

OVERALL MASS-TRANSFER COEFFICIENTS FOR A
HOMOLOGOUS SERIES OF POLY GLYCOL
ETHERS BETWEEN TOLUENE AND WATER

by

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I. INTRODUCTION

A problem which occurs frequently in the field of chemical engineering is the separation of the components of a liquid solution. There are several unit operations available which may be used to perform such separations depending on the physical and chemical properties of the system in question. A technique which has become of importance during the last few years is liquid extraction. Although the earlier applications of liquid extraction were in the petroleum industry, recent developments have brought about the use of liquid extraction in the wood chemicals industry, the perfume and flavoring industries, and in the manufacture of many other organic chemicals.

The applications of liquid extraction have advanced much more rapidly than the development of methods of design. In most cases design information has resulted from trial and error procedures in design and testing. To obtain more basic design of extraction equipment development of

correlations between rates of extraction and the operating variables and properties of the systems involved is necessary.

According to the two-film theory as applied to liquid extraction, the resistance to diffusion of a component from one phase to another can be represented by an effective film thickness for each phase. The rate at which diffusion occurs through these films is of major importance in the design and operation of extraction equipment. Most experimental work has been performed with emphasis on the overall resistance to mass transfer and the effect of flow rates. Very few investigations have been made to correlate the resistance to mass transfer with the physical properties of the system.

The purpose of this investigation was to determine the effect of the molecular weight of solute on mass-transfer coefficients for liquid-liquid extraction by evaluating these coefficients at 30 °C for the systems toluene-ethylene glycol dimethyl ether-water, toluene-diethylene glycol dimethyl ether-water, toluene-triethylene glycol

dimethyl ether-water, and toluene-tetraethylene glycol dimethyl ether-water, using a horizontal, countercurrent, liquid-liquid extractor.

II. LITERATURE REVIEW

This section contains a survey of extraction theory and principles, previous work performed using horizontal tube extractors, and previous correlations of mass-transfer coefficients with physical properties. The nomenclature for extraction and types of extraction equipment will not be discussed. This material has been collected by Elgin⁽⁶⁾.

Theory of Liquid-liquid Extraction

The distribution of a solute between two immiscible phases is governed by the concentration of the solute, temperature of the system, and the nature of the materials involved. The rate of solute transfer from one phase to the other is a function of the contact area of the phases and of the degree of mixing between the phases. If the time of contact is not sufficient for equilibrium conditions to be established, then the diffusion rate is a governing factor⁽⁶⁾.

The mechanism for diffusion in liquids is explained by applying treatment paralleling that

used for diffusion in gases. The kinetic theory cannot be readily applied to liquids, and variations of physical properties with concentration are not well developed for liquids⁽²⁵⁾. Therefore, the resulting expressions are not as reliable as those for gases.

For all diffusional operations there are certain common characteristics. In every case one fluid is brought into contact with another phase, a concentration gradient is established, and transfer of material from one phase to the other results⁽²³⁾. Thus, it seems possible to correlate one operation with another.

Molecular and Eddy Diffusion. In a liquid extraction operation two moving immiscible liquids are brought into contact for the purpose of transferring a solute from one phase across the interface into the other phase. The liquid films adjacent to the interface are in laminar flow⁽²³⁾. This film is characterized by orderly movement of the liquid particles in streamlines which follow the contour of the surface. In the outer regions of the liquid the flow is turbulent. An intermediate

buffer zone is produced between the turbulent and laminar zones due to the gradual transition from one type of flow to the other. For a substance to pass or diffuse through these various zones at least two different mechanisms are involved⁽²⁴⁾. Diffusion in the laminar region is called molecular diffusion, and that in the turbulent zone is known as eddy diffusion⁽²⁴⁾.

The phenomenon of molecular diffusion has been studied from several points of view, the most important being those of Fick and Maxwell-Stefan⁽¹⁸⁾. Due to the complexity of the transfer of material through a turbulent zone, eddy diffusion has been described in a manner analogous to molecular diffusion⁽¹⁹⁾.

In an effort to include the effect of both types of diffusion a fictitious laminar film is used, such that the "effective" film thickness is sufficient to account for the total resistance to mass transfer⁽¹⁹⁾.

Thus,

$$N_A = \frac{D_A S C (C_{A1} - C_{A2})}{C_{BM} l} \quad (1)$$

where:

- N_A = rate of mass transfer of component A, mol/hr
- D_A = diffusion coefficient of component A, sq ft/hr
- S = cross-sectional area perpendicular to the direction of diffusion, sq ft
- C = concentration of components, mol/cu ft
- C_{A1}, C_{A2} = concentration of component A at points 1 and 2, mol/cu ft
- C_{BM} = log mean concentration of solvent, mol/cu ft
- l = effective film thickness for combined eddy and molecular diffusion, ft.

This equation may be simplified by introducing a mass-transfer film coefficient, k ,

$$N_A = kS(C_{A1} - C_{A2}) \quad (2)$$

where:

$$k = \frac{D_A C}{C_{BM} l}$$

The mass-transfer coefficient used in equation (2) is a "local" coefficient⁽²⁶⁾ and varies from one position to another in the apparatus. To describe the entire system by a single coefficient, average conditions must be used.

Two-film Theory. Consider the transfer of solute from one liquid phase to a second immiscible phase, under steady state conditions. Assuming the two phases to be moving in a direction parallel to the interface between them, there will exist concentration gradients in each phase which act as driving forces for the transfer, and the resistance to diffusion can be represented by an "effective" film thickness for each phase. This picture of the mass transfer process was introduced by Whitman⁽¹⁹⁾. This concept assumes that equilibrium is established at the interface.

Figure 1 is a graphical representation⁽¹⁹⁾ of the two-film concept. The concentration of the diffusing solute is plotted as a function of distance through the two-phase system. The two liquid phases are designated E (extract) and R (raffinate). The subscripts refer to positions in the system, i for interface and E and R for the main portion of the corresponding phases. C_R is the concentration of solute in the bulk of the raffinate phase. C_{Ri} is the concentration of solute at the raffinate side of the interface. The transfer of solute through the effective film thickness, l_R , is due to the concentration gradient $(C_R - C_{Ri})$. Since C_{Ri} is in equilibrium with C_{Ei} there is no resistance to transfer at the interface, and the solute passes into the extract phase. The concentration gradient $(C_{Ei} - C_E)$ provides the driving force for the diffusion of the solute into the bulk of the extract phase where the concentration is C_E .

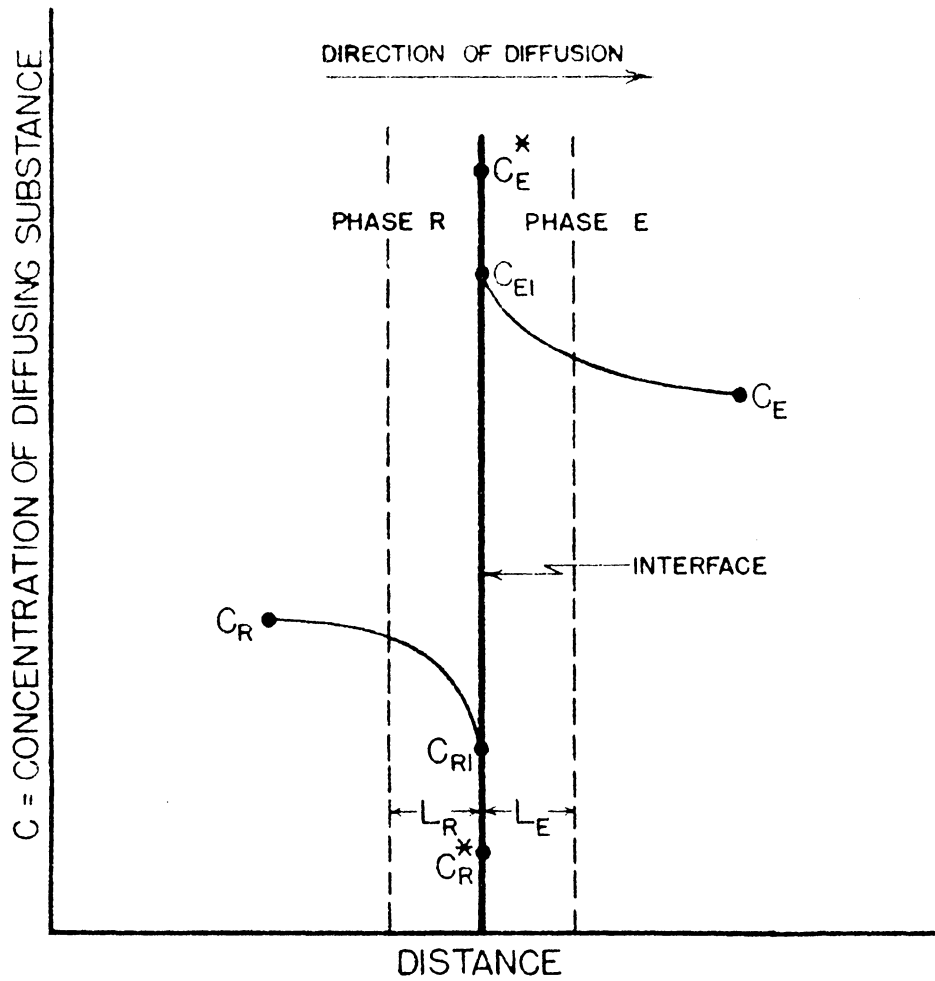


FIGURE 1. CONCENTRATION GRADIENTS IN A LIQUID-LIQUID SYSTEM

TREYBAL, R.E.: "LIQUID EXTRACTION," P. 119. MCGRAW-HILL BOOK CO., INC., NEW YORK, N.Y., 1951. 1 ED.

For a differential rate of transfer, dN , through a differential interfacial surface, dS ,

$$dN = k_R dS(C_R - C_{Ri}) = k_E dS(C_{Ei} - C_E) \quad (3)$$

where:

k_R = individual film coefficient based on R phase

k_E = individual film coefficient based on E phase.

Overall Mass-transfer Coefficients. In most practical situations it is impossible to determine k_E and k_R . The bulk concentrations C_E and C_R can be readily obtained by sampling the respective phases. However, ordinarily the interface cannot be approached sufficiently close to obtain samples which will give C_{Ei} and C_{Ri} accurately. The driving forces ΔC_R and ΔC_E cannot then be obtained. If the equilibrium-distribution curve is sufficiently straight for the concentration ranges under investigation, then

$$C_{Ei} = mC_{Ri} \quad (4)$$

where:

m = equilibrium distribution coefficient.

It is possible to define a concentration $\underline{C_E^*}$ which would be in equilibrium with the bulk concentration $\underline{C_R}$. Then,

$$C_E^* = mC_R. \quad (5)$$

The fictitious concentration $\underline{C_E^*}$ represents the concentration of solute in the E phase that would be in equilibrium with the bulk concentration in the R phase. Similarly, $\underline{C_R^*}$ can be defined as a concentration in equilibrium with $\underline{C_E}$.

The complete mass transfer process in both phases can then be expressed as

$$dN = K_E dS (C_E^* - C_E) = K_R dS (C_R - C_R^*) \quad (6)$$

where:

K_E, K_R = overall mass-transfer coefficients based on the overall concentration gradients ΔC_{OE} and ΔC_{OR} , respectively, lb mol/hr-sq ft-AC

dN = differential rate of mass transfer, lb mol/hr

dS = differential interfacial surface, sq ft

$(C_E^* - C_E), (C_R - C_R^*)$

= overall driving forces based on the E and R phases, respectively, lb mol/cu ft.

The relationship between the overall and the individual mass-transfer coefficients are given by⁽²⁰⁾:

$$1/K_E = 1/k_E + m/k_R \quad (7)$$

$$1/K_R = 1/k_R + 1/mk_E \quad (8)$$

$$K_R = mK_E \quad (9)$$

where:

$1/K$ = total resistance to mass transfer

$m = C_E/C_R^* = C_E^*/C_R$ equilibrium coefficient expressed in terms of mol/unit volume

$m/k, 1/k, 1/mk$ = individual film resistances

E, R = subscript references to extract and raffinate phases, respectively.

If the distribution of solute strongly favors the E phase, \underline{m} will be very large. If $\underline{k_E}$ and $\underline{k_R}$ are of comparable magnitude, $\underline{K_R}$ will nearly equal $\underline{k_R}$, and the principal resistance to diffusion lies in the R phase. In a like manner, if \underline{m} is very small, $\underline{K_E}$ will nearly equal $\underline{k_E}$, and the E phase resistance is controlling.

