures can be expressed as follows:[13b]

$$\frac{dT_c}{dP} = \left(\frac{\partial^2\bar{V}}{\partial x_2^2}\right)_C \Big/ \left(\frac{\partial^2\bar{S}}{\partial x_2^2}\right)_C. \qquad (16)$$

From equations (14), (15), and (16), we can see that for a L.C.S.T.,

$$\frac{dT_c}{dP} \text{ has the same sign as } \left(\frac{\partial^2\bar{V}}{\partial x_2^2}\right)_C \qquad (17)$$

and for a U.C.S.T.,

$$\frac{dT_c}{dP} \text{ has the opposite sign to } \left(\frac{\partial^2\bar{V}}{\partial x_2^2}\right)_C. \qquad (18)$$

The effect of pressure on the critical temperature is thus determined by the curvature of the mean molar volume, i.e., whether the volume of mixing is positive or negative at the critical point.

Until recently, the solution theory used almost exclusively for high molecular weight polymers has been the conventional Flory-Huggins liquid lattice theory[14]. Although this theory treats the phenomena of U.C.S.T.'s adequately, it does not explain many features of L.C.S.T.'s. The entropy and enthalpy of mixing expressions derived from the liquid lattice model require that the solvent-polymer interactions continually decrease as the temperature increases, and this would be manifested in a corresponding decrease in the value of the free energy parameter, χ . With this restriction imposed, it is not possible to fulfill the critical requirements (10) and (14) for a L.C.S.T. from this model. It has become evident, therefore, that a more rigorous theoretical treatment for polymer solutions is needed.

One quantitative treatment of this problem was proposed by Delmas, Patterson, and Somcynsky[5] who used an approximation of the quasicrystalline lattice or cell model of Prigogine[15]. From considerations of the intersegment potential energies they develop the following expression for the heat of mixing, ΔH_M:

$$\frac{\Delta H_M}{(\text{no. base moles polymer})\ v_1} = A - B(T/r_1)^2 \qquad (19)$$

where r_1 is the number of segments in the solvent molecule, and A and B are constants characteristic of a given solvent-polymer pair, and are defined as:

$$A = zwN = ze^*_{11}\delta^2 N/8 \qquad (20)$$

and $$B = 10.5(k^2/ze^*_{12})N. \qquad (21)$$

Here, z is the lattice coordination number, e^*_{ij} represents the minimum potential energy between segments i and j with subscripts 1 and 2 referring to the solvent and solute respectively, k is the Boltzman constant, N is Avogadro's number, and δ is given by $e^*_{22}/e^*_{11} - 1$. The authors subsequently develop an expression for the Flory free energy of interaction parameter, χ, which is given by

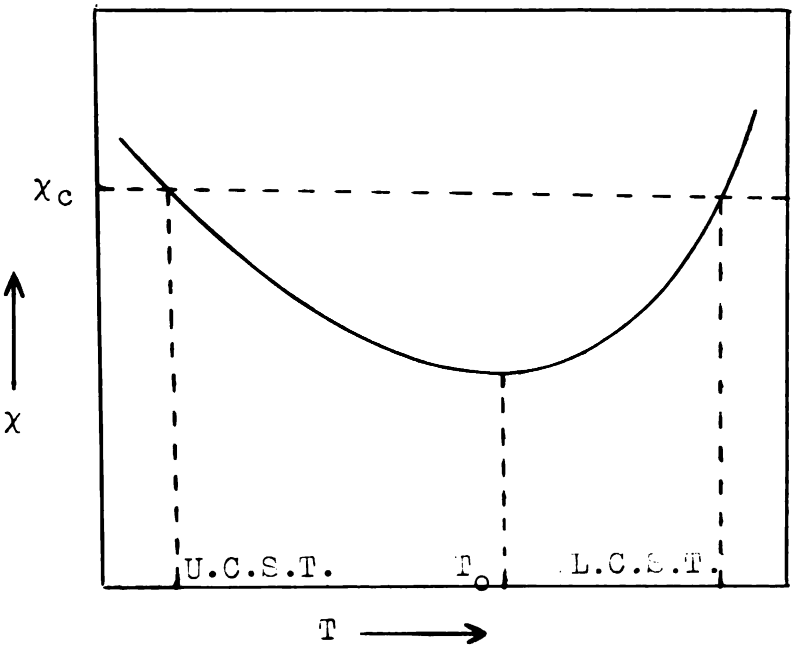
$$R\chi = A(r_1/T) + B(T/r_1). \qquad (22)$$

For a given solvent system, r_1 is constant, and for purely hydrocarbon systems, $r_1 = (n+1)/2$, where n is the number of carbon atoms in the solvent. The above equation is a quadratic in T and two roots are obtained for every value of χ; that is, χ passes through a minimum. The temperature, T_o, at which this minimum in χ occurs is given by

$$T_o^2 = (A/B)r_1^2. \qquad (23)$$

Therefore, either increasing or decreasing the temperature from T_o will result in an increase in χ and hence the solvent quality becomes poorer. At some critical value of χ, the polymer will precipitate from solution, and the roots of T at this point should correspond to the U.C.S.T. and the L.C.S.T. This behavior is illustrated in Figure 6. For a polymer of infinite molecular weight, the critical value, χ_c, is 1/2, and the U.C.S.T. and the L.C.S.T. become θ_U and θ_L respectively. For polymers of finite

Figure 6. Dependence of χ on T.



molecular weight, χ_c is somewhat larger than 1/2, and is given by

$$\chi_c = 1/2 + 1/x^{1/2} + 1/2x. \tag{24}$$

Solving equation (22) for T_c/r_1, we obtain

$$T_c/r_1 = \frac{R\chi_c \pm \left[(R\chi_c)^2 - 4AB\right]^{1/2}}{2B} . \tag{25}$$

Depending on the constants A and B, various particular cases may be distinguished. If A=0 (the liquids differ only in their chain lengths), one of the roots of T (the U.C.S.T.) is zero, and the other (the L.C.S.T.) is given by

$$T_c/r_1 = R/2B, \tag{26}$$

assuming that $\chi_c = 1/2$ (molecular weight of polymer is infinite). If $4AB<(\frac{1}{2}R)^2$, two real roots exist corresponding

to the L.C.S.T. and U.C.S.T. If $4AB>(½R)^2$, there are no real roots and hence no critical temperatures; the polymer and solvent are not soluble in all proportions at any temperature, there being only swelling of the polymer to a maximum value at T_o. The authors compare the results of the above treatment with experimental results obtained by Freeman and Rowlinson[1] with a considerable amount of success, and Tetreault[8] and Ballard[7] found fair agreement with experimental data on hydrocarbons. However the merits of this treatment with its many assumptions have yet to be adequately demonstrated.

Flory, Orwoll, and Vrij[16] have recently developed a configuration partition function for liquids and liquid mixtures of a homologous series. In this treatment they use as a model a linear sequence of segments, each of which has a hard sphere type repulsive potential and an intermolecular energy which depends only on the volume of the segments. This treatment results in a reduced equation of state which is parametric in character. The required parameters can be evaluated from volume, thermal expansion, and compressibility data. The authors derive expressions for the various thermodynamic functions including an expression for the chemical potential, $\mu_1 - \mu_1^o/RT$, as a function of the characteristic parameters of each of the components in a binary system. Application of the conditions for critical miscibility, as given in equation (6), to this expression for chemical potential results finally in the following equation:

$$3x_1c_1(1-T_1^{*}/T_\infty^{*})^2 / (1-4\tilde{v}_1T/T_1^{*})+2x_1\beta_{12}/T\tilde{v}_1 = 1 \qquad (27)$$

where x_1 is the number of segments in the solvent, c_1 and T_1^{*} are characteristic parameters of the solvent, T_∞^{*} is a characteristic temperature of a homolog of infinite chain length, $\tilde{v}_1$ is the reduced volume of the solvent, and β_{12} is a constant derived from the parameters of each of the components. By inspection of equation (27) we find that it has a quadratic form, and therefore gives two roots for T, which are the U.C.S.T. and the L.C.S.T. respectively. Although this treatment gives good to excellent agreement with experimental results for a number of the thermodynamic functions, the calculated and experimentally found values for the L.C.S.T. are in only moderate agreement. So it appears then that further refinement of the above approach will be required before the L.C.S.T. phenomena can be predicted accurately from a strictly theoretical standpoint.

EXPERIMENTAL

Equipment

All the lower critical solution temperature determinations were made using a variable temperature stirred bath containing Dow Corning 550 Fluid. The rate of heating of the bath was controlled by varying the voltage on a blade type heater with a Variac.

The polymer solutions were contained in small sealed ampules made of three mm. bore Pyrex capillary glass tubing. The tubes were suspended in the bath with a small wire basket which held up to four tubes at one time. Accurate temperatures were insured by using mercury thermometers that had been calibrated against a certified National Bureau of Standards thermometer.

Polymer Samples

All of the samples of polydimethylsiloxane used in this study were prepared and carefully fractionated at the research laboratories of Dow Corning Corporation. After preparing the polymer by conventional techniques, a solvent fractionation was carried out by dissolving the polymer in toluene, and then adding acetonitrile, a non-solvent, to cause precipitation of the successive fractions. The solvent was removed from the fractions by stripping at 100°C, 0.1 mm. Hg pressure for eight hours. The molecular weight of each fraction was determined also at Dow Corning Corporation using light-scattering techniques. Five of these fractions were selected for use in this study. The weight-average molecular weights of these five fractions are listed in Table I. Number-average molecular weights were also determined for two of these fractions by intrinsic viscosity measurements using the Barry equation[17]. These are also listed in Table I. The close agreement between the number and weight average molecular weights indicates that the fractions are fairly monodisperse.

TABLE I. Molecular Weight Data for Polydimethylsiloxane Fractions

Fraction	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$
A	24.8	-
B	19.6	-
C	8.01	-
D	4.78	4.25
E	1.17	.866

Solvents

Technical grade normal pentane was twice distilled on a 30" spinning band column, retaining only a center cut in each distillation. The pentane thus purified had a constant boiling point of 36.0°C. Research grade normal propane, and pure grade normal butane and neopentane were purchased from Phillips Petroleum Company. Purities of 99.84 mol.

per cent and 99 mol. per cent are claimed by the supplier for the research grade and the pure grade respectively. Dimethyl ether, having a stated purity of 99.0 mol. per cent, was purchased from the Matheson Company, and the tetramethylsilane was n.m.r. standard grade purchased from the Stauffer Chemical Company. The methyl chloride used in this study was a commercial grade obtained from the Dow Chemical Company. The purity of these solvents was determined or verified by passing a sample of each through an F and M Model 500 gas chromatograph. A two foot column packed with polydimethylsiloxane gum on Chromosorb P was used. Figures 19 through 24 in Appendix VIII show the chromatograms thus obtained, and the purity data are summarized in Table II.

TABLE II. Purity of Solvents

Solvent	Per Cent Purity Calculated from Chromatogram
n-Pentane	99.2
n-Butane	99.0
Propane	99.9
Neopentane	>99.9
Tetramethylsilane	>99.7
Dimethyl Ether	>99.9
Methyl Chloride	>99.9

Preparation of Tubes

The tubes containing pentane solutions were made up in the following manner. Solutions of known concentration of each of the five fractions of polymer were made up in small vials. Successive dilutions of each of these solutions were used to obtain other solutions of known concentrations. Samples of each solution were added to the tubes with a hypodermic syringe. The tubes were then attached one at a time to a vacuum line. After freezing the solutions with liquid nitrogen, the tubes were opened to the vacuum system to remove the permanent gases, and then sealed with a flame.

All of the other tubes contained solutions with either gaseous or very low boiling solvents and were prepared in the following way: Varying amounts of pentane solutions of each of the fractions were added to previously tared tubes with a hypodermic syringe. The pentane was removed by heating the tubes in a vacuum oven at 55°C, after which the tubes were re-weighed to determine the amount of polymer in each. The tubes were then attached one at a time to a vacuum line where they were evacuated, and the solvent distilled into the tubes. After cooling the tubes with liquid nitrogen, they were sealed off with a flame. The tubes were again re-weighed to determine the amount of solvent added to each. The polymer was soluble in all the solvents at room temperature and solution was effected by simply shaking the tubes.

Determination of Critical Solution Temperatures

With the tubes containing the polymer solutions immersed in the bath, the temperature was raised at a rate of about one degree per minute until the polymer just began to precipitate. Knowing the approximate precipitation temperature, the temperature of the bath was lowered a few degrees, and the tubes were shaken again to insure solution homogeniety. The temperature of the bath was then raised very slowly (at a rate of about 0.2 degree per minute) until the precipitation temperature, T_p, of each of the solutions was reached. This temperature was taken as the point where a very sudden increase in solution cloudiness occurred. Shortly before this temperature was reached (a few tenths of a degree below T_p) the solutions developed a very slight haziness which gradually increased until T_p was reached. The endpoint is very sharp and so easily recognized that T_p could be reproduced to within one tenth of a degree. Immediately or very shortly after T_p was reached, the heavier phase began to settle out. This phase separation occurs quite rapidly because of the low density of the solvent at these temperatures.

Measurement of Specific Volume of Solvent at Temperatures Corresponding to the L.C.S.T.

Samples of each of the pure solvents were introduced into tared 3 mm. I. D. glass capillary tubes similar to those used above. The tubes were then cooled with liquid nitrogen, evacuated, sealed off, and re-weighed to determine the weight of solvent in each. These tubes had been previously calibrated for volume by introducing weighed increments of mercury into the tubes, and noting the change in liquid column height with a cathetometer. Using the density of mercury at ambient temperature, the volume as a function of liquid column height was determined. The tubes containing the pure solvents were immersed one at a time in the bath, which was then brought to the desired temperature. Using a cathetometer, the liquid column height was measured, the corresponding volume determined from the calibration graph, and the specific volume computed from the weight of solvent in the tube. These tubes had been filled fairly full so the error due to solvent in the gas phase was minimized.