In continuously operating extraction processes, the concentrations in each phase undergo variations throughout the equipment. The concentrations used in the development of the previous equations are point conditions. Therefore, when applying these equations to practical operations, they will have to be integrated over the entire concentration ranges of the two phases⁽²⁰⁾. Also, if the distribution curve is not straight, there will be wide variations of $\underline{K_E}$ and $\underline{K_R}$ with concentration. Since the factors upon which $\underline{K_E}$ and $\underline{K_R}$ depend are also likely to vary, the use of the overall coefficient is limited. However, according to Treybal⁽²¹⁾ these expressions are used for all situations for lack of anything better.

The integrated form of equation (6), page 12, has been shown⁽²²⁾ to be,

$$N = KaSH\Delta C_{1m} = KA\Delta C_{1m} \quad (7)$$

where:

- N = rate of mass transfer, lb mol/hr
- K = overall mass-transfer coefficient, lb mol/hr-sq ft- ΔC
- a = constant area per unit tower volume, sq ft/cu ft
- S = tower cross-sectional area, sq ft
- H = effective tower height, ft
- A = total contact area = aSH, sq ft
- C_{1m} = log mean concentration difference, lb mol/cu ft.

Other Theories. There have been several other theories^(5,9) proposed for the mechanism of mass transfer. However, since they are not used frequently, they will not be discussed.

Extraction in Horizontal Tubes

Very few investigations have been performed using horizontal tube extractors. Most of the previous extraction work was done in packed columns, spray towers, and wetted-wall towers^(2,3,4,7,15,27). The advantage gained by using a horizontal tube was that the interfacial surface area may be accurately determined. This allowed calculation of the overall mass-transfer coefficients instead of the product of transfer coefficient and area.

Berglin, Lockhart, and Brown⁽¹⁾ studied the transfer of isopropyl alcohol from tetrachloroethylene to water in a horizontal tube extractor. They used a two-inch diameter, ten-foot long, horizontal tube extractor and varied the velocities of the phases over wide ranges. The water phase mass velocity was varied between 5,000 and 85,000 pounds per hour per square foot for solvent phase velocities of 17,500, 35,000, and 50,000 pounds per hour per square foot. The solvent phase mass velocity was varied from 5,000 to 112,000 pounds per hour per square foot for water phase velocities of 7,500, 22,000, and 32,000 pounds per hour per square foot. The same

concentration of alcohol was used for each test so that the effect of flow rate on overall mass-transfer coefficients could be determined. The overall mass-transfer coefficients based on the solvent phase when plotted versus the mass velocity of the water phase pass through a minimum. The minimum occurred at the point where the mass velocities were the same in both phases. This minimum was not observed when the coefficients were plotted versus the mass velocity of the solvent phase. The investigators explained that these minima were the result of the movement of the "plane of zero velocity"⁽¹⁾ from one phase to the other.

Skrzecz⁽¹⁶⁾ used a 1-1/2-inch diameter, eight-foot long, horizontal extractor for evaluating the individual mass-transfer coefficients for binary systems. The systems used were cyclohexanol, methyl ethyl ketone, furfural, normal butanol, and nitromethane with water. The individual mass-transfer coefficients for the water side were found to increase as the flow rate of the water phase was increased. Changes in the flow rate of the solvent phase had no effect on the water-side coefficients. The solvent-film coefficients were found to increase

as the flow rate of the solvent phase was increased, but decreased as the flow rate of the water phase increased.

Skrzec⁽¹⁶⁾ also evaluated the overall mass-transfer coefficients for several ternary systems. He measured the transfer of acetic acid from methyl ethyl ketone, normal butanol, and cyclohexanol with water. The flow rate of the water phase was varied from 1,000 to 15,000 pounds per hour, square foot for solvent-phase flow rates of 5,000 and 10,000 pounds per hour, square foot. The solvent-phase, flow rate was varied between 1,000 and 15,000 pounds per hour, square foot for water-phase flow rates of 5,000 and 8,000 pounds per hour, square foot. The overall mass-transfer coefficients based on the solvent phase were found to increase with increases in the flow rate of the water phase. However, when the coefficients were plotted versus the flow rate of the solvent phase a minimum was observed. These results were the converse of those found by Berglin, Lockhart, and Brown⁽¹⁾. Skrzec correlated the individual and the overall mass-transfer coefficients

with the physical properties of the respective phases⁽¹⁶⁾ for two component systems.

Lastovica⁽¹¹⁾ used the same apparatus as that used by Skrzec to study effects of physical variables on the film coefficients of mass transfer. He recalculated the binary data obtained by Skrzec using experimentally determined values of interfacial tension. Also, a more accurate correlation of film coefficients with the physical properties of the system was derived. Lastovica then attempted to predict film coefficients for ternary systems from data for binary systems, but found that the equation was not applicable.

Mote⁽¹³⁾ continued the work of Lastovica on the effect of interfacial tension. He used two, ternary systems: hexane-acetone-water and toluene-acetone-water. The interfacial tension was varied by varying the solute concentrations. The transfer of solute was attempted in both directions. However, the transfer coefficients for transfer of solute from water to toluene were approximately ten times larger than the coefficients obtained for transfer of solute from toluene to water. It was found that the overall

mass-transfer coefficients increased with increases in interfacial tension for the toluene-acetone-water system. However, for the hexane-acetone-water system the overall mass-transfer coefficients decreased with increases in interfacial tension.

Correlations of Mass-transfer Coefficients

There have been numerous^(2,3,7,8,11,13,16) correlations of mass-transfer coefficients with the physical and operational variables of the system. Most of these correlations involve effect of flow rate on the mass-transfer coefficients.

Gilliland and Sherwood⁽⁸⁾ investigated the evaporation of water into air in a wetted-wall column. They obtained a correlation of individual mass-transfer coefficients with the Reynolds and Schmidt numbers. Fallah, Hunter, and Nash⁽⁷⁾ were able to obtain a similar correlation for extraction of phenol between water and kerosene in a wetted-wall

tower. When kerosene was used as the core liquid the following correlation was obtained:

$$\frac{kd}{D_L} = 0.94 \left(\frac{du\rho}{\mu} \right)^{0.8} \left(\frac{\mu}{D_L\rho} \right)^{0.46}$$

where:

k = liquid film coefficient, ft/hr

d = diameter of tower, ft

D_L = diffusion coefficient of solute
through solvent, ft²/hr

u = velocity of liquid, ft/sec

ρ = density of liquid, lb/ft³

μ = viscosity of liquid, lb/hr-ft

Brinsmade and Bliss⁽²⁾ studied the extraction of acetic acid from methyl isobutyl ketone with water in a wetted-wall tower. They obtained a correlation of film coefficients with Reynolds and Schmidt numbers, and predicted that the flow rate of one fluid did not

affect the transfer coefficient for the other fluid.

The correlation for the core fluid was:

$$\frac{kd}{D_L} = 1.07 \left(\frac{du\rho}{\mu}\right)^{0.67} \left(\frac{\mu}{D_L\rho}\right)^{0.62}$$

and for the wall fluid:

$$\left(\frac{\mu^2}{\rho^2g}\right)^{1/3} \frac{k}{D_L} = 0.00135 \left(\frac{du\rho}{\mu}\right) \left(\frac{\mu}{D_L\rho}\right)^{0.62}$$

where:

k, μ, ρ, D_L, d, u = same as indicated above

g = gravitation acceleration, ft/hr²

Treybal and Work⁽²⁷⁾ also used a wetted-wall tower to study the system acetic acid-water-benzene. They predicted that neither film could be said to "control" and that the flow rate of either phase might affect the individual transfer coefficients.

Skrzec⁽¹⁶⁾, Lastovica⁽¹¹⁾, and Mote⁽¹³⁾, all used a horizontal extractor for evaluating transfer coefficients of ternary systems. They all expressed the transfer coefficients as a function of dimensionless groups of physical properties.

The equation presented by Mote⁽¹³⁾ for the overall mass-transfer coefficient in ternary systems is:

$$\frac{K_s d}{D_s} = 2.708 \times 10^{-21} \left(\frac{d\sigma}{\mu_s D_s} \right)^{0.7227} \left(\frac{\mu_w}{\mu_s} \right)^{4.0592} \left(\frac{\mu_s}{\rho_s D_s} \right)^{5.4361} \left(\frac{dG_s}{\mu_s} \right)^{0.4701} \left(\frac{dG_w}{\mu_w} \right)^{0.3027}$$

where:

- K = overall mass-transfer coefficient, lb/hr-sq ft-ΔC
- d = diameter of tube, ft
- D = diffusivity, sq ft/hr
- σ = interfacial tension, lb/hr
- ρ = average phase density, lb/cu ft
- μ = viscosity, lb/ft-hr
- G = mass velocity, lb/hr-sq ft
- s,w = refer to solvent and water phases, respectively.

III. EXPERIMENTAL

The purpose of the investigation, the plan of investigation, materials, apparatus, procedure, data and results, and sample calculations are presented in this section.

Purpose of Investigation

The purpose of this investigation was to determine the effect of molecular weight of solute on overall mass-transfer coefficients for liquid-liquid extraction by evaluating these coefficients at 30 °C for the systems toluene-ethylene glycol dimethyl ether-water, toluene-diethylene glycol dimethyl ether-water, toluene-triethylene glycol dimethyl ether-water, and toluene-tetraethylene glycol dimethyl ether-water, using a horizontal, countercurrent, liquid-liquid extractor.

Plan of Investigation

The plan of investigation for determining the effect of molecular weight of solute on the overall mass-transfer coefficients for liquid-liquid extraction involves a survey of the literature, determination of physical properties, determination of equilibrium data, operation of laboratory equipment, and correlation of data.

Literature Review. A survey of the literature was made to acquaint the investigator with the theory of liquid-liquid extraction, and especially to liquid-liquid extraction in horizontal tubes. To accomplish this purpose a study of extraction principles and of previous work concerning extraction in horizontal tubes was made. The relations between and the effects of the physical properties of the systems used was also studied.

Selection of Systems. Mono-, di-, tri-, and tetra-ethylene glycol dimethyl ethers were used for solutes since they were completely soluble in both water and toluene, were similar in structure, and their molecular weights varied over a wide range.

Determination of Physical Properties. The physical properties, density, viscosity, interfacial tension, and diffusivity, were measured or calculated. These properties were used in selecting the operating conditions for the experimental tests.

Determination of Equilibrium Data. The equilibrium distribution data, which was not available in the literature was determined by preparing samples of solute in both phases and titrating to the cloud point. The refractive indices at 30 °C versus concentration curves were obtained.

Operation of Laboratory Equipment. A 1-1/2-inch diameter, eight foot long, horizontal tube was used for the extraction tests. The solute concentrations were held approximately constant. The water and solvent phase flow rates were varied over a narrow range. Samples were obtained at steady state

conditions and analyzed by measuring their refractive index.

Correlation of Data. The overall coefficients of mass-transfer were determined from the experimental data. These coefficients were plotted against molecular weight to determine the relation, if any.

Materials

The materials used in the investigation are presented in this section. Table I shows the structure of the solutes used, and Table II lists some of their physical properties.

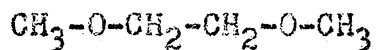
Diethylene Glycol Dimethyl Ether. Lot No 1439; E-141. Obtained from Ansul Chemical Co., Industrial Chemicals Division, Marinette, Wisc. Used as solute in extraction tests.

Ethylene Glycol Dimethyl Ether. Lot No 379; E-121. Obtained from Ansul Chemical Co., Industrial Chemicals Division, Marinette, Wisc. Used as solute in extraction tests.

Tetraethylene Glycol Dimethyl Ether. Lot No 220 and No 222; E-181. Obtained from Ansul

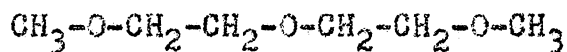
TABLE I

Structure of the Poly Glycol Ethers



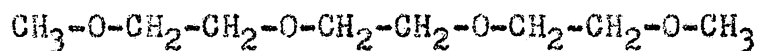
Ethylene Glycol Dimethyl Ether

E-121



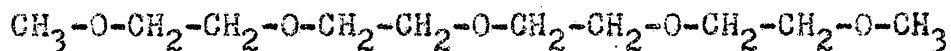
Diethylene Glycol Dimethyl Ether

E-141



Triethylene Glycol Dimethyl Ether

E-161



Tetraethylene Glycol Dimethyl Ether

E-181

Ansul Ether, Chemical Products Bulletin, p. 5.
Ansul Chemical Company, Marinette, Wisc.

TABLE II

Physical Properties of Glycol Dimethyl Ethers

Property	<u>E-121</u>	<u>E-141</u>	<u>E-161</u>	<u>E-181</u>
Molecular Weight	90.120	134.172	178.224	222.276
Specific Gravity, 20/20°C	0.8683	0.9451	0.9862	1.0130
Refractive Index, n ₂₀ ^D	1.3792	1.4078	1.4233	1.4322
Boiling Point, °C, 760 mm	85.2	162.0	216.0	275.3
Freezing Point, °C	-69	-64	-45	-27
Vapor Pressure, mm Hg at 20 °C	48.0	3.0	0.9	0.01
Viscosity, Absolute (cp) at 20 °C	1.1	2.0	3.8	4.05
Surface Tension, dynes/cm at 20 °C	22.9	27.0	29.4	31.1
Specific Heat, cal/gm/°C	0.438	0.403	0.424	0.427
Heat of Fusion, cal/gm	33.3	24.2	20.2	27.3
Heat of Combustion, K cal/mol	602.088	902.2	1190.5	1479.8
Heat of Formation, K cal/mol	117.5	142.8	178.5	216.7
Latent Heat of Vaporization, K cal/mol	6.720	9.940	14.280	18.680
Flash Point, °C open cup	1.11	70.0	111.11	140.5
Solubility				
(a) water	miscible	miscible	miscible	miscible
(b) ethanol	miscible	miscible	miscible	miscible
(c) acetone	miscible	miscible	miscible	miscible
(d) benzene	miscible	miscible	miscible	miscible
(e) ether	miscible	miscible	miscible	miscible
(f) octane	miscible	miscible	miscible	miscible
Color	water white	water white	water white	water white
Odor	etheral	faint pleasant	mild	very mild
pH	neutral	neutral	neutral	neutral

Chemical Co., Industrial Chemicals Division, Marinette, Wisc. Used as solute in extraction tests.

Toluene. Purified, lot No 6481 and No 90429.

Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. Used as extracting solvent in extraction tests and in determination of phase diagrams.

Toluene. Certified, reagent, lot No 771780.

Obtained from Fisher Scientific Co., Silver Spring, Md. Used as solvent in determination of equilibrium data.

Triethylene Glycol Dimethyl Ether. Lot No 77

and No 81; E-161. Obtained from Ansul Chemical Co., Industrial Chemicals Division. Marinette, Wisc. Used as solute in extraction tests.

Water. Tap. Obtained from water mains at

Virginia Polytechnic Institute, Blacksburg, Va. Used as carrier solvent in extraction tests.

Apparatus

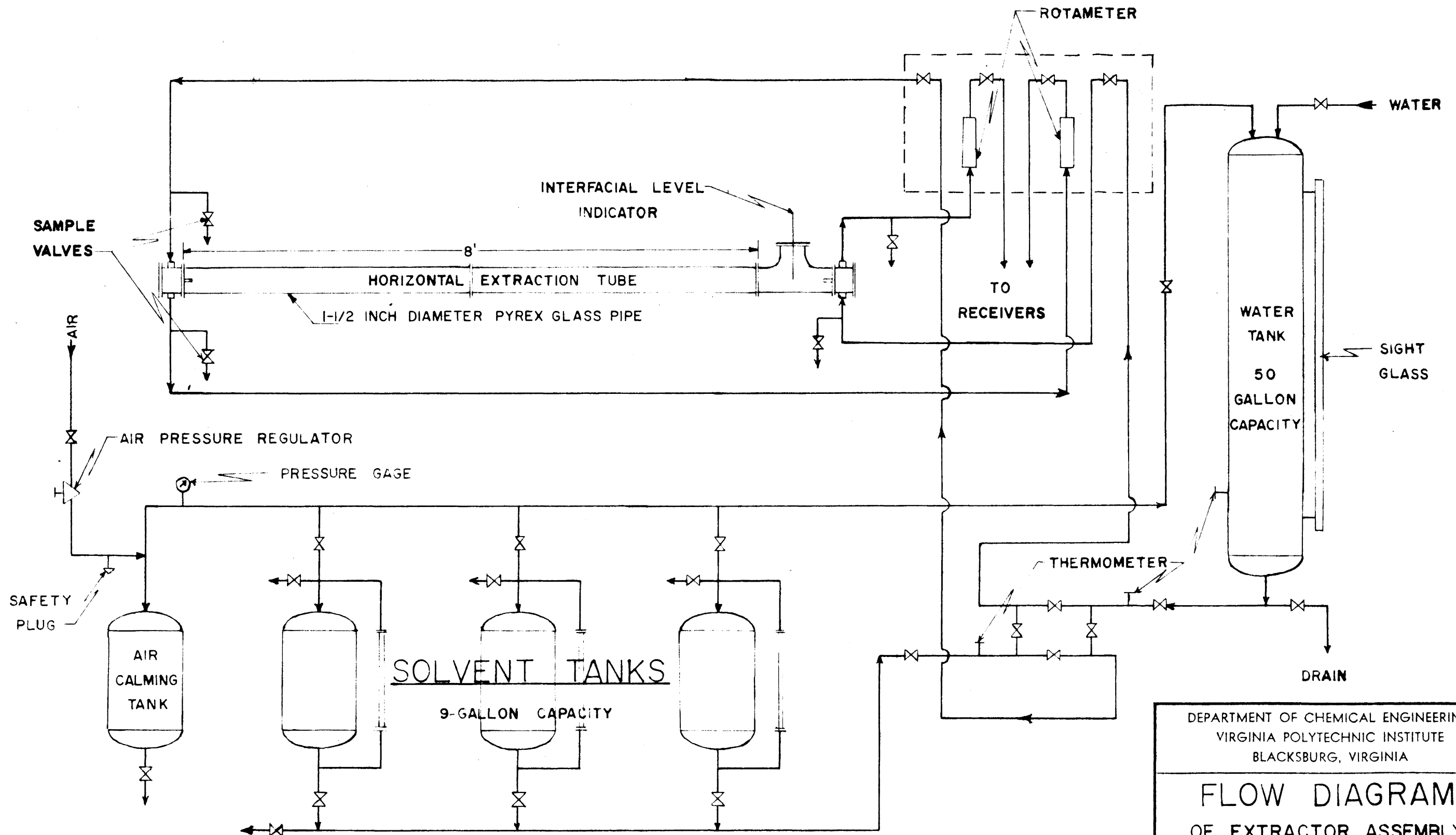
The apparatus used in this investigation is described in this section.

Balance, Analytical. Model No 2201-D, serial No M-16009. Manufactured by Voland and Sons, Inc., New Rochelle, N. Y. Used to weigh samples in determination of solubility data.

Balance, Beam. Triple beam type construction; capacity, 610 grams; sensitivity, 0.05 gram; catalog No 3-3423. Obtained from Phipps and Bird, Inc., Richmond, Va. Used to determine the weight rate of flow of raffinate and extract streams from the extractor.

Bath, Constant Temperature. Serial No J-4, catalog No 66600, 115 v, 50/60 cy, 4 amp, 450 w, single phase. Manufactured by Precision Scientific Co., Chicago, Ill. Used to maintain samples at constant temperature.

Extractor, Horizontal Tube. The extractor used in this investigation is shown in the flow diagram of the extractor assembly, Figure 2. The assembly is the same as that used by Mote⁽¹³⁾. A



NOTE: FLOW LINES ARE 3/8-INCH COPPER TUBING

DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

FLOW DIAGRAM OF EXTRACTOR ASSEMBLY

SCALE: NONE	DATE: 12/1/57	CASE NO: 50
DRAWN BY: JWP	12/1/57	FILE NO: 598
CHECKED BY: JWP	12/1/57	FIGURE NO: 2
APPROVED BY: JWP	12/1/57	SHEET NO: 1

detailed description of the extraction apparatus is given by Lastovica ⁽¹¹⁾ and Mote ⁽¹³⁾.

Glassware, Assorted. Sample bottles, burets, pipets, flasks, and other general laboratory glassware. Obtained from Fisher Scientific Co., Silver Spring, Md. Used in determination of phase diagrams.

Lamp, Sodium Vapor. Adjustable, self-contained unit including housing and support base; full power, 650 lumens of monochromatic light; catalog No 11-985. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as light source for refractometer.

Motor. Model No S60SBZ-1820, frame 567, type S, 1/4 hp, 1725 rpm, 115 v, 4.6 amp, 60 cy, single phase, code R. Manufactured by Emerson Electric Co., St. Louis, Mo. Used as power source for vacuum pump.

Pump. Serial No 10M16272, model No 13-061, 50/60 cy, 1550 rpm, 1.3 amp, 95 w. Manufactured by Universal Electric Co., Owosso, Mich. Used to circulate water in constant temperature bath.

Pump, Vacuum. Cenco-Pressovac 4. Manufactured by Central Scientific Co., Chicago, Ill. Used to fill feed and solvent tanks.

Refractometer, Dipping. Immersion type with constant temperature bath, serial No KM878, catalog No 33-45-26. Manufactured by Bausch and Lomb Optical Co., Rochester, N. Y. Used to measure refractive indices of samples.

Tanks, Storage. Five-gallon solvent cans and fifty-gallon, aluminum drop tanks. Manufacturers unknown. Used as receiving and storage tanks for exit streams from extractor.

Timer. Kodak, No 3X28922A, range 0-60 minutes, 0.5 second increments. Manufactured by Eastman Kodak Co., Rochester, N. Y. Used to time extraction tests.

Procedure

The methods of procedure used in this investigation are presented in this section.

Determination of Solubility Curves. Solubility curves were determined for each of the four systems. For the water phase, weighed amounts of water and ether were placed in a glass stoppered bottle. Toluene was added by means of a buret until the cloud point was reached. The bottle was placed in a constant temperature bath at 30 °C for approximately one hour. If at the end of this time the solution had become clear, additional toluene was added to make the solution cloudy again. A similar procedure was followed to find the solubility of ether in the toluene phase.

Refractive Index-concentration Curves. No data for the refractive index as a function of solute concentration were available for the systems used in this investigation. The refractive indices of the above samples were measured at 30 °C with a dipping refractometer. A curve of refractive index versus solute concentration was plotted.

Tie-line Data. Tie-line data were determined for each system by preparing two phase solutions of solute, toluene and water in varying concentrations, separating the phases, and measuring the refractive index of each phase at 30 °C. Before separating the phases the solutions were placed in a constant temperature bath at 30 °C for at least two hours. The concentration of solute in each phase was read from the refractive index-concentration curve.

Estimation of Plait Point. The plait points of the ternary systems investigated were estimated by the method proposed by Hand⁽¹⁷⁾.

Operation of Horizontal Tube Extractor. A horizontal tube extractor was used in this investigation to obtain extraction data for ternary systems which had solutes of varying molecular weight. The molecular weight of these solutes varied from 90 to 222. The feed concentrations used for the tests were approximately 13 to 15 weight per cent of solute in water. These concentrations were used since the viscosity, density, and interfacial tension of the two phases were approximately the same between systems at these concentrations. Two tests were made on each

system. The solvent phase flow rate varied from 19 to 34 pounds per hour, and the water phase flow rate varied from 15 to 35 pounds per hour.

The feed solution and solvent were transferred to the feed and solvent tanks by applying a vacuum at the top of the tanks and sucking the liquid through rubber tubing into the bottom of the tanks. The liquids were then transferred to the extractor by applying an air pressure of ten pounds per square inch, gauge, to the top of the feed and solvent tanks. The feed valve was opened and feed was forced into the extractor until it was half full. The feed valve was closed and the solvent valve was opened. Solvent was forced into the tube until it was completely full. The solvent valve was closed and any entrapped air bubbles were allowed to escape. The extraction tube was leveled and the interface adjusted to the half-way mark. The solvent, feed, extract, and raffinate valves were then adjusted to give the desired rotameter settings. A sample of the solvent and feed was obtained.