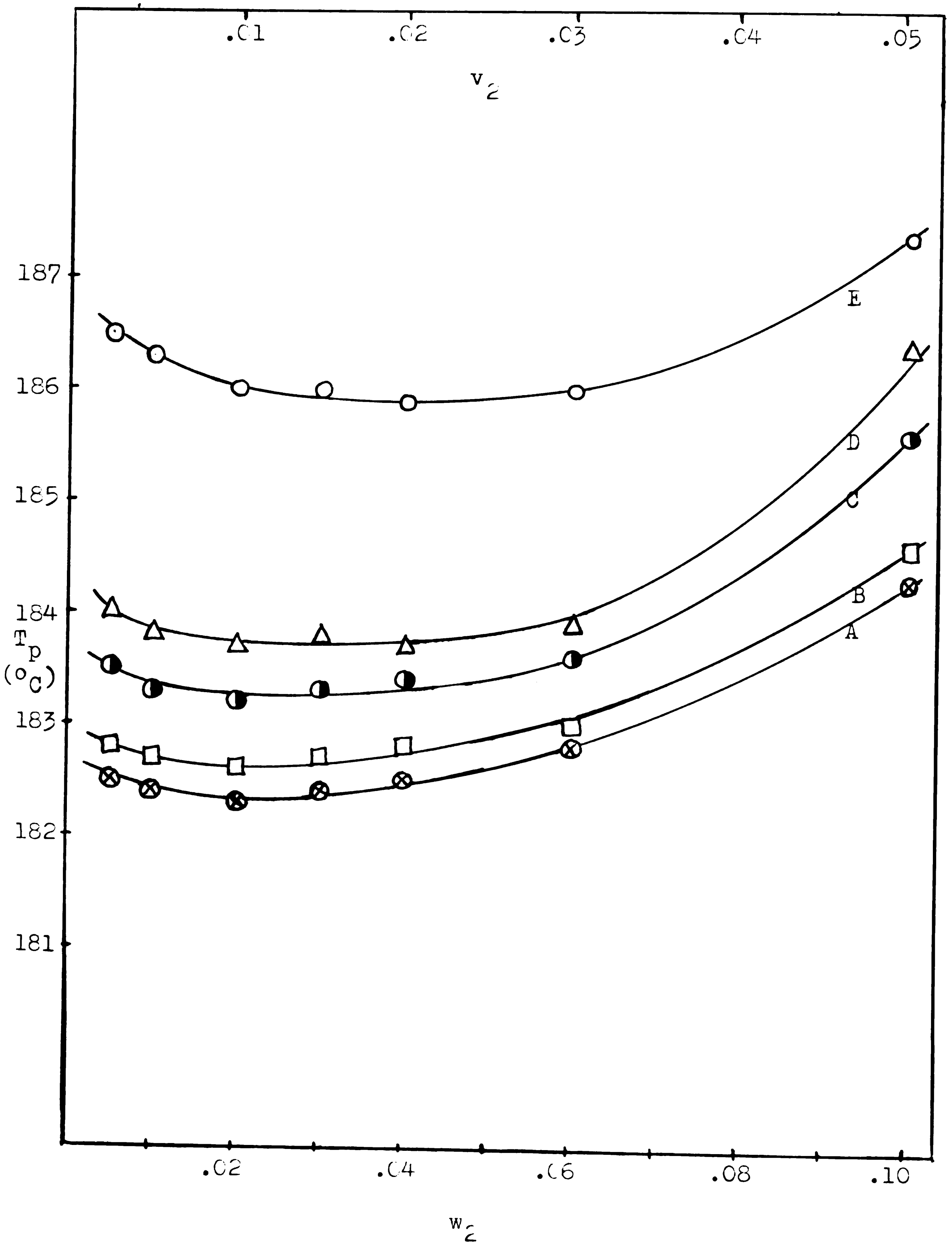
RESULTS AND DISCUSSION

Phase Diagrams

Lower critical solution temperatures for solutions of five fractions of polydimethylsiloxane (PDMS) in various solvents were determined. The precipitation temperatures, T_p, were determined as a function of concentration for each polymer fraction. The L.C.S.T.'s were taken as the minima in the resulting phase diagrams, plotting T_p against the concentration in weight fraction. These phase diagrams are shown in Figures 7 through 12. Because of higher than normal pressures, which resulted in rupture of nearly all of the tubes containing the methyl chloride solutions, insufficient data was obtained to construct phase diagrams for this system.

Volume fraction is also shown on the phase diagrams across the upper abscissa, since it is the conventional concentration unit in the treatment of U.C.S.T. data. Volume fractions were calculated from the specific volumes of the solvent and of the polymer at the temperatures corresponding to the approximate L.C.S.T. with the assumption that the excess volume of mixing is negligible. The specific volumes of the solvents were determined experimentally and the specific volume of the polymer was calculated from data in the literature[18]. The values obtained for these specific volumes are listed in Table III. The molar volumes of the solvents are also included since they will be used to calculate the size function, x, of the polymer fractions (see equation 2).

Figure 7. Phase diagrams for PDMS fractions in n-pentane



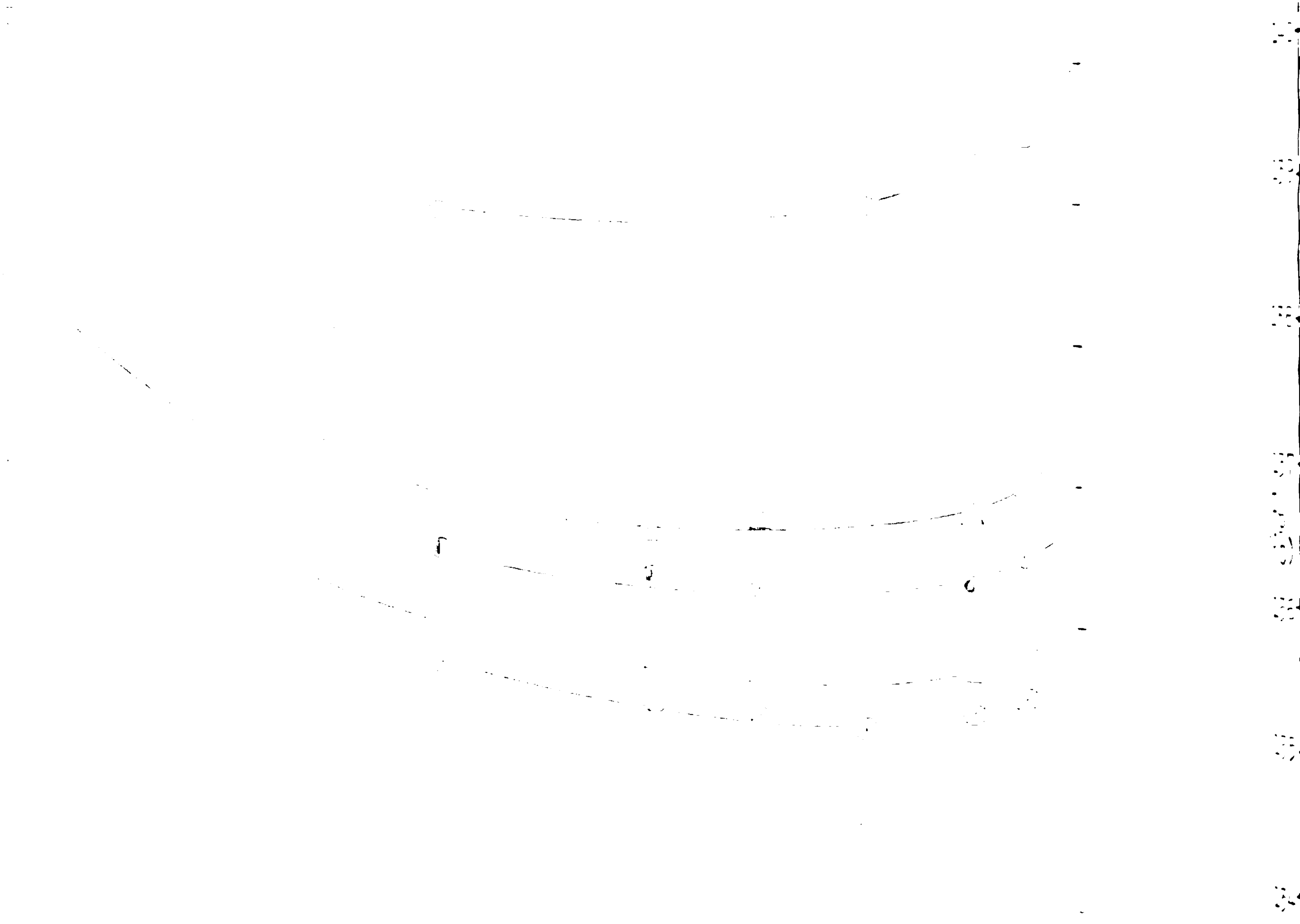


Figure 8. Phase diagrams for PDMS fractions in n-butane

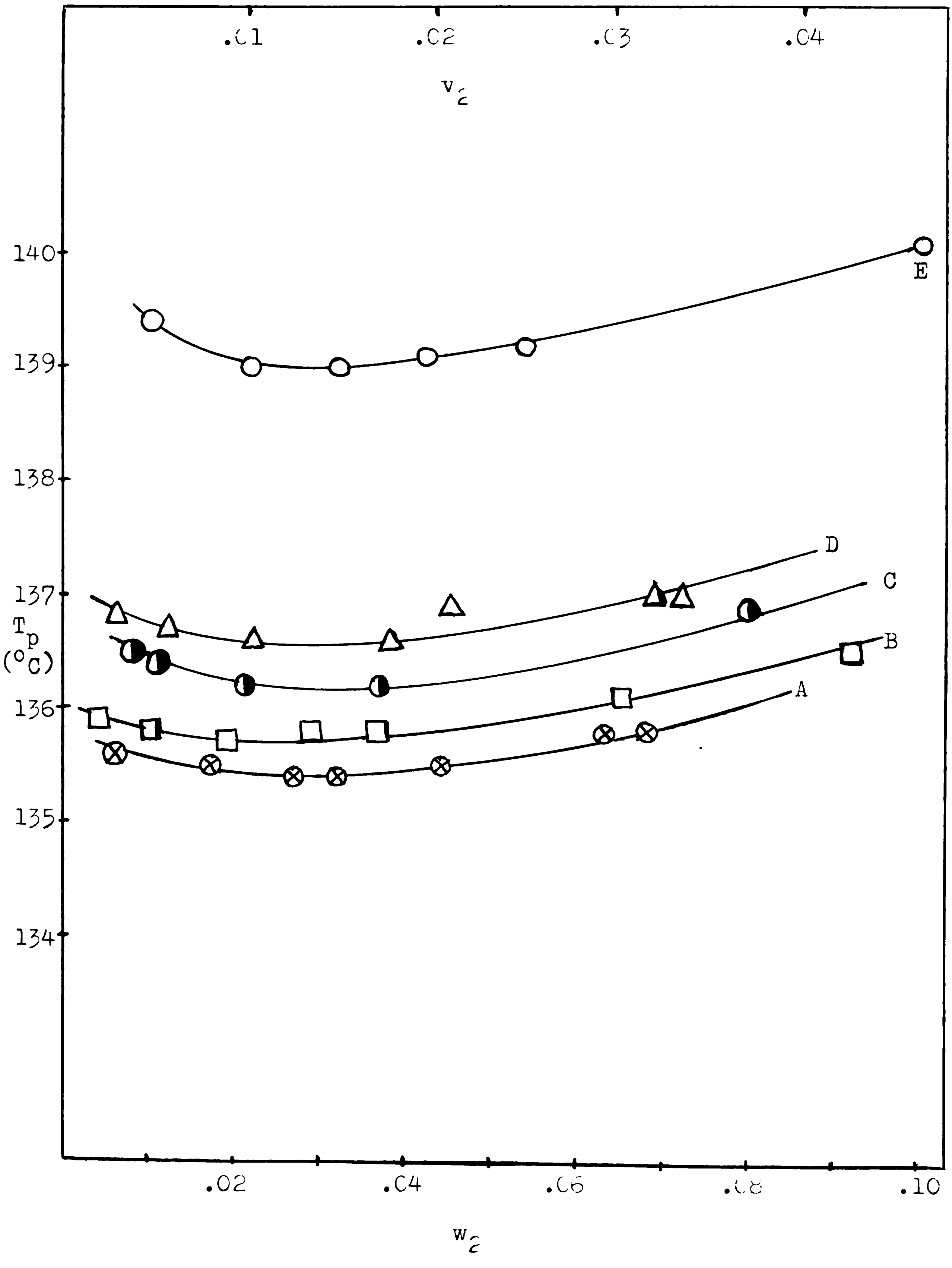


Figure 9. Phase diagrams for PDMS fractions in propane

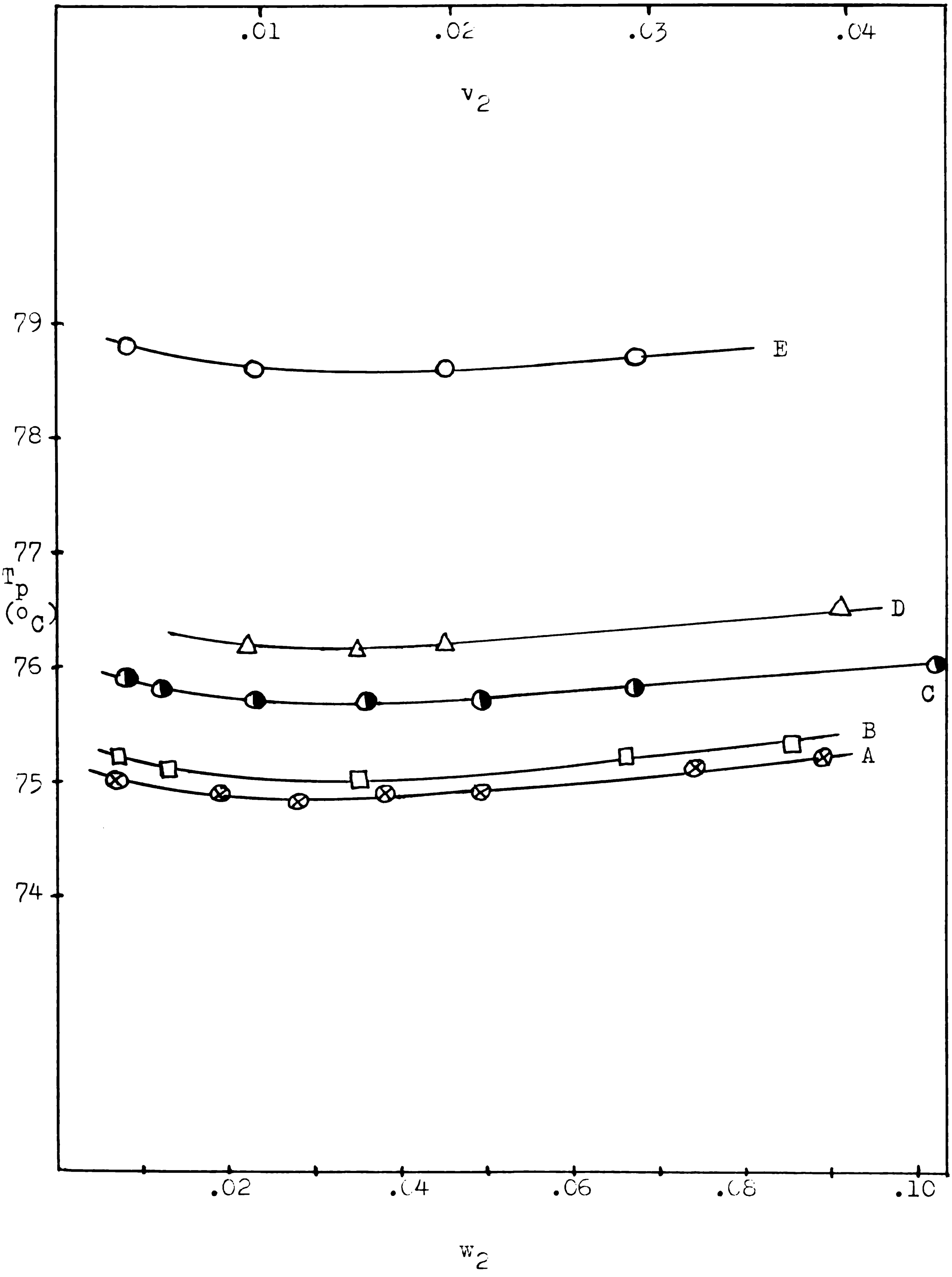


Figure 10. Phase diagrams for PDMS fractions in neopentane

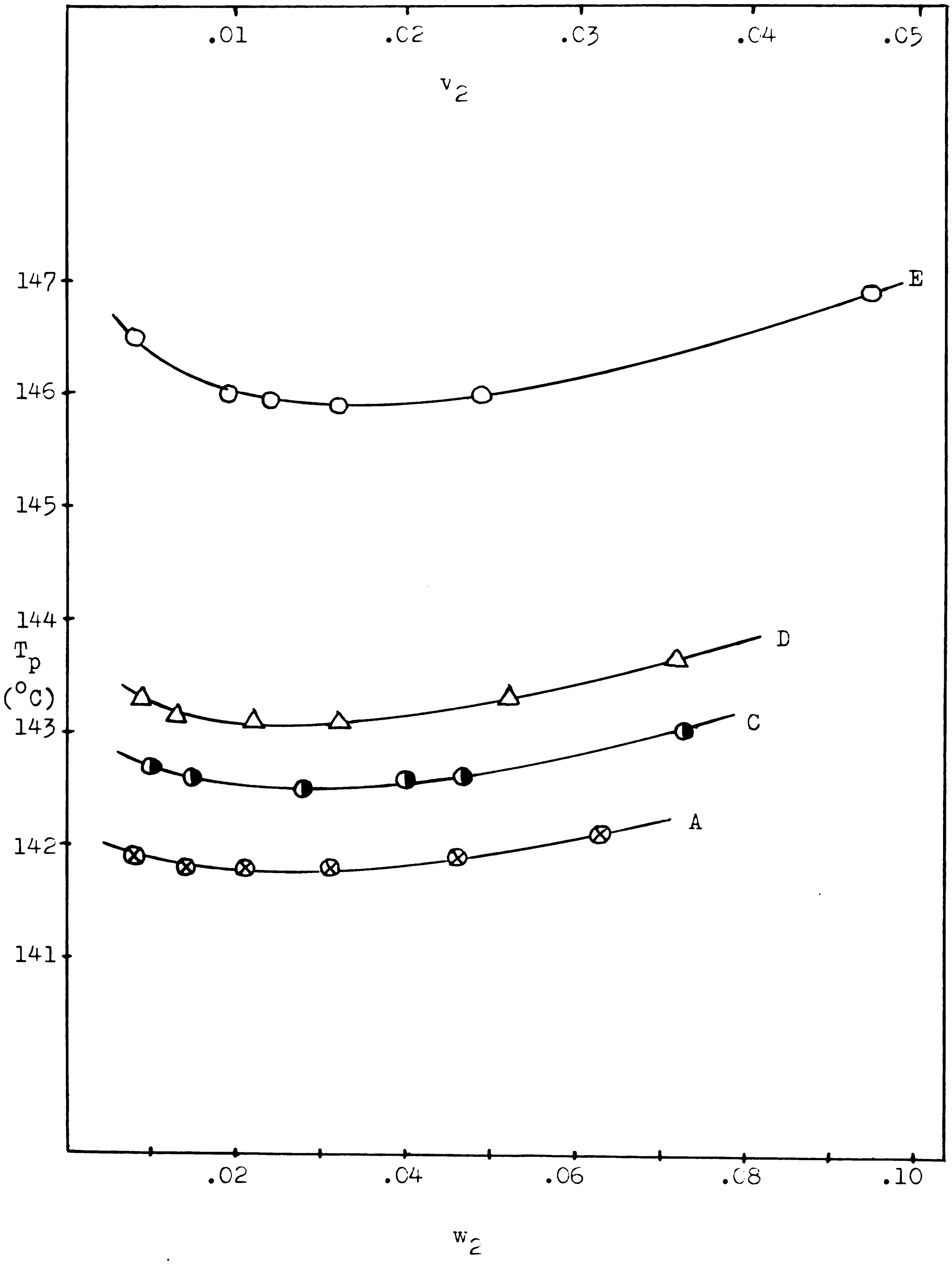


Figure 11. Phase diagrams for PDMS fractions in tetramethylsilane

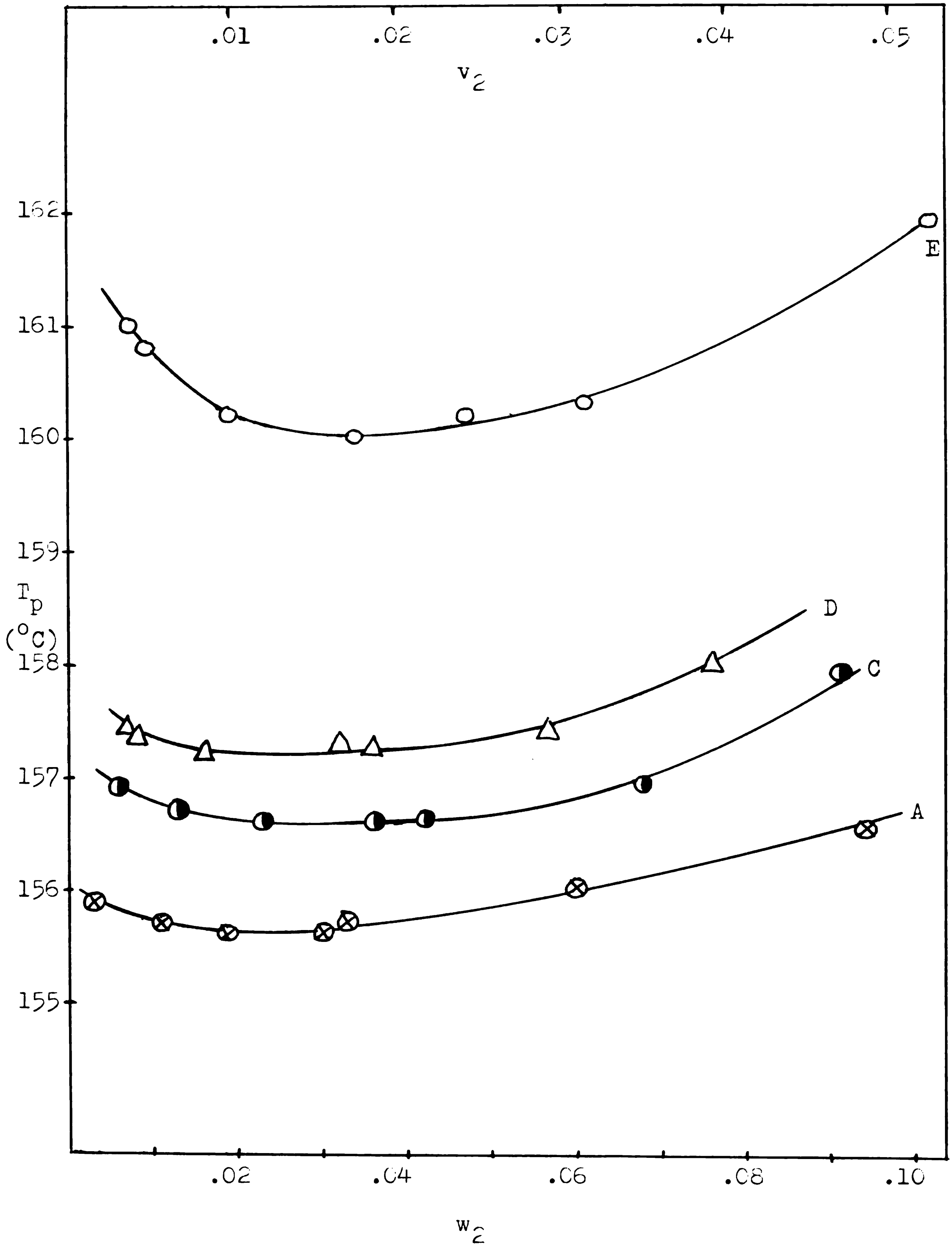
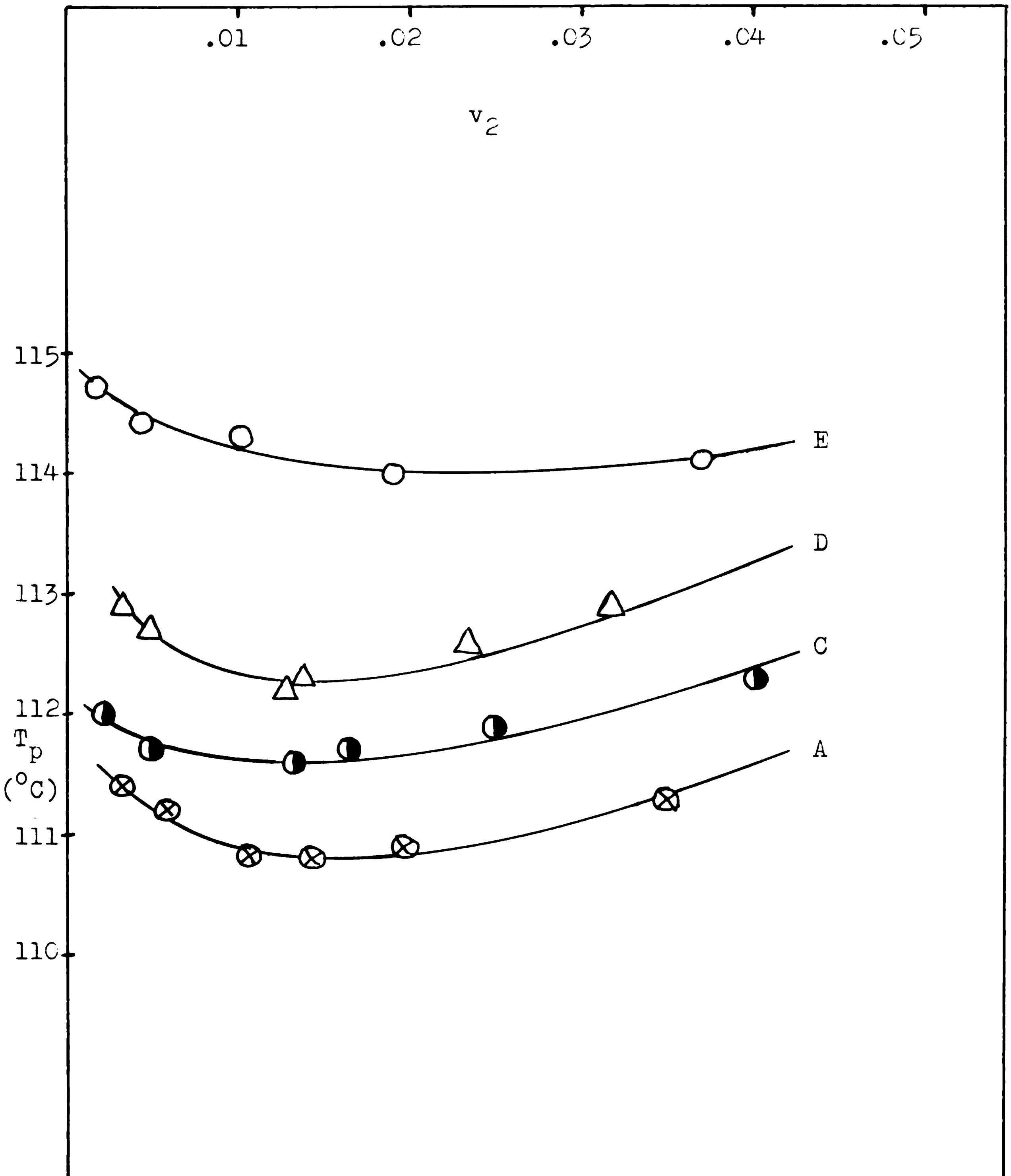