After the extraction tube was in operation for approximately 30 to 50 minutes, a sample was taken of all terminal streams. The extract and raffinate

streams were then sampled at ten-minute intervals for approximately 40 to 60 minutes. The feed and solvent streams were sampled at approximately 20- to 30-minute intervals over this same period of time. The flow rate of each phase was determined by collecting and weighing the leaving streams for a given time interval. At least three of these determinations were made for each phase during the test.

Analysis of Samples. The terminal streams of the extractor were analyzed by measuring the refractive index of the samples at 30 °C with a dipping refractometer. The solute concentrations were then read from the refractive index-concentration curves.

Determination of Physical Properties. The procedure for determining density, viscosity, surface tension, interfacial tension, and diffusivity is described by Landis⁽¹⁰⁾.

Data and Results

The data and results obtained during this investigation are presented in this section.

Refractive Index-concentration Data. The data obtained for analysis of samples by refractive index are shown in Tables III, V, VII, and IX. These data are shown graphically in Figure 3.

Phase Diagrams. The data obtained for determining the phase diagrams for the systems investigated are shown in Tables III, V, VII, and IX. The diagrams are plotted in Figures 4, 5, 6, and 7.

Physical Properties. The values for the physical properties determined by Landis⁽¹⁰⁾ are presented in Tables IV, VI, VIII, and X. These data are shown graphically in Figures 8, 9, 10, 11, and 12.

Equilibrium Distribution Data. The equilibrium distribution data are graphically represented in Figure 13.

Plait Points. Figures 14, 15, 16, and 17, were used to estimate the plait points for the systems investigated.

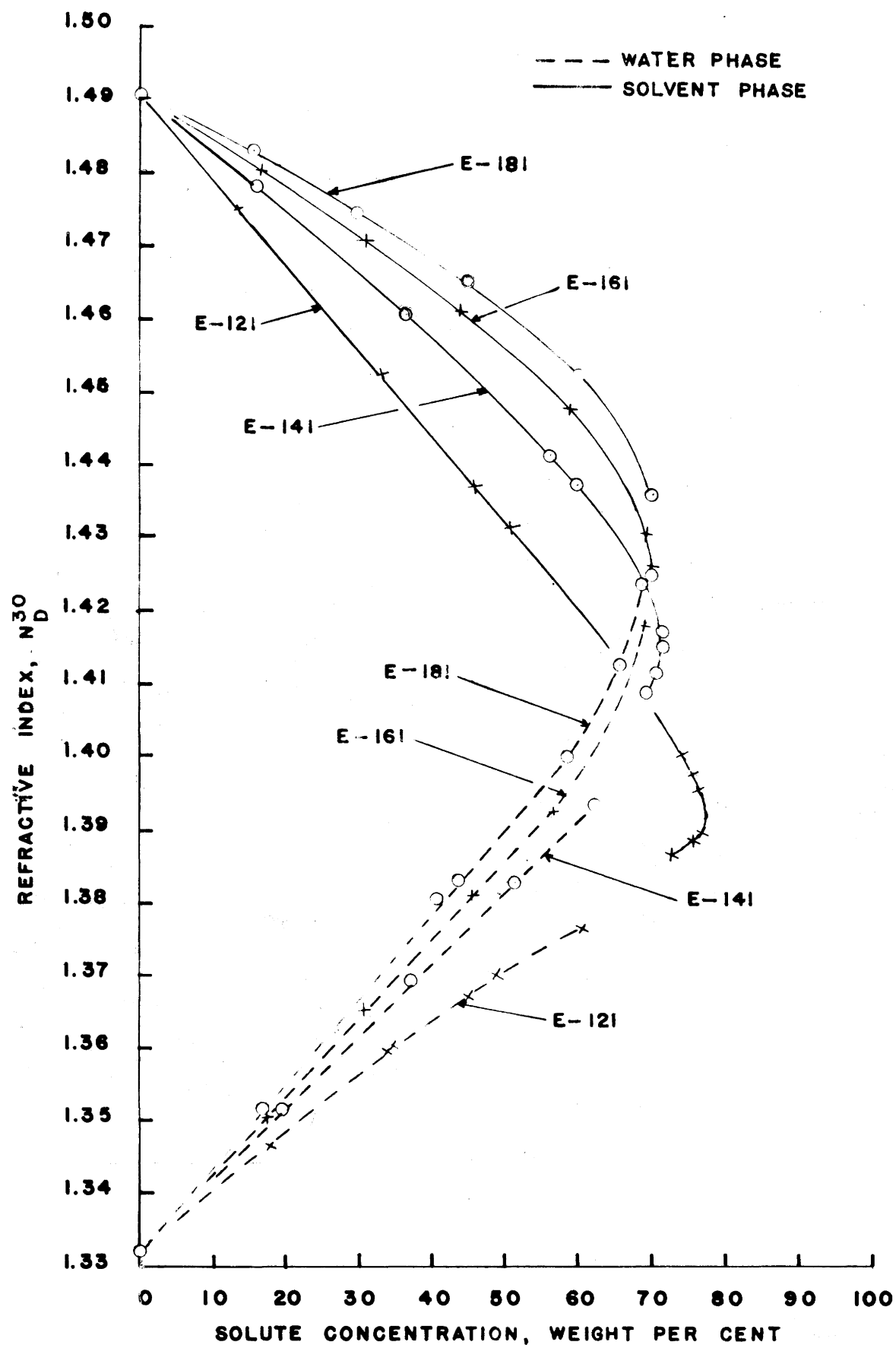


FIGURE 3. REFRACTIVE INDICES FOR SYSTEMS OF TOLUENE-POLY GLYCOL ETHERS-WATER AT 30 °C

TABLE III

Solubility and Tie Line Data for Toluene-Ethylene

Glycol Dimethyl Ether-Water System at 30 °C

Solubility Data

Refractive Index n_d^{30}	Concentration,		
	Solute wt %	Water wt %	Toluene wt %
1.47511	13.40	0.14	86.46
1.45233	33.09	0.17	66.74
1.43696	45.91	0.59	52.50
1.43138	50.86	0.51	48.63
1.40031	74.00	5.51	20.49
1.39744	75.48	6.63	17.89
1.39545	76.24	7.43	16.33
1.38954	76.73	11.95	11.32
1.38951	75.58	14.80	9.62
1.38644	72.27	20.74	6.99
1.37650	60.56	37.10	2.34
1.37628	60.36	37.20	2.44
1.37006	48.80	50.38	0.82
1.36733	44.89	54.85	0.26
1.36043	34.63	64.94	0.43
1.35975	33.84	66.10	0.06
1.34670	17.76	82.20	0.04
Estimated Plait Point			
	67.3	27.6	4.6

Tie Line Data

Refractive Index		Solute Concentration	
Water Phase	Toluene Phase	Water Phase	Toluene Phase
n_d^{30}		wt %	wt %
1.33617	1.48558	5.0	4.5
1.33984	1.47990	9.4	9.3
1.34336	1.47170	13.7	16.2
1.34749	1.46522	18.6	21.7
1.35372	1.45158	26.3	33.5
1.36338	1.42242	39.2	58.2
1.36387	1.42288	39.2	57.8
1.3705	1.40239	50.2	72.5
1.33206		water saturated with toluene	
	1.49096	toluene saturated with water	

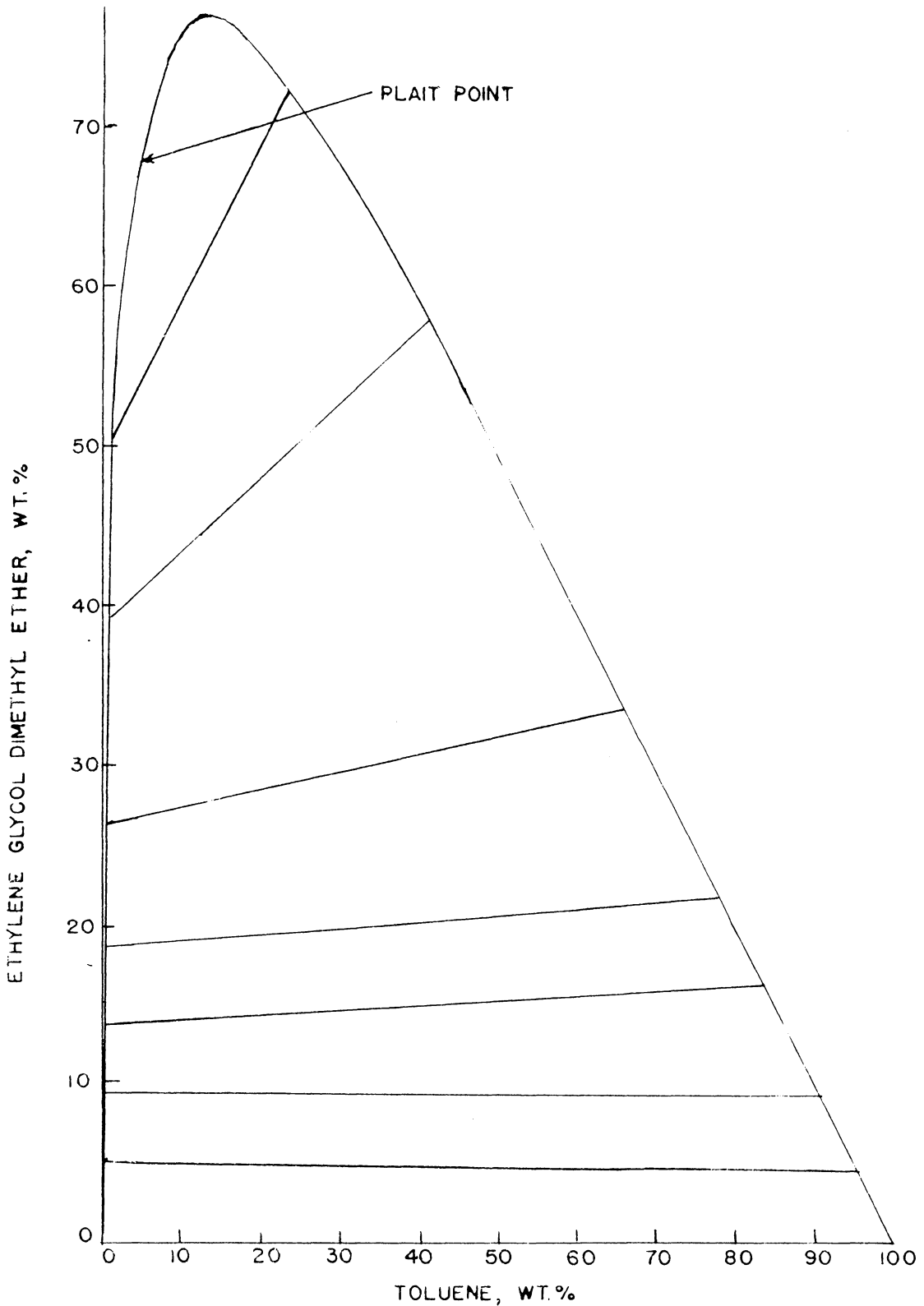


FIGURE 4. TERNARY PHASE DIAGRAM FOR THE SYSTEM
TOLUENE-ETHYLENE GLYCOL DIMETHYL ETHER-WATER
AT 30°C

TABLE IV

Physical Properties of Systems of Toluene and Water Containing E-121 at 30 °C

Test No	Phase	Composition			Density gm/ml	Viscosity cp	Surface Tension dynes/cm	Inter- facial Tension dynes/cm	Diffu- sivity X 10 ³ sq ft/hr
		E-121 wt%	Toluene wt%	Water wt%					
1-A	H ₂ O	0.0	0.0	100.0	0.9952	0.801	69.1	24.4	4.06
	Tol	0.0	100.0	0.0	0.8572	0.525	30.4		8.76
2-A	H ₂ O	5.0	0.07	94.83	0.9926	0.924	60.7	17.6	---
	Tol	4.5	95.25	0.25	0.8575	0.521	29.1a		8.84
3-A	H ₂ O	9.4	0.2	90.4	0.9900	1.049	56.2	14.6	3.10
	Tol	9.3	90.4	0.3	0.8575	0.514	29.3		8.94
4-A	H ₂ O	13.7	0.3	86.0	0.9886	1.157	47.1a	13.4a	2.82
	Tol	16.2	83.4	0.4	0.8571	0.506	29.5a		9.10
5-A	H ₂ O	18.6	0.35	81.05	0.9862	1.302	48.2	11.9a	2.50
	Tol	21.7	77.8	0.5	0.8573	0.504	29.05		9.12
6-A	H ₂ O	26.3	0.4	73.3	0.9828	1.3175a	43.95	7.5	---
	Tol	33.5	65.8	0.7	0.8583	0.4925	28.9		9.34
7-A	H ₂ O	39.2	0.5	60.3	0.9735a	1.508a	37.0	3.1a	---
	Tol	58.2	40.6	1.2	0.8615a	0.481a	28.35a		---
8-A	H ₂ O	39.2	0.5	60.3	0.9730	1.751	37.8a	3.1	1.86
	Tol	57.8	41.0	1.2	0.8622	0.484	27.9		9.50
9-A	H ₂ O	50.2	0.9	48.9	0.9599	1.697	31.4	0.95	1.92
	Tol	72.5	23.0	4.5	0.8687	0.514	26.9		8.96

a) refers to experimental points not used in plotting the curves

TABLE V

Solubility and Tie Line Data for Toluene-Diethylene
Glycol Dimethyl Ether-Water System at 30 °C