Figure 12. Phase diagrams for PDMS fractions in dimethyl ether



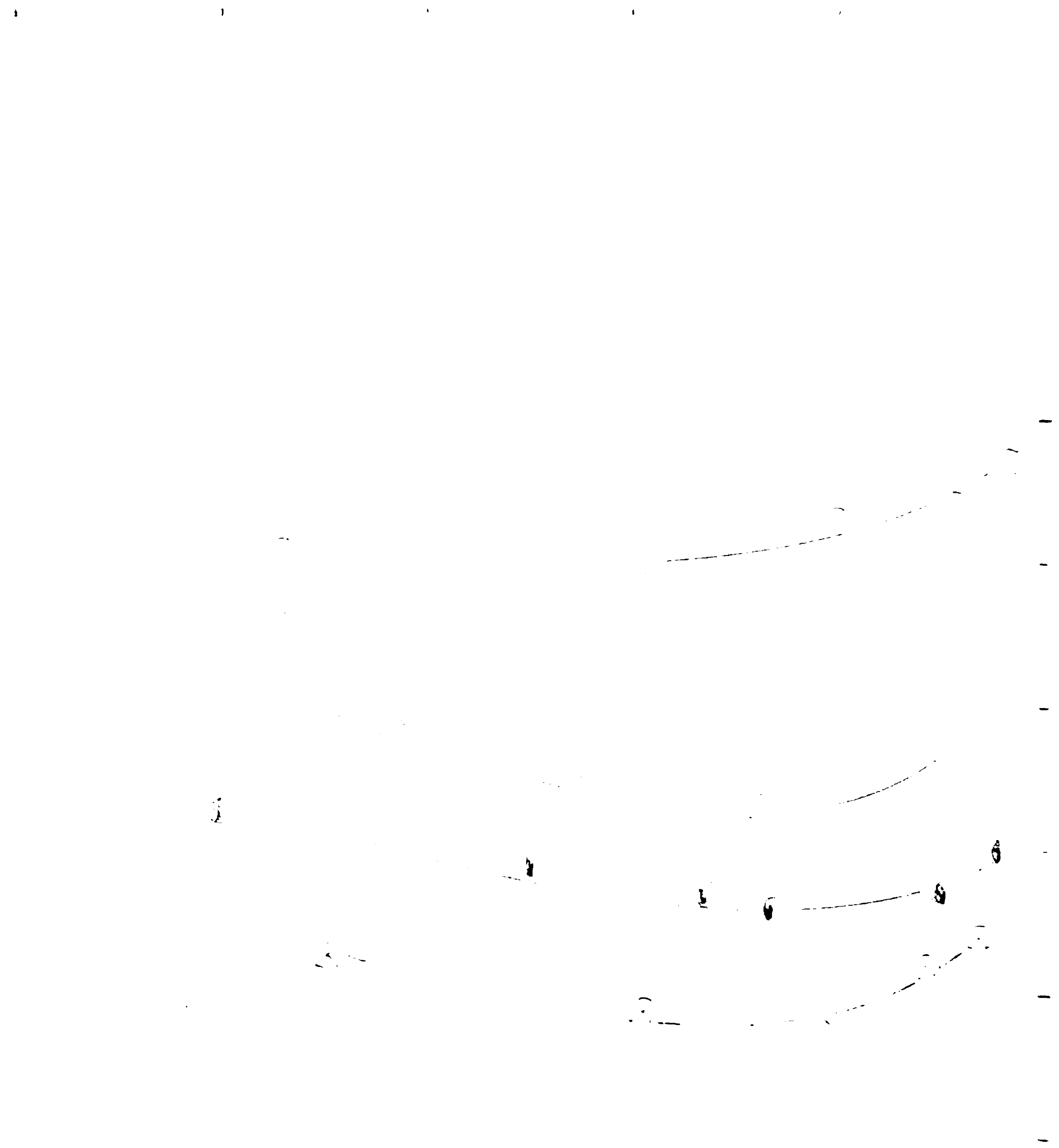


TABLE III. Specific Volume for Solvents and Polydimethylsiloxane

Temp.* (°C)	Solvent	Sp. Vol. Solvent (cc./g.)	Molar Vol. Solvent (cc./mol.)	Sp. Vol.** PDMS (cc./g.)
73.9	Propane	2.48	109.1	1.076
110.1	Dimethyl Ether	2.13	98.0	1.116
129.3	Methyl Chloride	1.58	79.8	1.140
134.6	Butane	2.50	146.2	1.146
140.7	Neopentane	2.33	167.8	1.154
154.6	Tetramethylsilane	2.29	201.5	1.171
181.6	Pentane	2.42	174.2	1.207

*These temperatures correspond to the θ_L temperature of the polymer solutions in the respective solvents (see page 37).

**These are specific volumes of PDMS at $T = \theta_L$.

In most respects the phase diagrams are quite similar in character to those found for hydrocarbon polymer systems by previous authors.[4,6,7,9] The general shape is the same, the L.C.S.T.'s occur in roughly the same concentration range, and the increase of L.C.S.T. with decreasing molecular weight is a similar characteristic. There does appear to be, however, a dependence of the critical volume fraction on molecular weight. Although this dependence ranges from very slight in some solvents (propane, butane) to fairly pronounced in others (pentane, tetramethylsilane), it is nevertheless present in all cases. This type of behavior would be anticipated if the L.C.S.T. assumed the same character as the familiar U.C.S.T., in which case the critical volume fraction is given by $v_{2c} = 1/x^{1/2}$[14a]. This behavior is notably absent from previously reported L.C.S.T. data, however.

In Table IV are listed the L.C.S.T.'s, and the molecular weights for each of the polymer fractions in the various solvents.

TABLE IV. L.C.S.T. and Molecular Weight Data for Polydimethylsiloxane Fractions in Various Solvents.

Solvent	Polymer Fraction	Mol. Wt. ($\times 10^{-6}$)	L.C.S.T. (°K)
n-Pentane	A	2.48	455.5
"	B	1.96	455.8
"	C	.801	456.4
"	D	.478	456.9
"	E	.117	459.1
n-Butane	A	2.48	408.6
"	B	1.96	408.9
"	C	.801	409.4
"	D	.478	409.8
"	E	.117	412.2

TABLE IV. Continued

Solvent	Polymer Fraction	Mol. wt.(X10^{-6})	L.C.S.T.(^{o}K)
Propane	A	2.48	348.0
"	B	1.96	348.2
"	C	.801	348.9
"	D	.478	349.4
"	E	.117	351.8
Neopentane	A	2.48	414.9
"	C	.801	415.7
"	D	.478	416.3
"	E	.117	419.1
Tetramethylsilane	A	2.48	428.8
"	C	.801	429.8
"	D	.478	430.4
"	E	.117	433.2
Dimethyl Ether	A	2.48	384.0
"	C	.801	384.8
"	D	.478	385.3
"	E	.117	387.2
Methyl Chloride	A	2.48	403.4
"	E	.117	407.7

As is the case with organic polymers, the L.C.S.T. phase diagrams for polydimethylsiloxane are quite broad; much broader than the corresponding U.C.S.T. phase diagrams. The exact significance of this is not known; however, this broadness suggests that the solubility parameter χ is much less concentration dependent in the L.C.S.T. region than in the lower temperature U.C.S.T. region.

Molecular Weight Dependence of L.C.S.T.

The molecular weight dependence of the familiar U.C.S.T. (for sufficiently large molecular weights) is expressed in the Flory-Huggins treatment as follows[14b]:

$$\frac{1}{T_c} = \frac{1}{\theta}\left[1 + (1/\psi_1)(1/x^{1/2})\right] \qquad (14)$$

where ψ_1 is the entropy of dilution parameter, and x is the polymer size function previously defined (equation 2). If the assumption is made that the L.C.S.T.'s exhibit a molecular weight dependence of this same character, then a plot of $1/T_{CL}$ vs. $1/x^{1/2}$ should give a straight line. Plots of this type were made for each of the solvents used, and are shown in Figures 13 through 15. It is to be noted that all of these plots are, indeed, remarkably linear. Previous authors[6,7,8] also have found such linear relationships with other polymer-solvent systems. So it appears from these findings that, at least within the range of experimental results reported, the L.C.S.T. and the U.C.S.T. data can be similarly treated in this one respect.