Solubility Data			
Refractive Index 30 n _d	Concentration,		
	Solute wt %	Water wt %	Toluene wt %
1.47790	15.89	0.16	83.95
1.46037	36.38	0.76	62.96
1.44128	56.16	2.58	41.26
1.43714	59.78	3.38	36.84
1.42478	69.34	7.66	23.00
1.41698	71.23	12.15	16.62
1.41493	71.32	14.16	14.52
1.41164	70.56	16.33	13.51
1.41166	70.80	17.47	11.73
1.41121	70.30	18.07	11.63
1.40850	69.33	20.08	9.87
1.39332	62.06	35.36	2.58
1.38274	51.32	48.06	0.61
1.36915	37.08	62.59	0.33
1.35163	19.53	80.43	0.04
Estimated Plait Point			
	68.1	24.0	7.9

Tie Line Data			
Refractive Index		Solute Concentration	
Water Phase	Toluene Phase	Water Phase	Toluene Phase
30 n _d		wt %	wt %
1.33825	1.48759	6.2	4.1
1.34398	1.48387	12.0	8.6
1.34921	1.47956	17.9	13.9
1.35515	1.47500	23.2	19.4
1.36422	1.46527	32.3	30.8
1.37971	1.44234	47.8	55.1
1.38291	1.43770	51.1	59.2
1.39173	1.42442	60.0	69.4
1.36942	1.46062	37.5	36.1
1.37706	1.44889	45.1	48.6

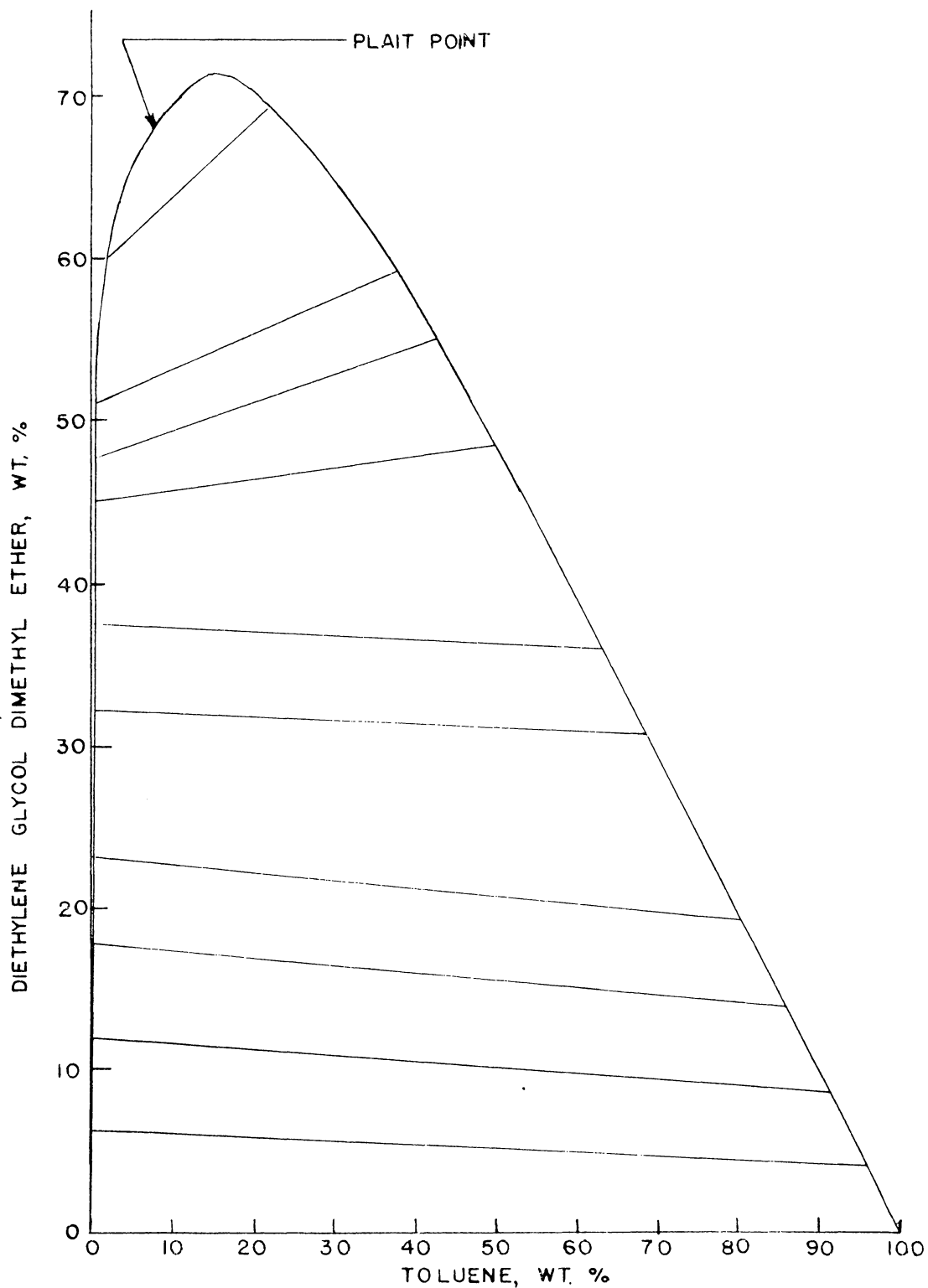


FIGURE 5. TERNARY PHASE DIAGRAM FOR THE SYSTEM
TOLUENE-DIETHYLENE GLYCOL DIMETHYL
ETHER-WATER AT 30°C

TABLE VI

Physical Properties of Systems of Toluene and Water Containing E-141 at 30 °C

Test No	Phase	Composition			Density gm/ml	Viscosity cp	Surface Tension dynes/cm	Inter-facial Tension dynes/cm	Diffusivity X 10 ³ sq ft/hr
		E-141 wt%	Toluene wt%	Water wt%					
1-B	H ₂ O	0.0	0.0	100.0	0.9952	0.801	69.1	24.4	3.57
	Tol	0.0	100.0	0.0	0.8572	0.525	30.4		6.77
2-B	H ₂ O	6.2	0.17	93.63	0.9965	0.955 ^a	59.45	18.0	—
	Tol	4.1	95.75	0.15	0.8596	0.535 ^a	30.25		—
3-B	H ₂ O	12.0	0.22	87.78	0.9980	1.041	55.2	13.1	2.75
	Tol	8.6	91.2	0.2	0.8629	0.550	30.4		6.46
4-B	H ₂ O	17.9	0.3	81.8	0.9999	1.193	52.55	10.5	2.40
	Tol	13.9	85.7	0.4	0.8671	0.565	30.5		6.29
5-B	H ₂ O	23.2	0.34	76.46	1.0010	1.362	49.65	8.6	2.10
	Tol	19.4	80.1	0.5	0.8711	0.576	30.5		6.17
6-B	H ₂ O	32.3	0.4	67.3	1.0031	1.660	46.4 ^a	5.9	1.72
	Tol	30.8	68.5	0.7	0.8806	0.621	30.7		5.72
7-B	H ₂ O	47.8	0.5	51.7	1.0006	2.140	39.6	2.1	1.34
	Tol	55.1	42.4	2.5	0.9042	0.756	31.2		4.70
8-B	H ₂ O	51.1	0.5	48.4	0.9995	2.155	37.4	1.67	1.33
	Tol	59.2	37.5	3.3	0.9116	0.777	30.85		4.57
9-B	H ₂ O	60.0	1.8	38.2	0.9900	2.100	34.0	0.17	1.36
	Tol	69.4	22.2	8.4	0.9291	0.932	31.7		3.82

^a) refers to experimental points not used in plotting the curves

TABLE VII

Solubility and Tie Line Data for Toluene-Triethylene
Glycol Dimethyl Ether-Water System at 30 °C

Refractive Index n_d^{30}	Solubility Data		
	Concentration,		
	Solute wt %	Water wt %	Toluene wt %
1.48010	16.51	0.20	83.29
1.47078	30.66	0.33	69.01
1.46096	43.87	0.76	55.37
1.44774	58.85	3.24	37.91
1.43052	69.17	10.08	20.03
1.42548	69.85	14.16	15.99
1.42474	69.74	14.63	15.63
1.41793	69.05	20.42	10.53
1.39236	56.35	43.43	0.22
1.38113	45.30	54.65	0.05
1.36540	30.69	69.29	0.02
1.35076	17.44	82.50	0.06
	Estimated Plait Point		
	69.3	19.2	11.5

Refractive Index		Solute Concentration	
Water Phase n_d^{30}	Toluene Phase n_d^{30}	Water Phase wt %	Toluene Phase wt %
1.33862	1.48947	6.1	2.0
1.34486	1.48769	12.0	4.9
1.35144	1.48553	18.1	8.1
1.35752	1.48298	23.8	12.0
1.36790	1.47699	33.3	21.0
1.38621	1.45921	50.2	46.0
1.39010	1.45506	53.9	51.0
1.39949	1.44292	62.6	62.8
1.37876	1.46921	43.3	32.8

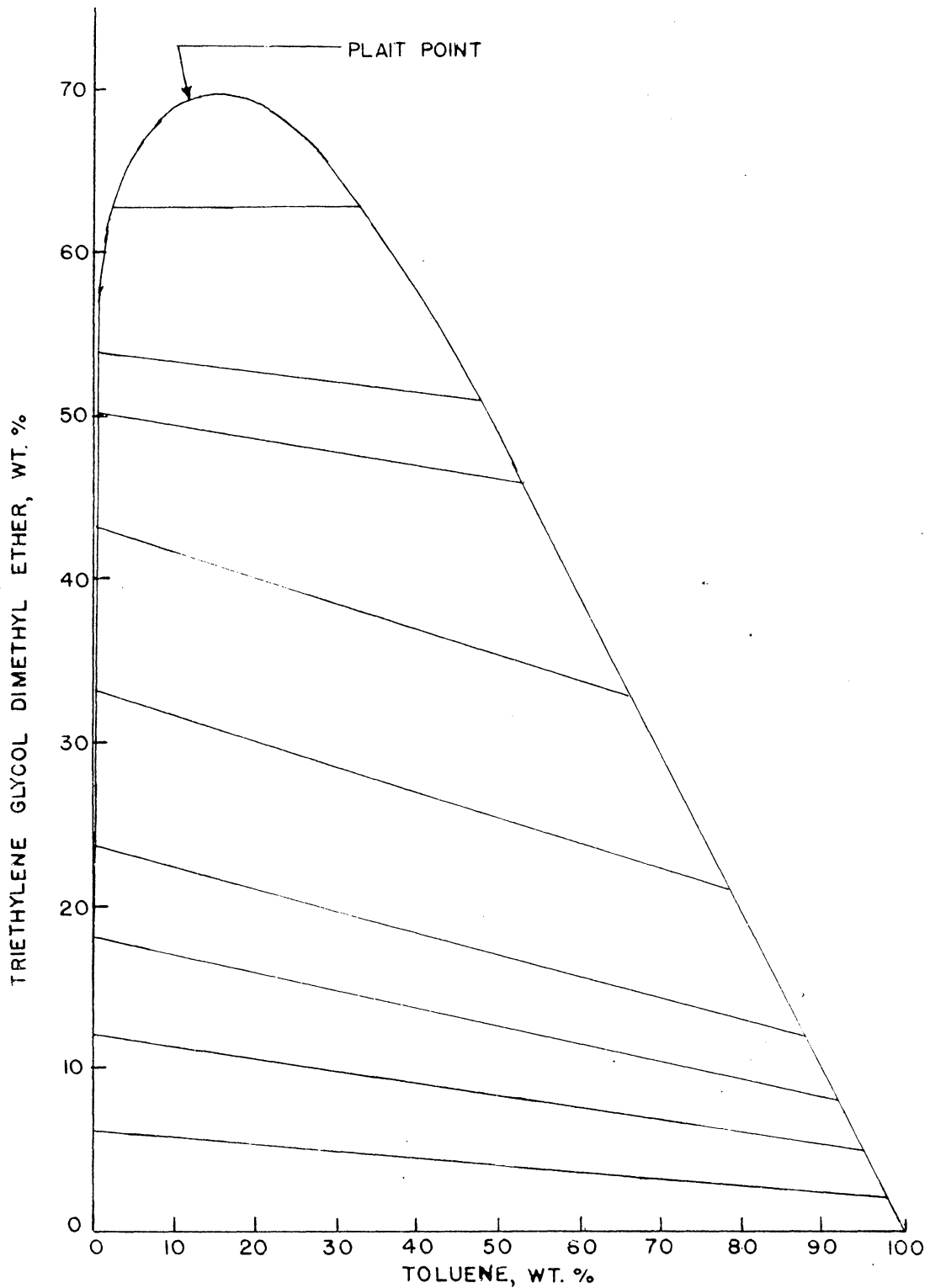


FIGURE 6. TERNARY PHASE DIAGRAM FOR THE SYSTEM
TOLUENE-TRIETHYLENE GLYCOL DIMETHYL
ETHER-WATER AT 30°C

TABLE VIII

Physical Properties of Systems of Toluene and Water Containing E-161 at 30 °C

Test NO	Phase	Composition			Density	Viscosity	Surface Tension	Interfacial Tension	Diffusivity
		E-161 wt%	Toluene wt%	Water wt%	gm/ml	cp	dynes/cm	dynes/cm	X 10 ⁵ sq ft/hr
1-C	H ₂ O	0.0	0.0	100.0	0.9952	0.801	69.1	24.4	2.76
	Tol	0.0	100.0	0.0	0.8572	0.525	30.4		5.78
2-C	H ₂ O	6.1	0.1	93.8	0.9986	0.918 _a	60.9	17.3	2.41
	Tol	2.0	97.9	0.1	0.8596 _a	0.537 _a	30.15 _a		---
3-C	H ₂ O	12.0	0.12	87.88	1.0029	1.055	57.7	14.5	2.10
	Tol	4.9	94.95	0.15	0.8624	0.552 _a	30.3		---
4-C	H ₂ O	18.1	0.15	81.75	1.0062	1.236	54.7	11.5	1.79
	Tol	8.1	91.7	0.2	0.8660 _a	0.5715 _a	30.4		---
5-C	H ₂ O	23.8	0.17	76.03	1.0099	1.446	52.6	9.0	1.53
	Tol	12.0	87.7	0.3	0.8711	0.592	30.45		5.07
6-C	H ₂ O	33.3	0.2	66.5	1.0161	1.872	48.9	6.6	1.18
	Tol	21.0	78.6	0.4	0.8814	0.650	30.5		4.62
7-C	H ₂ O	50.2	0.25	49.55	1.0219	2.768	43.2	3.0	0.798
	Tol	46.0	53.0	1.0	0.9130	0.839	31.5		3.58
8-C	H ₂ O	53.9	0.25	45.85	1.0218	2.908	42.2	2.15	0.766
	Tol	51.0	47.6	1.4	0.9925	0.913	32.3 _a		3.29
9-C	H ₂ O	62.6	3.3	34.1	1.0174	3.097	38.8	0.60	0.714
	Tol	62.8	32.8	4.4	0.9451	1.157	32.3		2.60

a) refers to experimental points not used in plotting the curves

TABLE IX

Solubility and Tie Line Data for Toluene-Tetraethylene
Glycol Dimethyl Ether-Water System at 30 °C

Solubility Data			
Refractive Index 30 n_d	Concentration,		
	Solute wt %	Water wt %	Toluene wt %
1.48293	15.15	0.14	94.71
1.47470	29.62	0.31	70.07
1.46491	44.67	1.29	54.04
1.45203	59.96	4.01	36.13
1.43574	69.94	11.78	18.28
1.42355	68.63	21.25	10.12
1.41248	65.30	30.47	4.23
1.39972	58.15	41.68	0.17
1.38316	43.24	56.69	0.07
1.38046	40.53	59.04	0.43
1.35149	16.83	83.11	0.06
Estimated Plait Point			
	69.0	19.8	11.2

Tie Line Data			
Refractive Index		Solute Concentration	
Water Phase	Toluene Phase	Water Phase	Toluene Phase
30 n_d		wt %	wt %
1.33997	1.49017	6.6	1.5
1.34716	1.48911	12.9	3.6
1.35394	1.48769	18.7	6.5
1.36091	1.48582	24.6	9.9
1.37237	1.48113	34.4	18.0
1.39201	1.46612	51.3	42.7
1.39610	1.46201	54.9	48.5
1.40624	1.45046	62.2	61.1
1.38287	1.47540	43.4	28.1

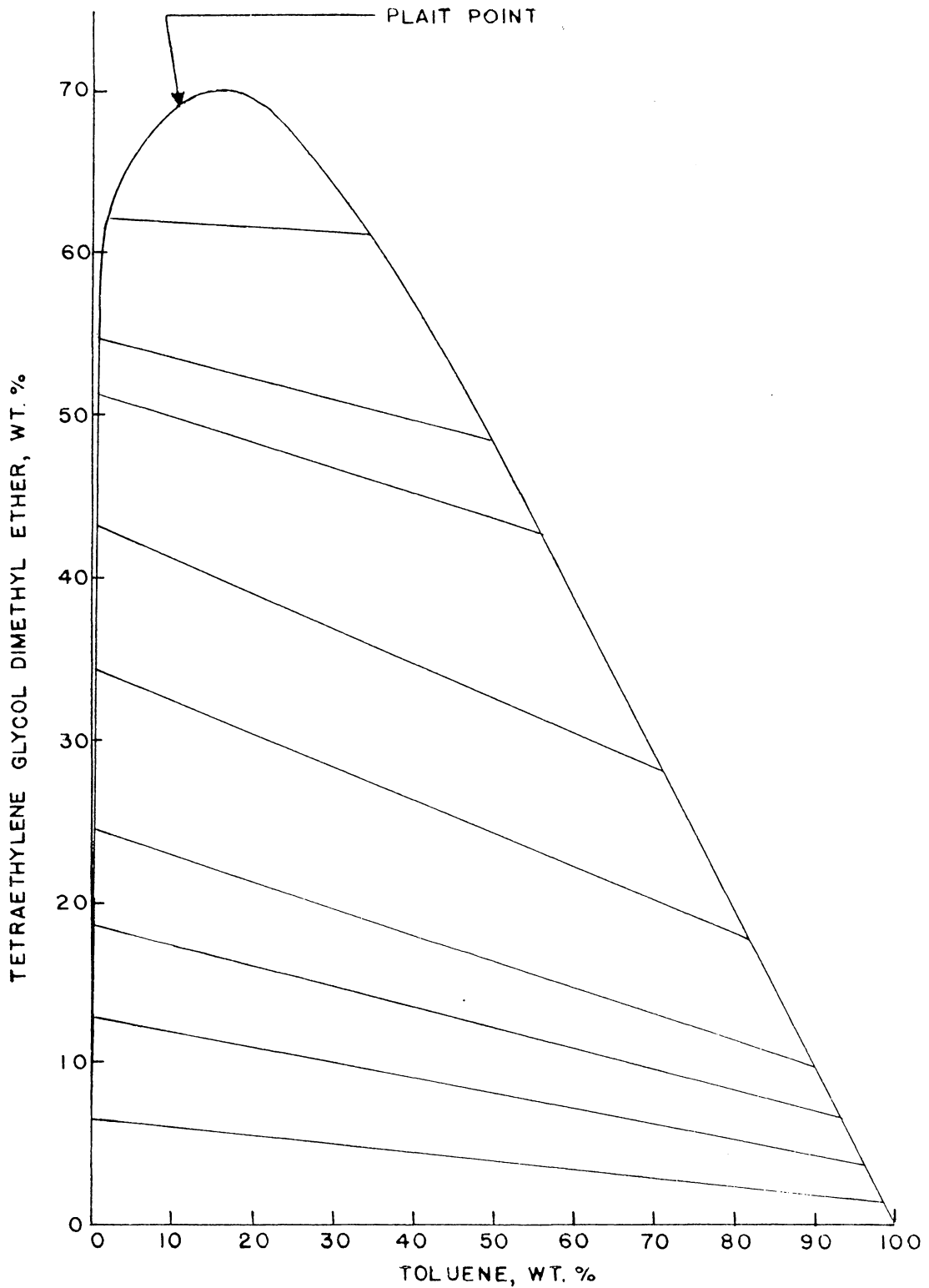


FIGURE 7. TERNARY PHASE DIAGRAM FOR THE SYSTEM
TOLUENE-TETRAETHYLENE GLYCOL DIMETHYL
ETHER-WATER AT 30° C

TABLE I

Physical Properties of Systems of Toluene and Water Containing E-181 at 30 °C

Test No	Phase	Composition			Density gm/ml	Viscosity cp	Surface Tension dynes/cm	Inter- facial Tension dynes/cm	Diffu- sivity X 10 ⁵ sq ft/hr
		E-181 wt%	Toluene wt%	Water wt%					
1-D	H ₂ O	0.0	0.0	100.0	0.9952	0.801	69.1	24.4	2.48
	Tol	0.0	100.0	0.0	0.8572	0.525	30.4		5.19
2-D	H ₂ O	6.6	0.17	93.23	1.0006	0.937	60.2	13.6a	---
	Tol	1.5	98.4	0.1	0.8586a	0.5415a	29.9a		---
3-D	H ₂ O	12.9	0.25	86.85	1.0058	1.120	57.3	12.5	1.78
	Tol	3.6	96.3	0.1	0.8614	0.586a	30.1a		---
4-D	H ₂ O	18.7	0.3	81.0	1.0104	1.339a	55.45	10.0	---
	Tol	6.5	93.3	0.2	0.8644	0.6035	30.25		4.52
5-D	H ₂ O	24.6	0.35	75.05	1.0154	1.602	53.6	8.5	1.24
	Tol	9.9	89.8	0.3	0.8695	0.619a	30.65a		---
6-D	H ₂ O	34.4	0.4	65.2	1.0233	2.179	50.5	6.5	0.912
	Tol	18.0	81.5	0.5	0.8806	0.673	30.7		4.05
7-D	H ₂ O	51.3	0.5	48.2	1.0326	3.449	44.9a	2.7	0.576
	Tol	42.7	55.9	1.4	0.9162	0.907	31.9		3.00
8-D	H ₂ O	54.9	0.5	44.6	1.0326	3.741	42.0	2.02	0.531
	Tol	48.5	49.6	1.9	0.9276a	1.0165	30.25a		2.68
9-D	H ₂ O	62.2	1.8	36.0	1.0295	4.067	38.7	0.52	0.489
	Tol	61.1	34.5	4.4	0.9545	1.421	33.2		1.92