Therefore, as is done in the case of U.C.S.T. data,

Figure 13. Plot of $1/T_{CL}$ vs. $1/x^{1/2}$ for PDMS in n-pentane and n-butane

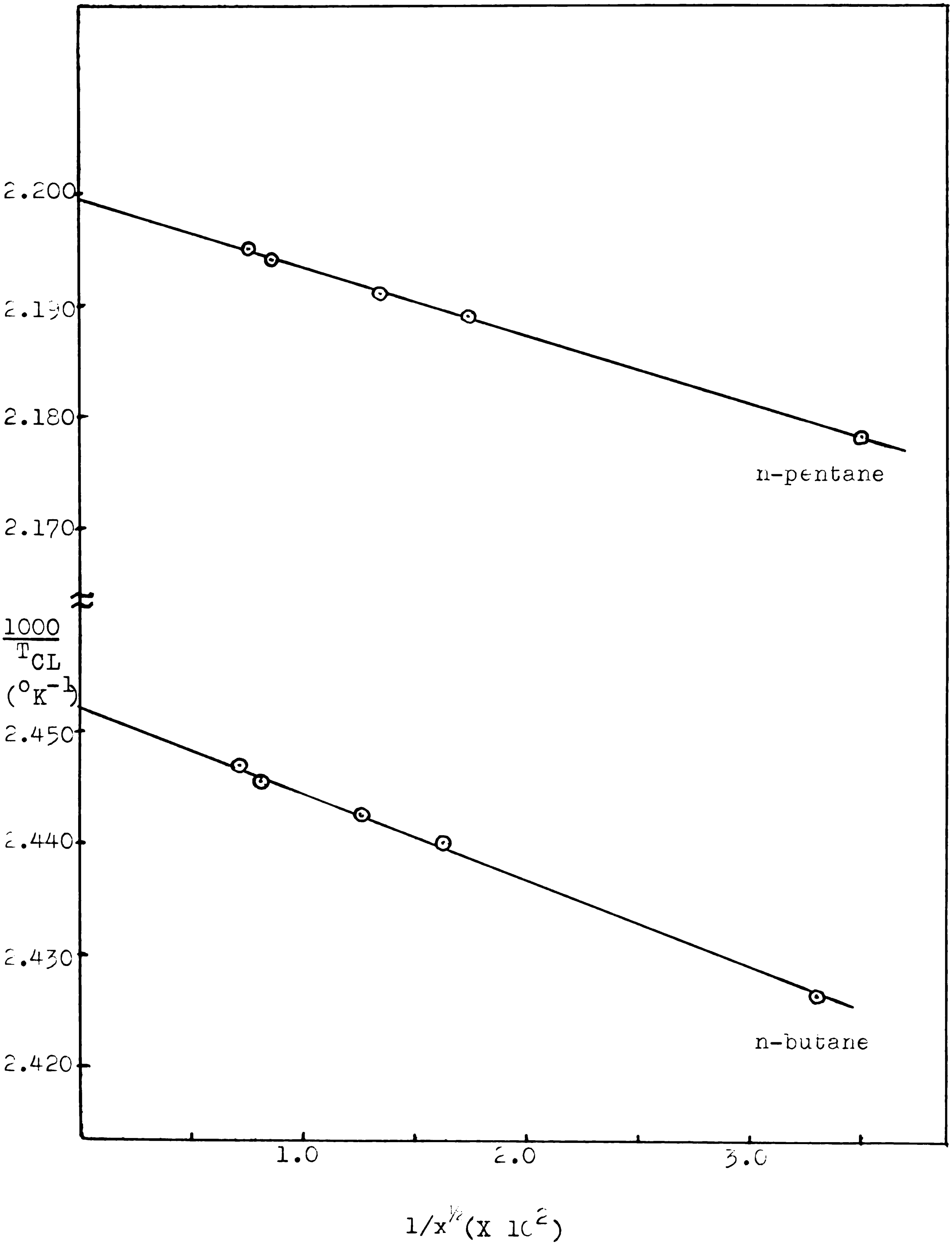


Figure 14. Plot of $1/T_{CL}$ vs. $1/x^{1/2}$ for PDMS in propane and neopentane

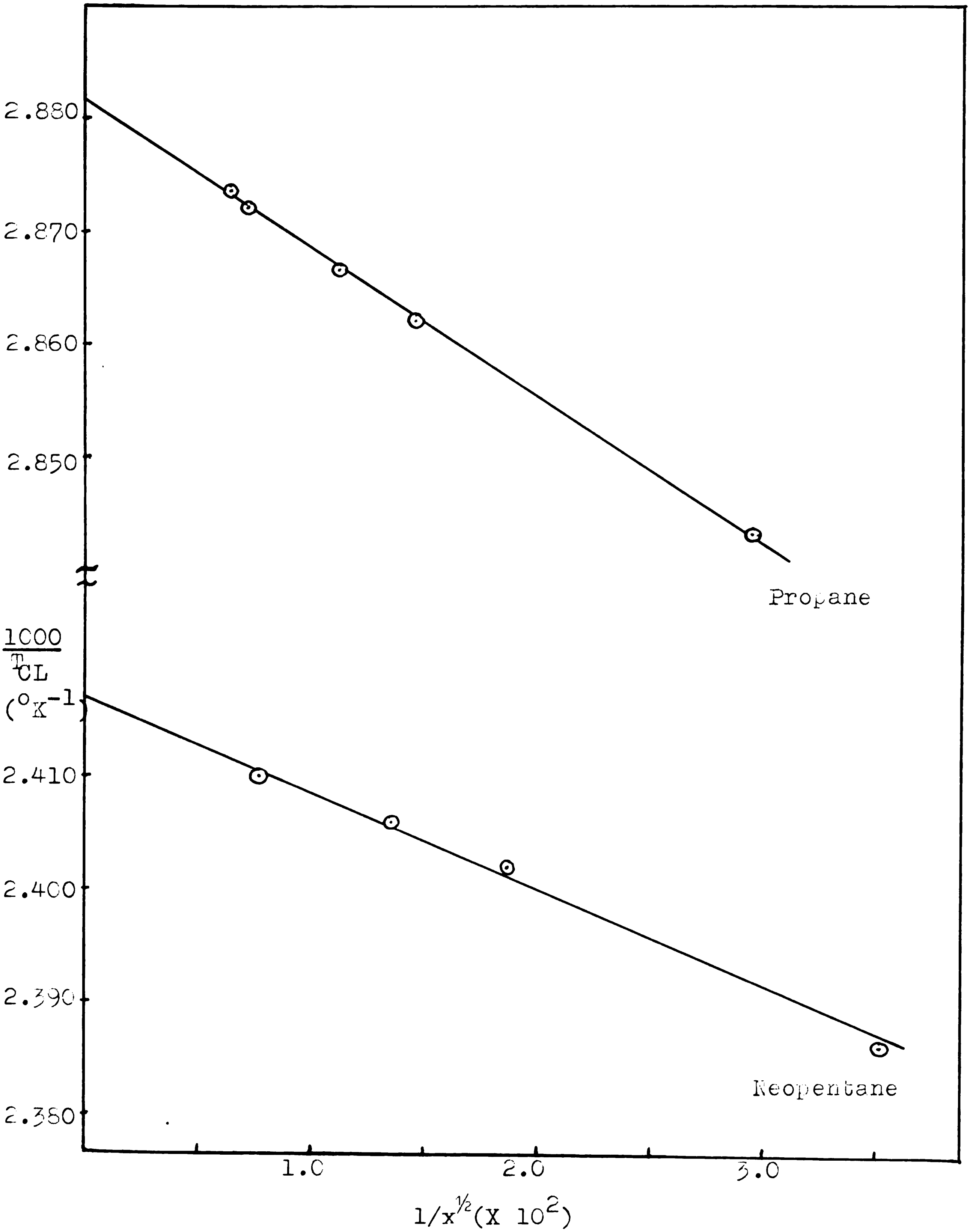
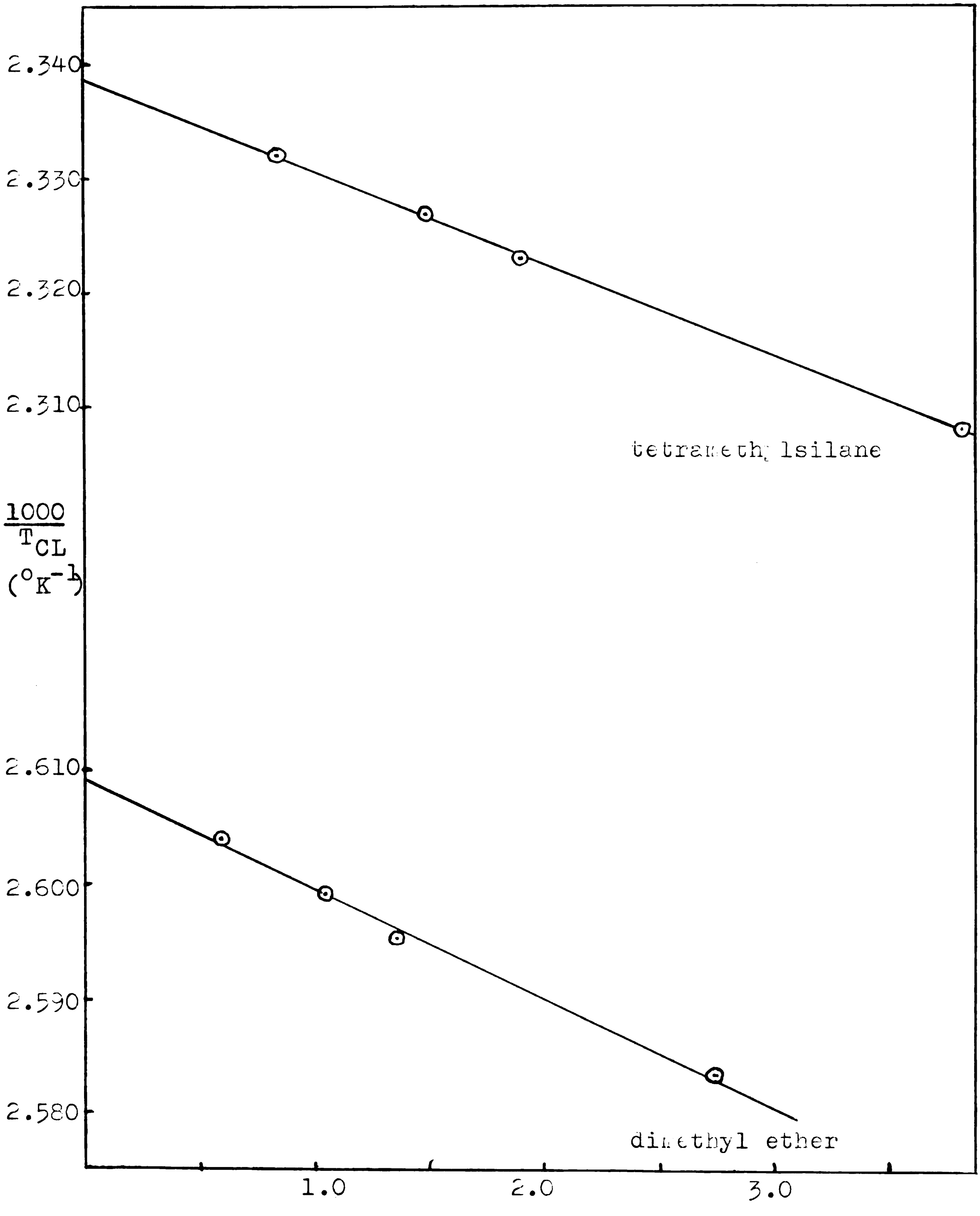


Figure 15. Plot of $1/T_{CL}$ vs. $1/x^{1/2}$ for PDMS in tetramethylsilane and dimethyl ether



the above graphs were used to calculate the entropy of dilution parameter, ψ_1, and the critical miscibility temperature for polymer of infinite molecular weight, θ_L. These values are easily obtained from the slope and intercept of the graphs. The values of ψ_1 and θ_L thus computed are listed in Table V.

TABLE V. Entropy of Dilution Parameter and θ_L Data for PDMS in Various Solvents

Solvent	Slope	Intercept $(^{\circ}K^{-1} \times 1000)$	ψ_1	θ_L $(^{\circ}K)$
Pentane	-.000617	2.1994	-3.56	454.7
Butane	-.000778	2.4520	-3.15	407.8
Propane	-.001323	2.8814	-2.18	347.1
Neopentane	-.000851	2.4170	-2.84	413.7
Tetramethylsilane	-.000798	2.3385	-2.93	427.6
Dimethyl Ether	-.000973	2.6090	-2.68	383.3
Methyl Chloride	(-.00134)	(2.4860)	(-1.86)	(402.3)

Values in parentheses only approximate.

There are a number of things to be noted about the calculated values of the entropy of dilution parameter: They are all negative in sign which requires that the excess entropies of mixing for these solutions at their lower critical temperature are also negative. Baker and coworkers[4] have shown this to be true in the system polyisobutene-n-pentane. Although the calculated values of ψ_1 are relatively constant with changing solvent, there is a definite trend for the absolute value of ψ_1 to increase as the solvent size increases. Finally, they are all of relatively large magnitude which indicates that excess entropy contributions are quite important in determining solution properties near its L.C.S.T.

In the treatment of upper critical solution temperature data, the determination of the Flory temperature, θ_U, is of significance since it represents a temperature where there are no net thermodynamic interactions in solutions of polymers of infinite molecular weight. It has been suggested similarly[6,8] that the temperature θ_L determined from L.C.S.T. data also represents a temperature where thermodynamic departures from ideality vanish. It is pointed out, however, that in the latter case, the balance of thermodynamic forces assumes a different character; namely, that favorable solvent-polymer interactions just balance the solvent-solvent interactions which cause the solvent to expand as it nears its critical temperature.

In considering the treatment of L.C.S.T.'s given by Delmas, Patterson, and Somcynsky[5], which results in equation (25), if either $A = 0$, or the product $4AB \ll (R\chi_c)^2$, then the equation can be re-written as

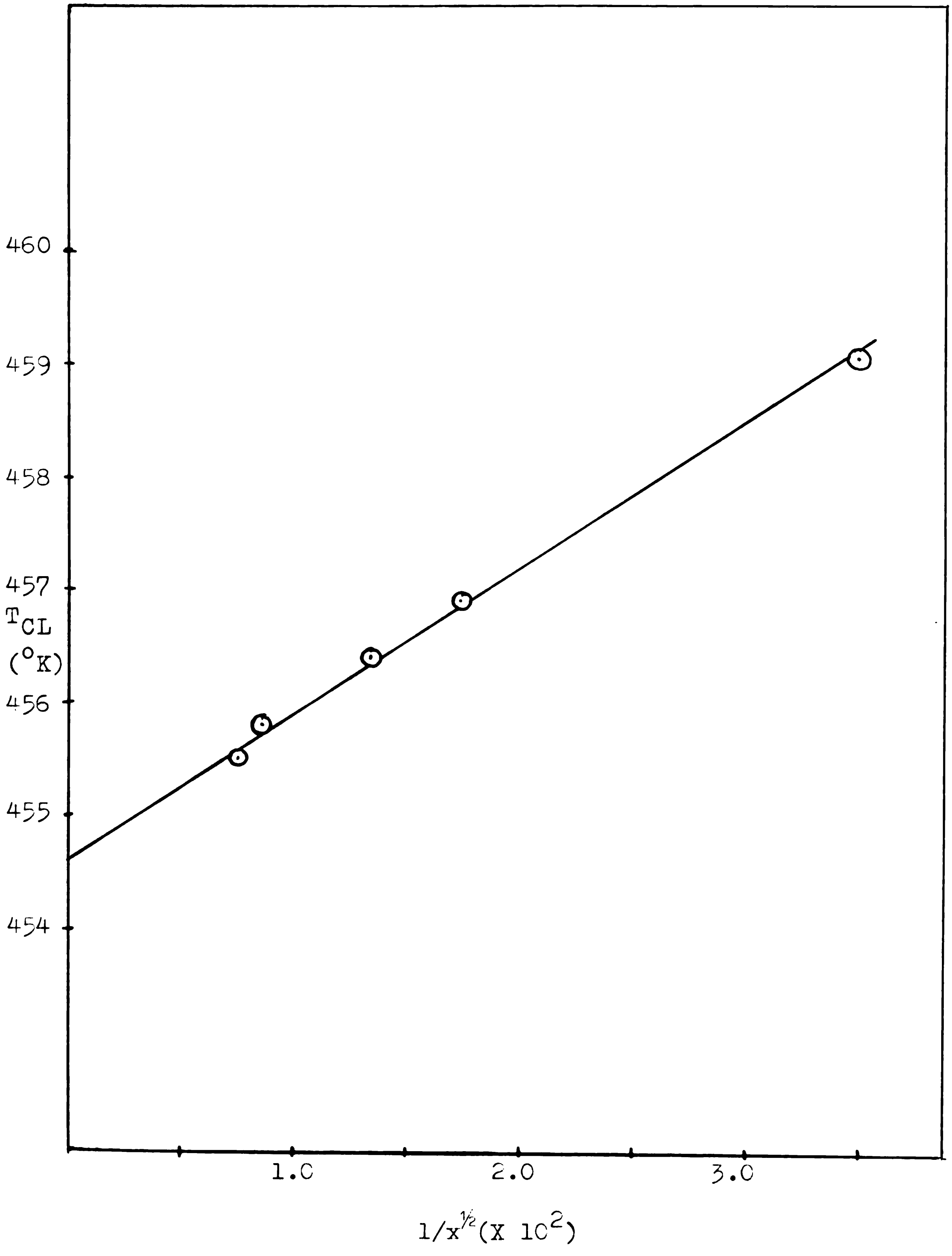
$$T_{CL} = r_1 R \chi_c / B. \qquad (28)$$

Since from equation (24) it is seen that χ_c is proportional to $1/x^{1/2}$, the above equation indicates that a plot of T_c vs. $1/x^{1/2}$ should give a straight line (still assuming either of the above mentioned conditions). One plot of this type, for the pentane-PDMS system, is shown in Figure 16, and it can be seen that the data does indeed give a straight line. The data from the other solvent systems give similar linear relationships.

In the above treatment, the first condition (that A = C) seems hardly justifiable in the present case since it has been shown[5] that this condition is true when the polymer and solvent differ only in chain length. Polydimethylsiloxane in a hydrocarbon type solvent obviously does not fall into this category. This means that if the Delmas-Patterson-Somcynsky treatment is valid for this system, then the second condition, $4AB \ll (R\chi_c)^2$, must hold, at least within the range of the experimental results. Unfortunately, the independent evaluation of the constants A and B is not possible at the present time, due to lack of sufficient thermodynamic data on the PDMS system. Likewise, the value of r_1 is also unknown for the PDMS system.

From the experimental results obtained then, no distinction can be made between the theory of Delmas, Patterson and Somcynsky and treatment which is analogous to the Flory-Huggins theory. The probable reason for this is that the range of experimental data is not sufficiently broad to allow this distinction. If the L.C.S.T.'s were studied over a much broader polymer molecular weight range,

Figure 16. T_{CL} vs. $1/x^{1/2}$ for PDMS in pentane



and therefore a broader temperature range; perhaps some distinction could be made.

It is not possible to attempt any correlations of the experimental results obtained with Flory's most recent theoretical treatment of this problem[16] in which he derives equation (27) from a configuration partition function, because the data required to calculate the necessary parameters for the PDMS were not experimentally obtained and are not in the literature.