a) refers to experimental points not used in plotting the curves

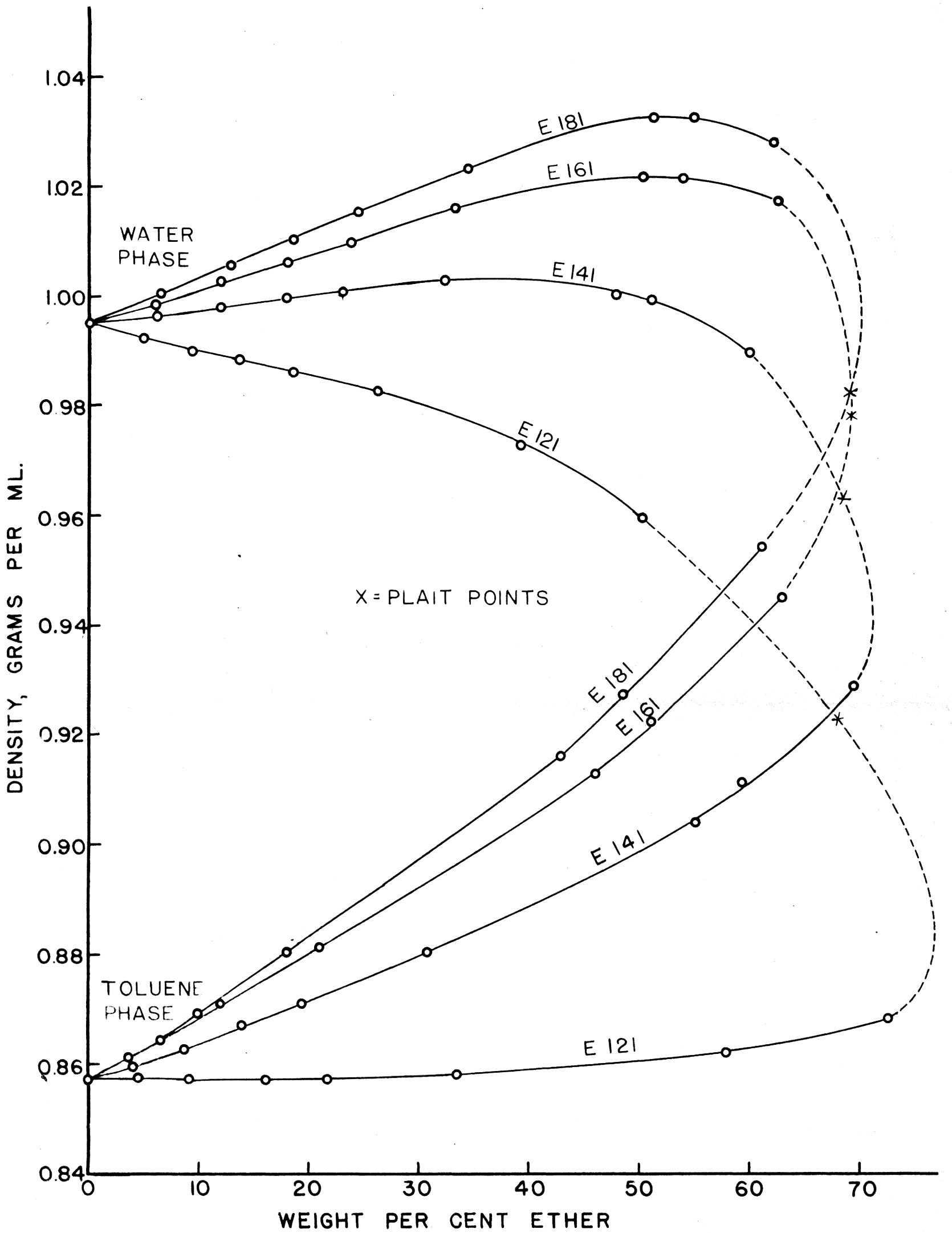


FIGURE 8. VARIATION OF DENSITY WITH CONCENTRATION OF ETHER FOR SYSTEMS OF GLYCOL ETHERS - TOLUENE - WATER AT 30°C.

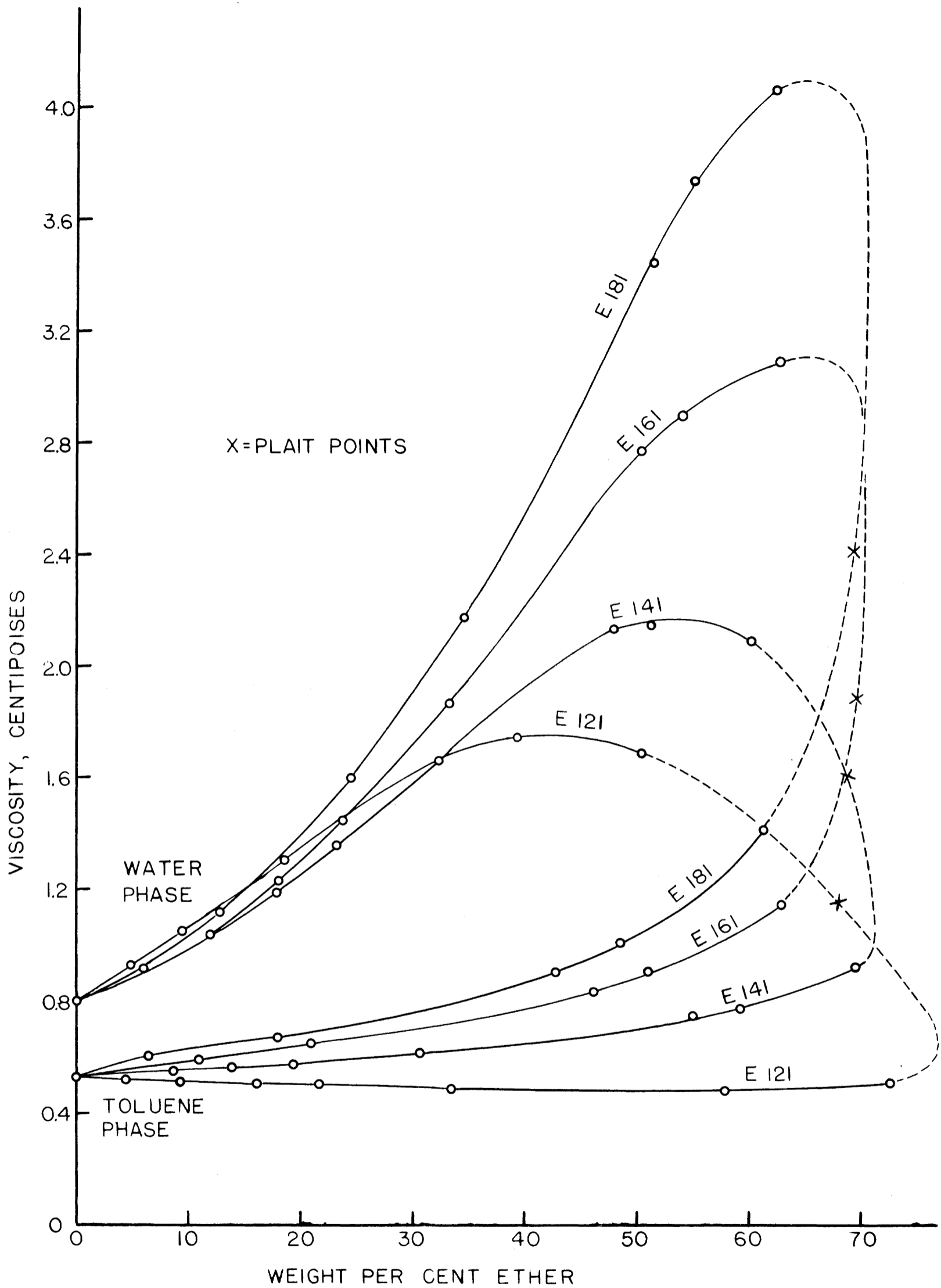


FIGURE 9. VARIATION OF VISCOSITY WITH CONCENTRATION OF ETHER FOR SYSTEMS OF GLYCOL ETHERS-TOLUENE-WATER AT 30°C.