Solvent Dependence of L.C.S.T.

A variety of solvents were used in this investigation in order to study the effect of changes in solvent character on the position of the L.C.S.T. The choice of solvents was limited, however, by two factors: The polymer had to be completely miscible in the solvent at some temperature, and also, to avoid thermal rearrangement of siloxane bonds in the polymer, solvents in which the lower critical temperatures were not over ca. 200°C had to be chosen.

For the PDMS system, it is observed that in any given solvent, the θ_L temperature is considerably higher than those found for pure organic polymers[1,4,7,8,9] This is interpreted to be mainly a reflection of the relative magnitudes of the heats of mixing for PDMS and organic polymers in these solvents at room temperature. Newling[19], for example, has found large values of ΔH_M for PDMS compared to those of most organic polymers, and this would account for the greater miscibility (higher θ_L) observed in the PDMS system.

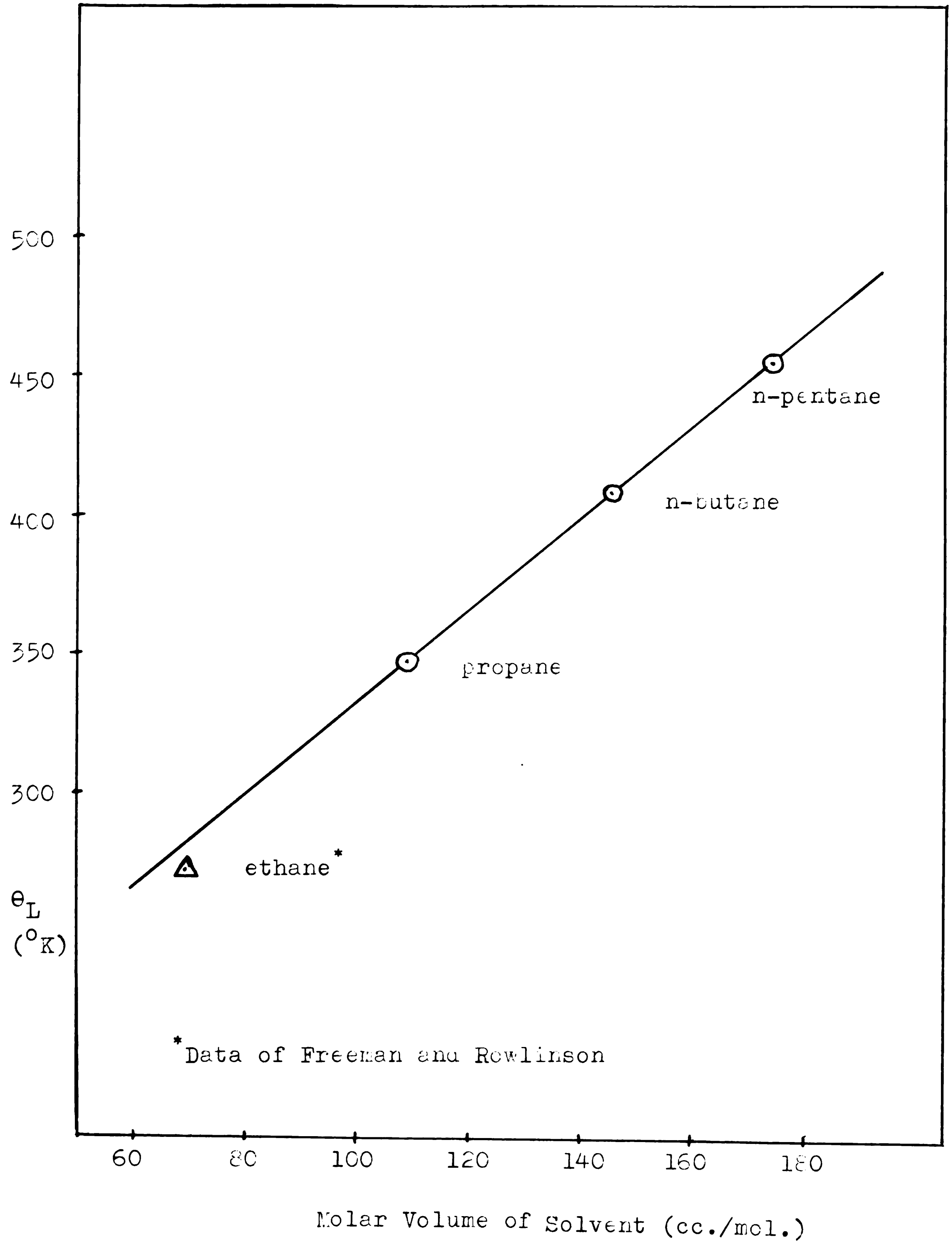
As Allen and Baker[9] have pointed out, the position of a L.C.S.T. depends both on the chemical nature of the two components, and on the relative molecular sizes of the solvent and solute. If we examine, therefore, solvents of a similar chemical nature, such as the homogolous series of n-alkanes, then the dependence of the L.C.S.T. should be strictly one of molecular size. In Figure 17, the θ_L temperatures of PDMS in propane, n-butane, and n-pentane are plotted against the molar volumes of the solvents at the corresponding θ_L temperatures. It is found that the dependence is indeed linear. It is of interest to note that the L.C.S.T. of -1°C reported by Freeman and Rowlinson[1] for a silicone polymer in ethane also falls nearly on this line. Their polymer, however, was not a true PDMS but a dimethyl-phenylmethyl siloxane copolymer.

If, on the other hand, we examine solvents of the same molecular size, the L.C.S.T.'s should be in some way dependent on the chemical nature of the solvent. This can be illustrated by examining the solvents propane, dimethyl ether, and methyl chloride, which are roughly comparable in size (see Table III). If the chemical nature of these solvents is expressed in terms of their dipole moments, they fall in the order

$$\text{propane} < \text{dimethyl ether} < \text{methyl chloride.}$$

It is noted that the θ_L temperatures also fall in this same order.

Figure 17. θ_L temperatures as a function of solvent size



The effects of both the molecular size of a solvent and its chemical nature, as reflected in the magnitude of the intermolecular forces, are manifested in the gas-liquid critical temperature of the solvent. An attempt was therefore made, to correlate the θ_L temperatures with the solvent critical temperatures, T_c. Table VI shows both the ratio θ_L/T_c and $T_c-\theta_L$. It can be noted that all the θ_L temperatures are quite near the corresponding gas-liquid critical temperatures, and that the ratio θ_L/T_c is relatively constant. On the other hand, one can still note trends in the values of $T_c-\theta_L$; i.e., in the n-alkanes the observed order is n-pentane $<$ n-butane $<$ propane, and similarly for the solvents of comparable size, the trend in $T_c-\theta_L$ is methyl chloride $<$ dimethyl ether $<$ propane.

TABLE VI. Correlation of θ_L Data with Solvent T_c.

Solvent	$T_c(^oK)$	$\theta_L(^oK)$	$\frac{\theta_L}{T_c}$	$T_c-\theta_L(^oK)$
Pentane	470.4	454.7	.967	15.7
Butane	426.2	407.8	.957	18.4
Propane	368.8	347.1	.941	21.7
Neopentane	433.8	413.7	.954	20.1
Tetramethylsilane	458.2	427.6	.933	30.6
Methyl Ether	400.3	383.3	.958	17.0
Methyl Chloride	416.3	(402.3)	(.966)	(14.0)

Values in Parentheses only approximate.

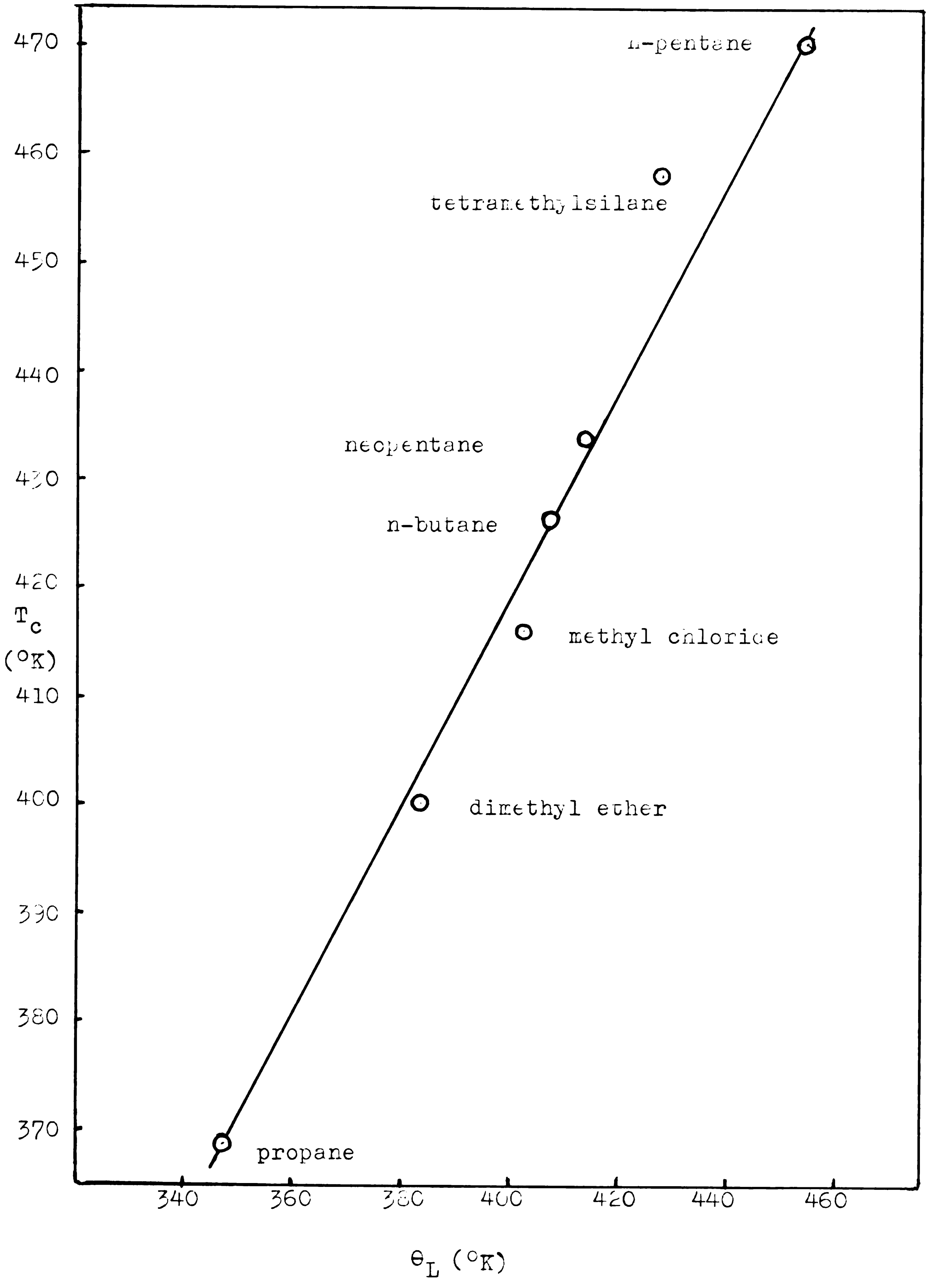
In Figure 18, θ_L is plotted against T_c for each of the solvents. A reasonable relationship is observed, with the pure hydrocarbon solvents falling on a straight line. Similar relationships were found by Tetreault[8] for hydrocarbon polymer systems. Even the more polar solvents dimethyl ether and methyl chloride are not too far removed from the line. However, tetramethylsilane, which is chemically similar to PDMS, lies considerably off the line, and exhibits a proportionately lower degree of miscibility with PDMS.

The effect of branching in the solvent can be observed by examining the data for n-pentane and neopentane. It is seen that the branched isomer, neopentane, exhibits a lower degree of miscibility with PDMS than the normal isomer. This is in contrast to the findings of Davenport and Rowlinson[3] who found in pure hydrocarbon systems that branching in the solute caused greater miscibility.

Pressure Dependence of L.C.S.T.

The marked dependence of L.C.S.T.'s on pressure has been adequately demonstrated by Allen and Baker[9], and should not be ignored in any discussion on the subject. They found pressure coefficients, $\frac{dT_{cL}}{dP}$, of 0.46 and 0.40 deg. atm.$^{-1}$ for two different fractions of polyisobutene in isopentane. This type of behavior would be anticipated since the appearance of a L.C.S.T. requires that the molar volume of the solvent should increase rapidly with temperature; this would be suppressed by increasing the pressure. The sign

Figure 18. θ_L temperature vs. solvent critical temperature



of the above pressure coefficients is also in agreement with that predicted thermodynamically. From equation (17) it can be seen that the pressure coefficient will be positive if the system exhibits a negative volume of mixing, i.e., $\frac{\partial^2 V}{\partial x_2^2}$ is positive. It has been shown[4] that polymer-solvent systems near their L.C.S.T. do indeed exhibit negative volumes of mixing.

Existing polymer solution theories do not take into account this pressure effect, and this is probably a reason that the correlation of experimentally determined L.C.S.T. data with values predicted from the various theories has not been wholly successful to date.

In the present work, the vapor pressures of the solutions at their respective L.C.S.T.'s are moderately high (ca. 20-30 atm.); there is therefore likely to be a considerable pressure effect reflected in the data obtained. The vapor pressures of the different solutions are of roughly the same order of magnitude, so any pressure correction required would be comparable in all solvents. The trends noted in the θ_L data are therefore at least qualitatively valid. This pressure effect is reflected in a more subtle way in the values of the entropy of dilution parameter, ψ_1. For any one polymer-solvent system, there are small vapor pressure differences between solutions of the various molecular weight fractions (due to T_{CL} differences). In the pentane system, for example, the vapor pressure difference between solutions of fractions A and E is ~1.4 atm.

Assuming a pressure coefficient of 0.4 deg. atm.$^{-1}$, an error of $\sim 0.6^{\circ}$ in T_{CL} would result. This would cause a 20 per cent error in the value of ψ_1. Even so, the values of ψ_1 obtained are at least qualitatively, if not quantitatively accurate.

Perhaps the best way to treat this problem would be to measure the L.C.S.T.'s at a number of pressures, and extrapolate back to some standard pressure such as 1 atm. or zero pressure. This would require, however, going to even higher pressures, and more sophisticated equipment. We are near the maximum pressure limit of the existing equipment, and indeed have surpassed this limit in the case of the methyl chloride solutions. The alternative to this would be to have available a theoretical treatment which adequately takes into account the pressure of the system.

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APPENDICES

APPENDIX I

Phase separation temperatures for PDMS fractions in n-pentane

Wt. Fraction Polymer	T_p (°C)
Fraction A	
0.005	182.5
0.010	182.4
0.020	182.3
0.030	182.4
0.040	182.5
0.060	182.8
0.100	184.3
Fraction B	
0.005	182.8
0.010	182.7
0.020	182.6
0.030	182.7
0.040	182.8
0.060	183.0
0.100	184.6
Fraction C	
0.005	183.5
0.010	183.3
0.020	183.2
0.030	183.3
0.040	183.4
0.060	183.6
0.100	185.6
Fraction D	
0.005	184.0
0.010	183.8
0.020	183.7
0.030	183.8
0.040	183.7
0.060	183.9
0.100	186.4
Fraction E	
0.005	186.5
0.010	186.3
0.020	186.0
0.030	186.0
0.040	185.9
0.060	186.0
0.100	187.4

APPENDIX II

Phase separation temperatures for PDMS fractions in n-butane

Mg. Polymer	Mg. Solution	Wt. Fraction Polymer	T_p(°C)
Fraction A			
0.7	112.0	0.006	135.6
1.6	91.8	0.017	135.5
2.9	109.3	0.027	135.4
4.3	136.4	0.032	135.4
6.0	137.2	0.044	135.5
8.4	133.9	0.063	135.8
13.7	200.7	0.068	135.8
Fraction B			
0.4	113.0	0.004	135.9
1.3	132.2	0.010	135.8
2.4	127.2	0.019	135.7
3.9	136.1	0.029	135.8
5.2	142.5	0.037	135.8
8.2	126.8	0.065	136.1
13.9	151.7	0.092	136.5
Fraction C			
0.8	100.1	0.008	136.5
1.5	141.2	0.011	136.4
2.5	120.5	0.021	136.2
4.4	118.5	0.037	136.2
8.4	104.9	0.080	137.0
14.2	112.8	0.126	137.6
Fraction D			
0.6	106.5	0.006	136.8
1.5	122.2	0.012	136.7
2.7	120.5	0.022	136.6
4.3	96.4	0.045	136.9
5.4	142.4	0.038	136.6
8.6	124.9	0.069	137.0
13.2	182.8	0.072	137.0
Fraction E			
1.4	133.9	0.010	139.4
2.8	130.1	0.022	139.0
3.9	119.9	0.032	139.0
5.4	129.1	0.042	139.1
8.3	155.3	0.054	139.2
13.2	132.5	0.100	140.1

APPENDIX III

Phase separation temperatures for PDMS fractions in propane

Mg. Polymer	Mg. Solution	Wt. Fraction Polymer	T_p(°C)
Fraction A			
0.9	136.2	0.007	75.0
2.0	107.5	0.019	74.9
3.6	127.4	0.028	74.8
4.5	117.7	0.038	74.9
6.2	126.3	0.049	74.9
9.2	124.8	0.074	75.1
14.3	160.9	0.089	75.2
Fraction B			
0.8	121.4	0.007	75.2
1.6	122.2	0.013	75.1
4.5	129.5	0.035	75.0
8.3	125.0	0.066	75.2
13.8	161.6	0.085	75.3
Fraction C			
1.0	119.4	0.008	75.9
1.7	142.0	0.012	75.8
3.0	132.0	0.023	75.7
4.0	111.6	0.036	75.7
6.2	126.8	0.049	75.7
8.8	131.6	0.067	75.8
12.8	125.7	0.102	76.0
Fraction D			
3.0	137.2	0.022	76.2
4.5	129.2	0.035	76.1
6.0	133.4	0.045	76.2
12.8	140.6	0.091	76.5
Fraction E			
0.8	102.1	0.008	78.8
2.9	124.6	0.023	78.6
5.7	127.0	0.045	78.6
8.4	126.2	0.067	78.7

APPENDIX IV

Phase separation temperatures for PDMS fractions in neopentane

Mg. Polymer	Mg. Solution	Wt. Fraction Polymer	T_p ($^\circ$C)
Fraction A			
1.0	122.3	0.008	141.9
1.8	126.7	0.014	141.8
2.4	116.2	0.021	141.8
3.8	124.3	0.031	141.8
6.4	140.8	0.046	141.9
10.2	161.2	0.063	142.1
Fraction C			
1.2	116.4	0.010	142.7
1.9	125.4	0.015	142.6
3.3	117.4	0.028	142.5
4.9	121.8	0.040	142.6
6.1	130.2	0.047	142.6
10.5	126.1	0.073	143.0
Fraction D			
1.0	115.7	0.009	143.3
1.7	126.1	0.013	143.2
2.6	119.2	0.022	143.1
4.0	127.0	0.032	143.1
6.0	115.8	0.052	143.3
10.2	139.0	0.072	143.7
Fraction E			
0.9	108.5	0.008	146.5
2.0	106.9	0.019	146.0
2.8	115.1	0.024	146.0
4.1	124.6	0.032	145.9
5.7	116.0	0.049	146.0
8.6	183.8	0.047	146.1
13.4	141.6	0.095	146.9

APPENDIX V

Phase separation temperatures for PDMS fractions in tetramethylsilane

Mg. Polymer	Mg. Solution	Wt. Fraction Polymer	T_p (°C)
	Fraction A		
0.3	122.1	0.003	155.9
1.4	127.8	0.011	155.7
2.7	142.7	0.019	155.6
4.2	140.8	0.030	155.6
6.0	181.8	0.033	155.7
8.3	158.8	0.060	156.0
13.0	138.9	0.094	156.5
	Fraction C		
0.8	135.8	0.006	156.9
1.8	138.5	0.013	156.7
2.8	122.2	0.023	156.6
4.4	122.5	0.036	156.6
5.5	131.7	0.042	156.6
8.7	128.1	0.068	156.9
13.0	142.5	0.091	157.9
	Fraction D		
0.9	122.3	0.007	157.5
1.1	133.0	0.008	157.4
2.2	134.0	0.016	157.2
4.2	132.8	0.032	157.3
4.6	126.4	0.036	157.3
8.3	146.6	0.057	157.4
10.0	131.4	0.076	158.0
	Fraction E		
1.3	145.5	0.009	160.8
1.1	145.7	0.008	161.0
2.6	138.1	0.019	160.2
4.6	134.4	0.034	160.0
6.0	128.1	0.047	160.2
8.3	136.9	0.061	160.3
13.5	131.9	0.102	161.9

APPENDIX VI

Phase separation temperatures for PDMS fractions in dimethyl ether

Mg. Polymer	Mt. Solution	Wt. Fraction Polymer	T_p (°C)
Fraction A			
1.2	205.2	0.006	111.4
2.1	189.0	0.011	111.2
3.6	180.6	0.020	110.8
4.7	174.9	0.027	110.8
6.0	161.2	0.037	110.9
10.1	153.9	0.066	111.3
Fraction C			
0.7	171.7	0.004	112.0
1.6	177.9	0.009	111.7
3.4	136.9	0.025	111.6
4.4	140.1	0.031	111.7
5.2	160.9	0.032	111.8
8.1	174.4	0.047	111.9
13.0	170.2	0.076	112.3
Fraction D			
1.0	176.5	0.006	112.9
1.4	157.7	0.009	112.7
3.1	129.3	0.024	112.2
4.3	164.6	0.026	112.3
6.0	136.9	0.044	112.6
8.8	146.8	0.060	112.9
13.8	119.4	0.115	114.8
Fraction E			
0.5	159.6	0.003	114.7
1.4	174.8	0.008	114.4
3.7	198.9	0.019	114.3
7.1	196.2	0.036	114.0
12.2	175.7	0.070	114.1

APPENDIX VII

Phase separation temperatures for PDMS fractions in methyl chloride *

Mg. Polymer	Mg. Solution	Wt. Fraction Polymer	T_p (°C)
Fraction A			
2.2	212.2	0.010	130.2
Fraction E			
8.2	216.1	0.039	134.4
13.0	281.9	0.046	134.7

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* Due to greater than normal pressures, nearly all the tubes containing methyl chloride solutions ruptured during the run, so appreciable data could not be obtained for this system.

APPENDIX VIII

Gas Chromatograms of Solvents

Figure 19. Gas chromatogram for n-pentane

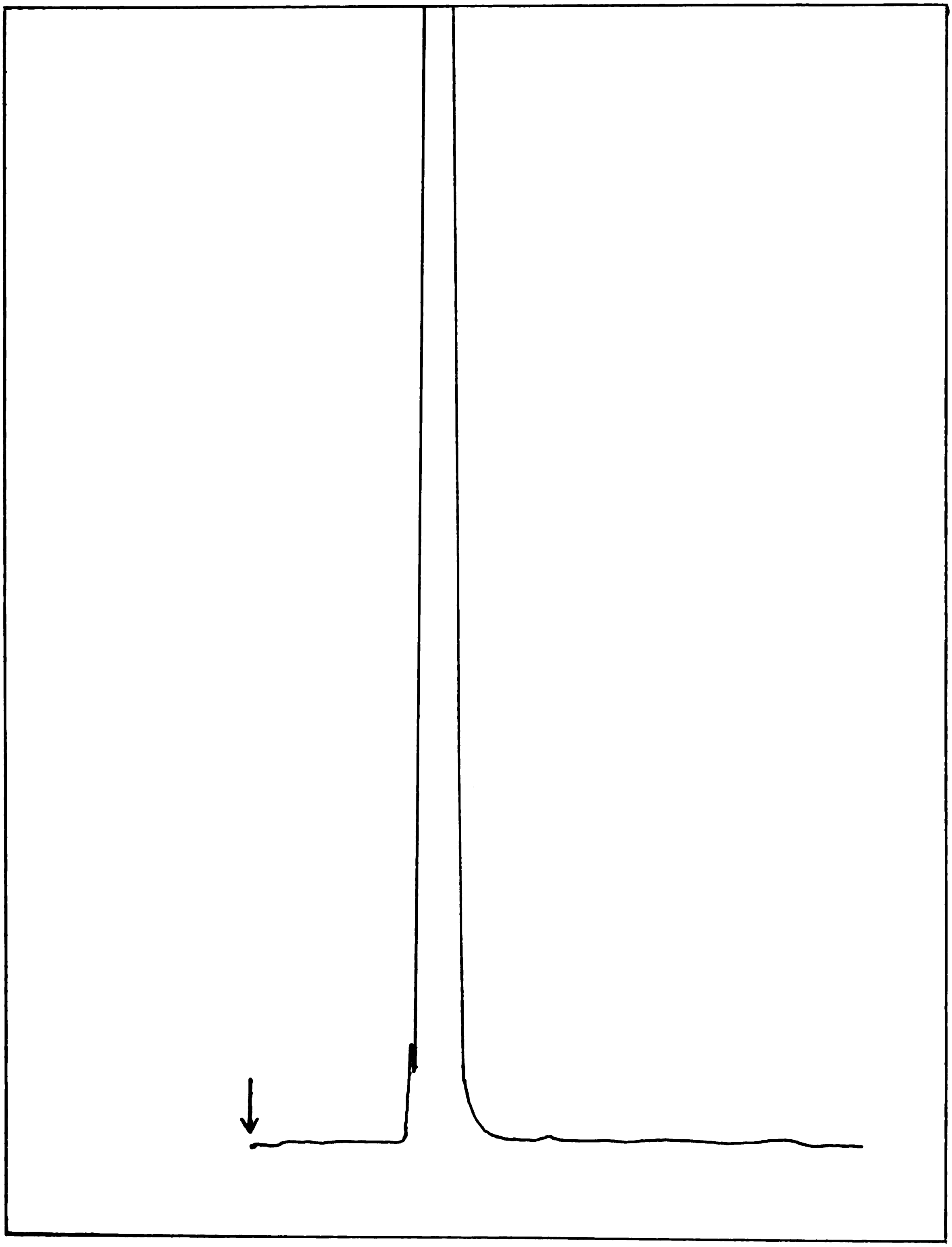

Figure 20. Gas chromatogram for n-butane

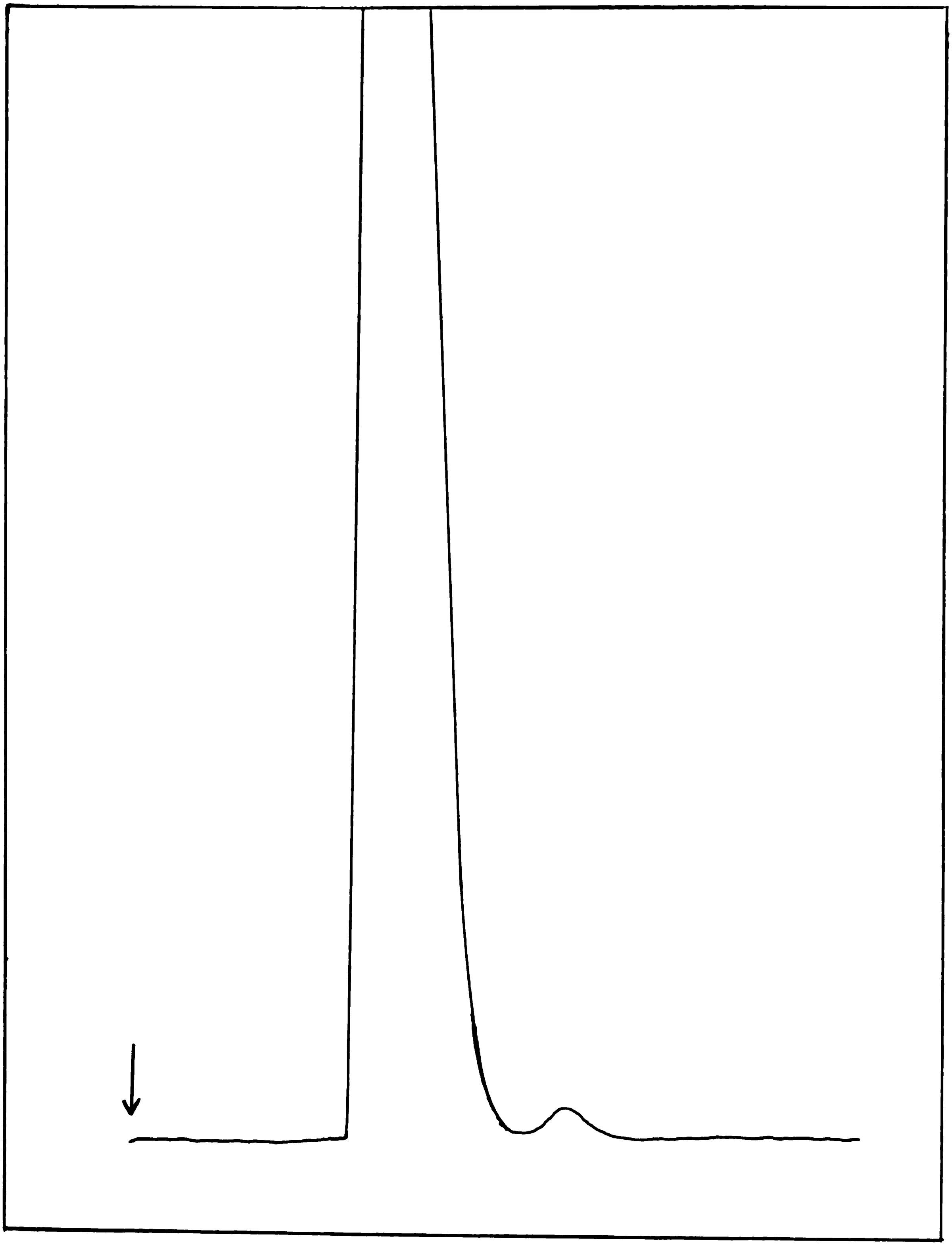

Figure 21. Gas chromatogram for neopentane

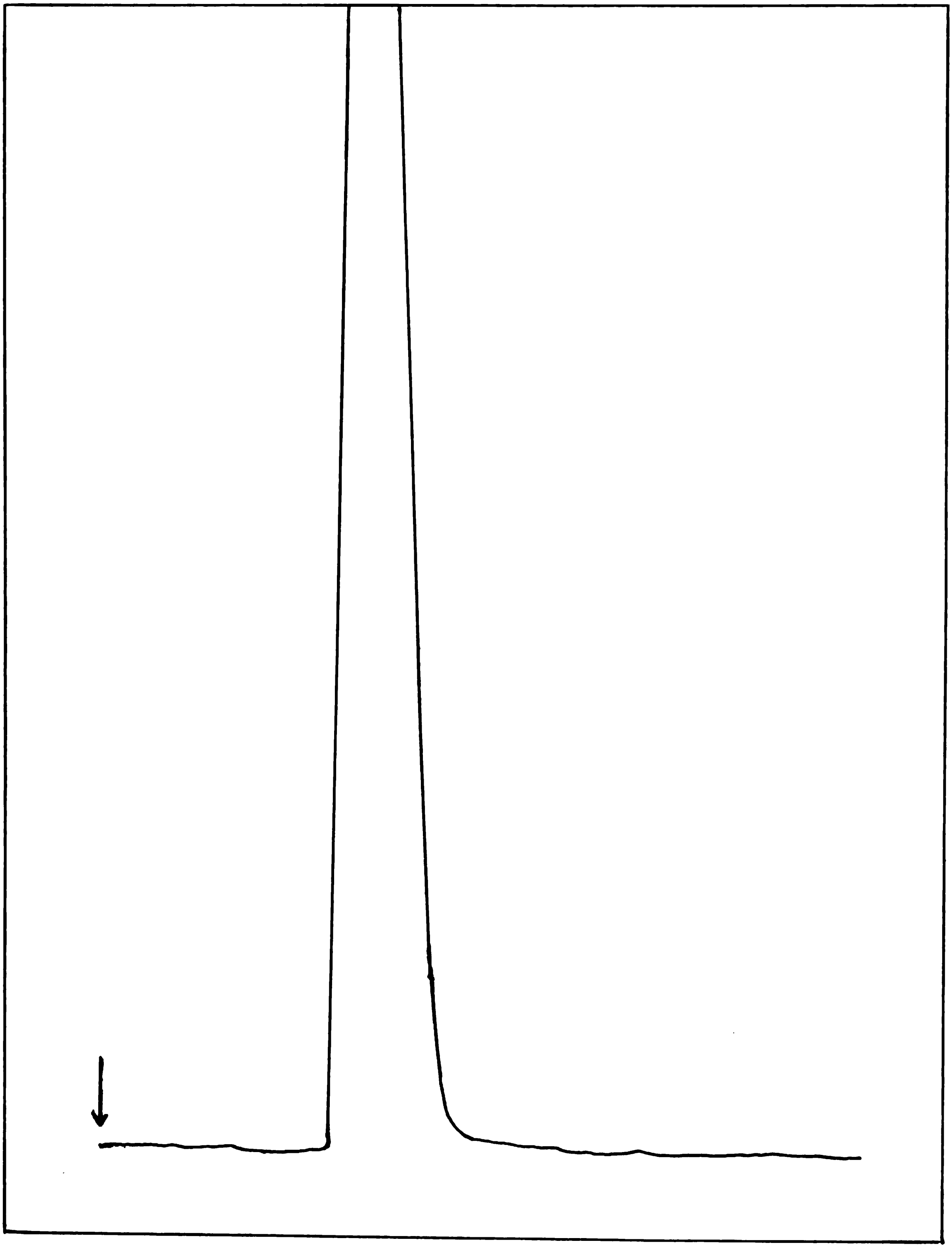

Figure 22. Gas chromatogram for tetramethylsilane

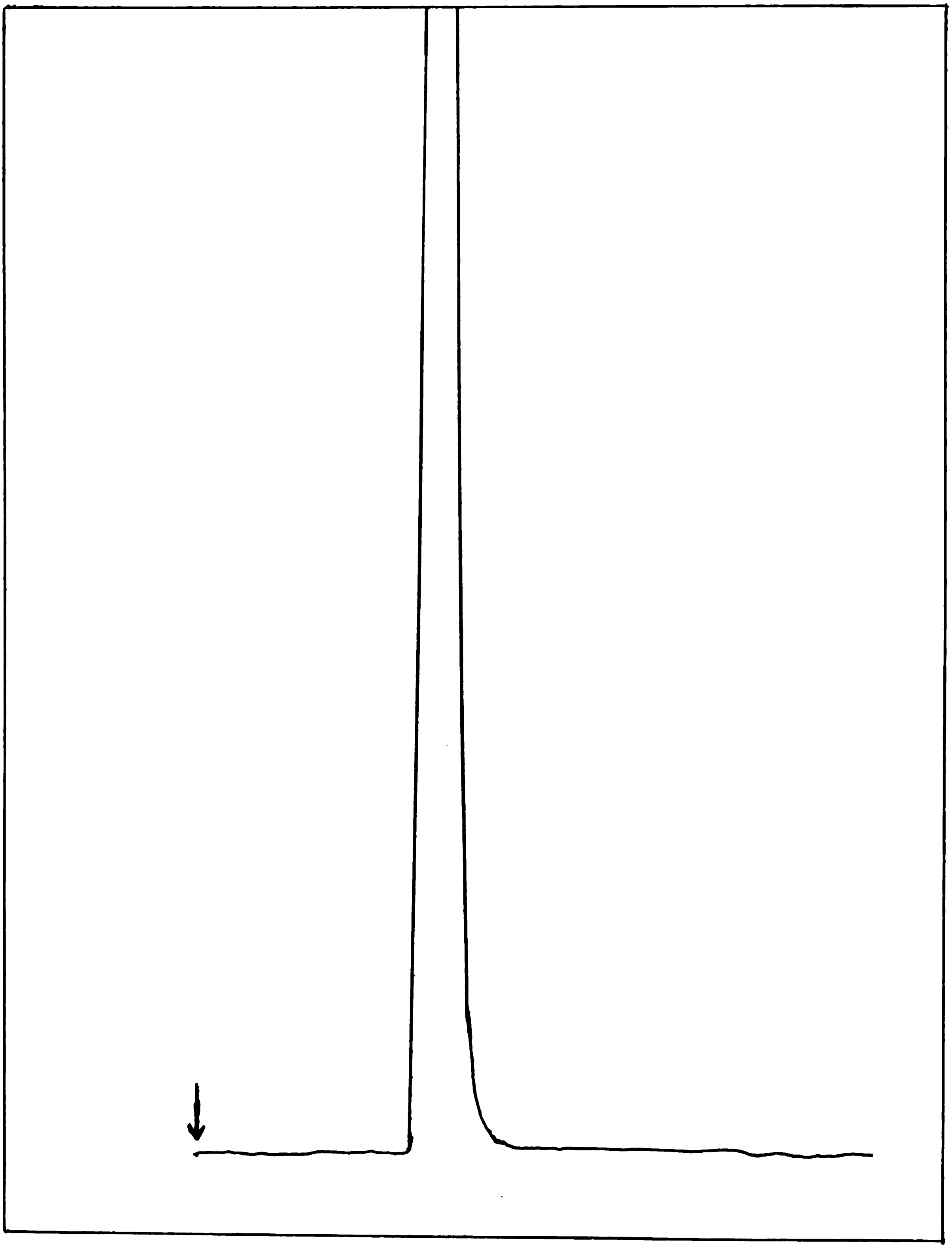

Figure 23. Gas chromatogram for dimethyl ether

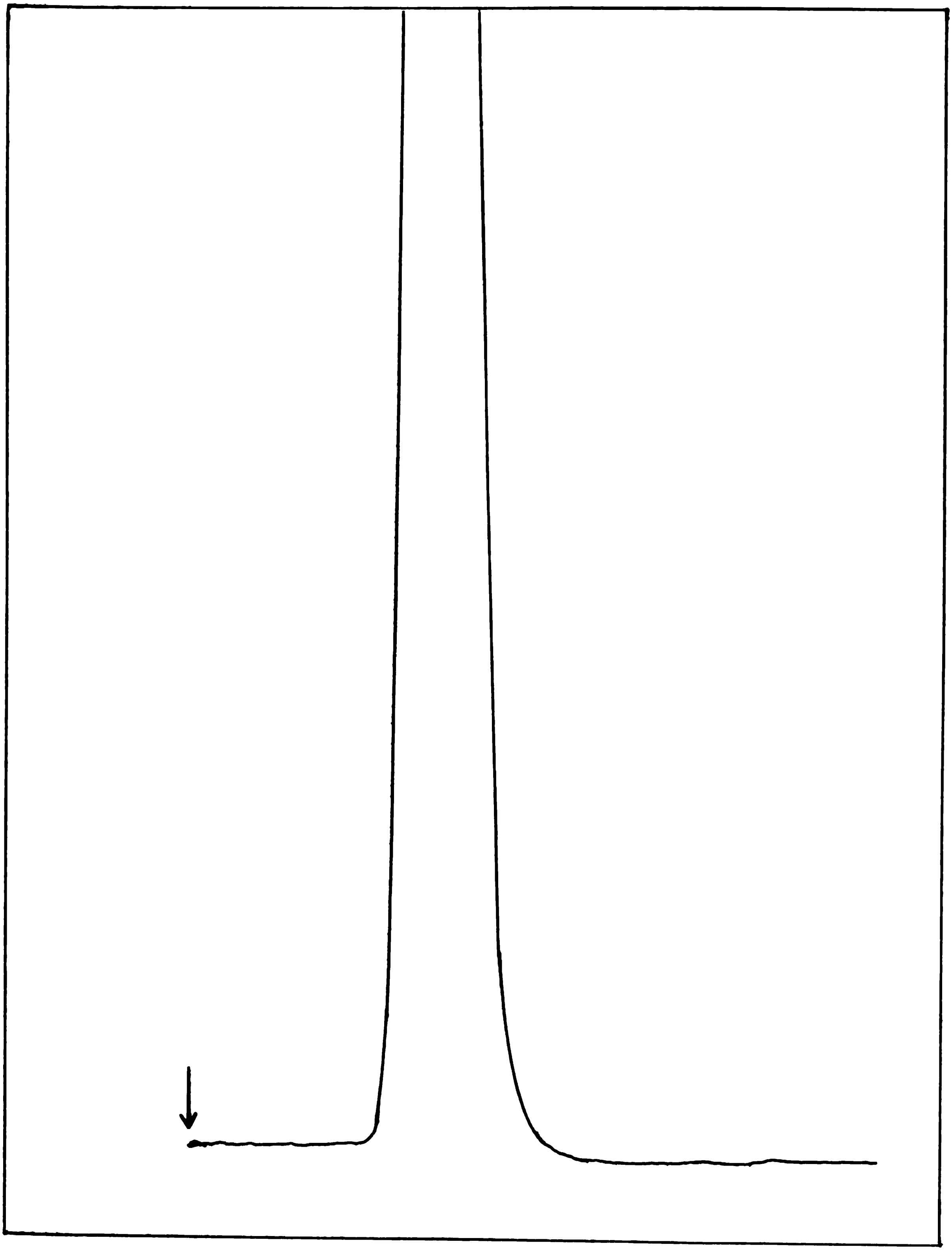

Figure 24. Gas chromatogram for methyl chloride