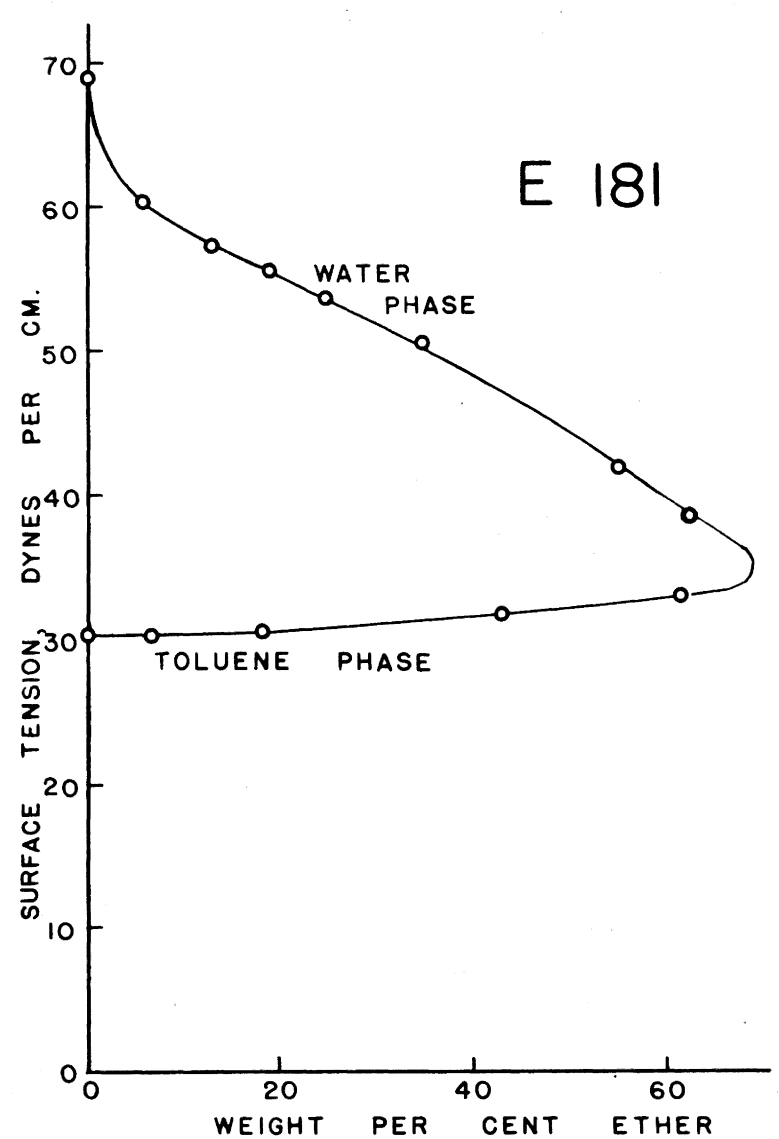
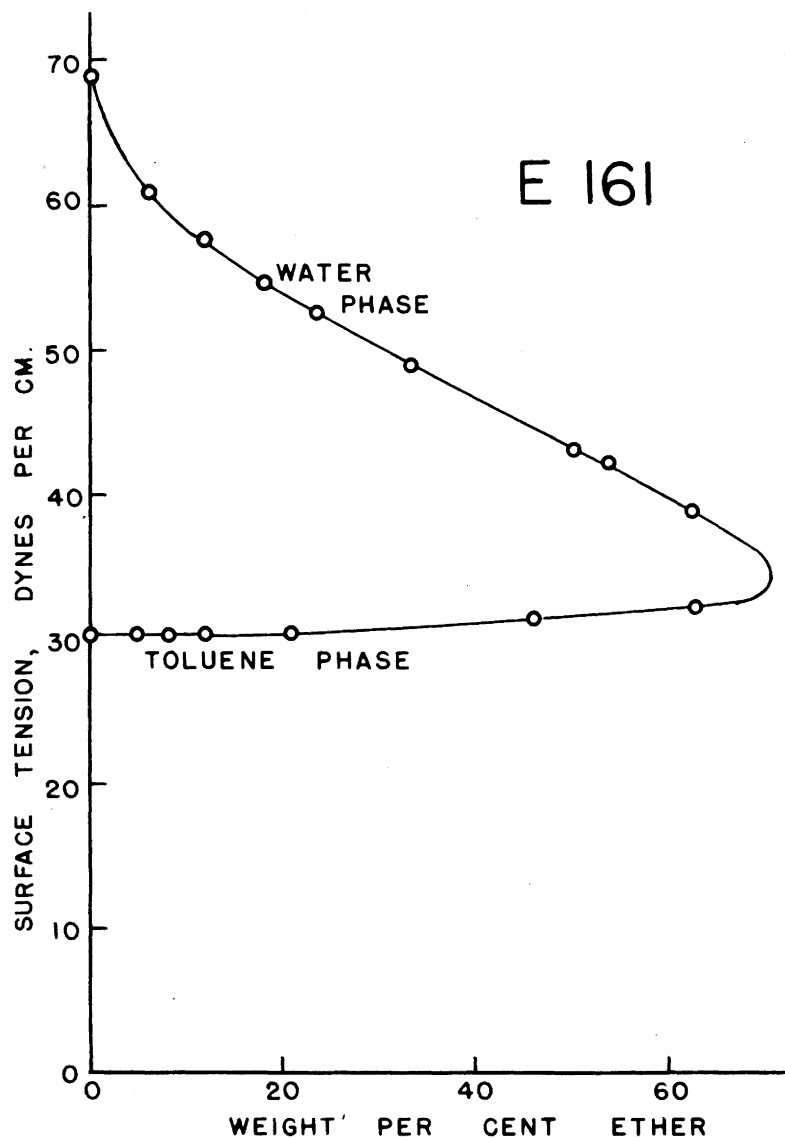
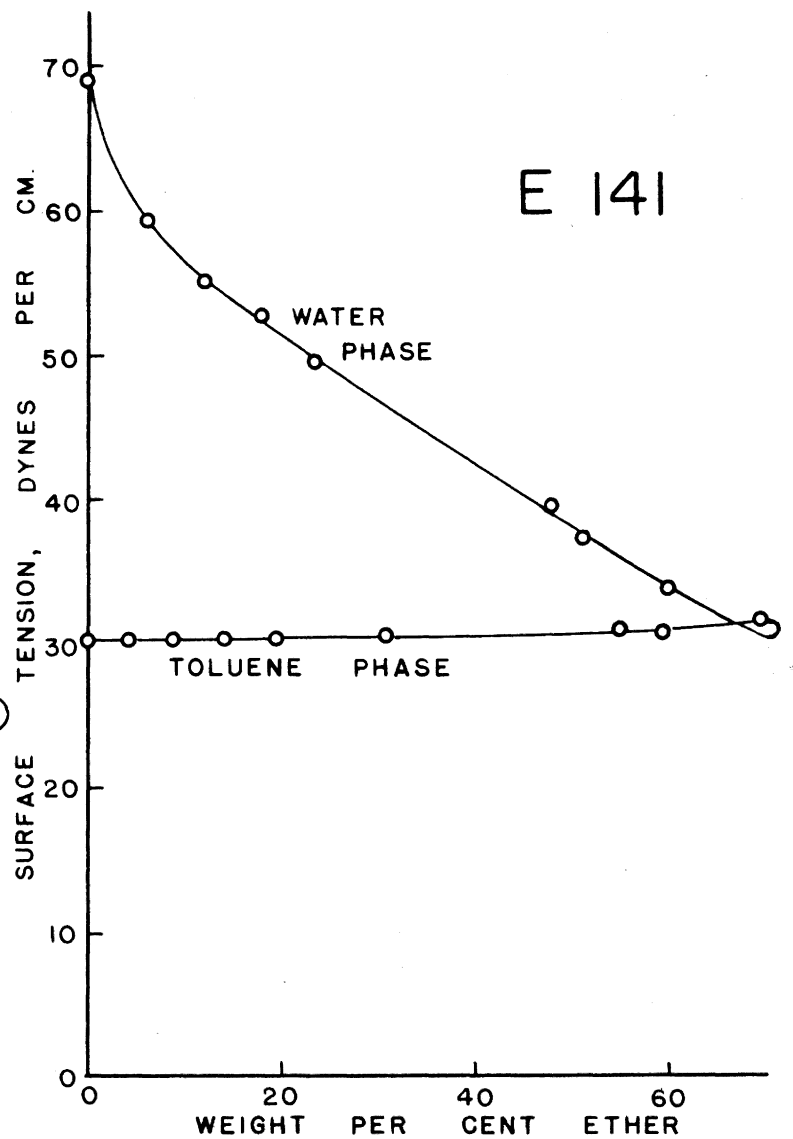
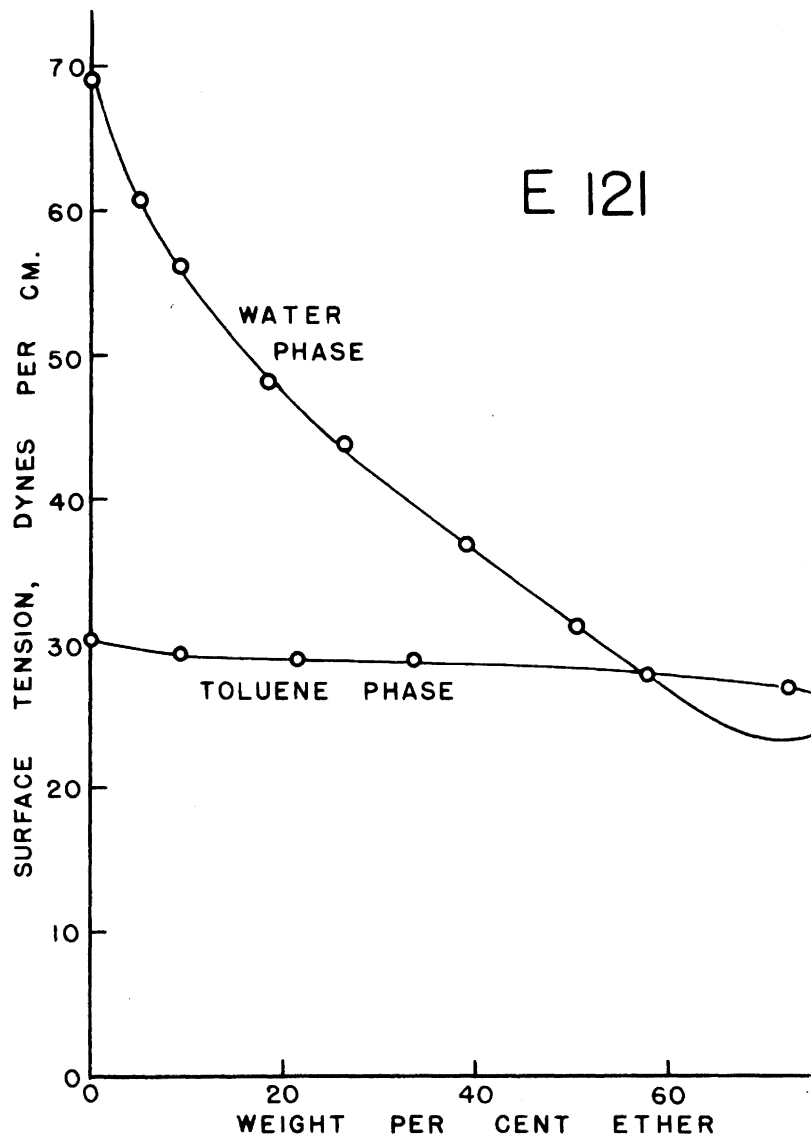


FIGURE 10. VARIATION OF SURFACE TENSION WITH CONCENTRATION OF ETHER FOR SYSTEMS OF GLYCOL ETHERS-TOLUENE-WATER AT 30°C.

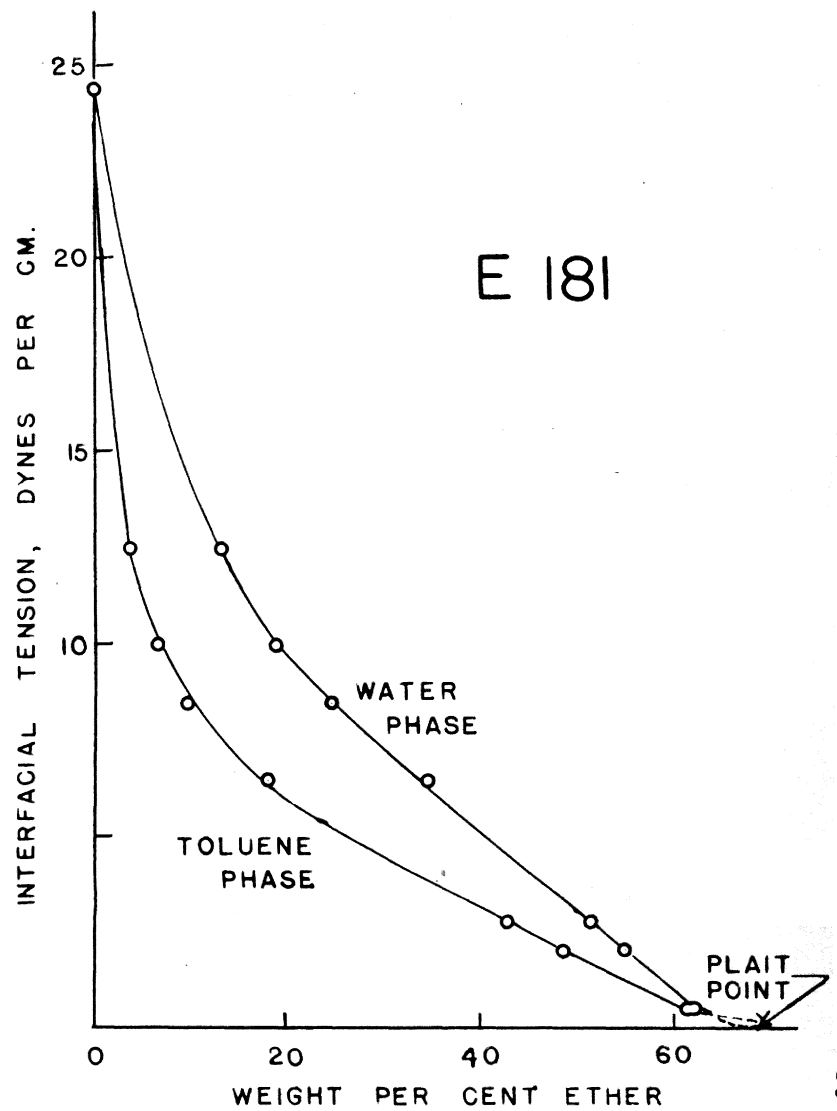
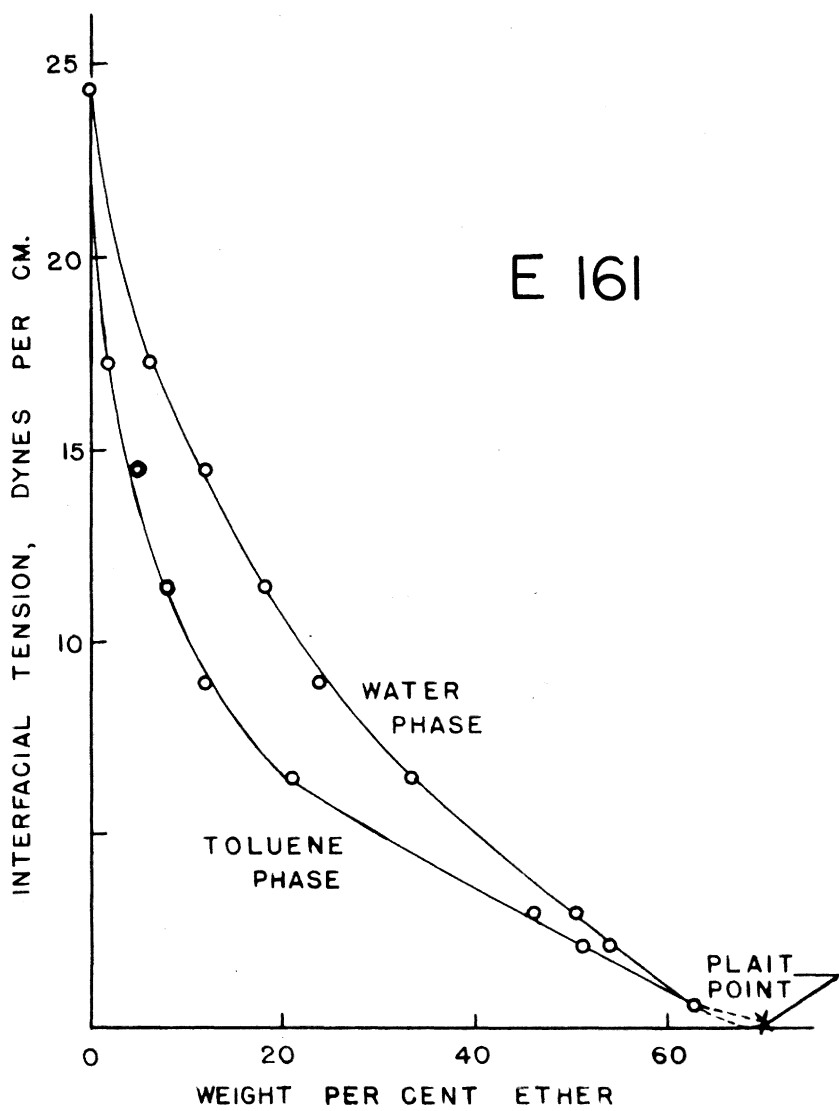
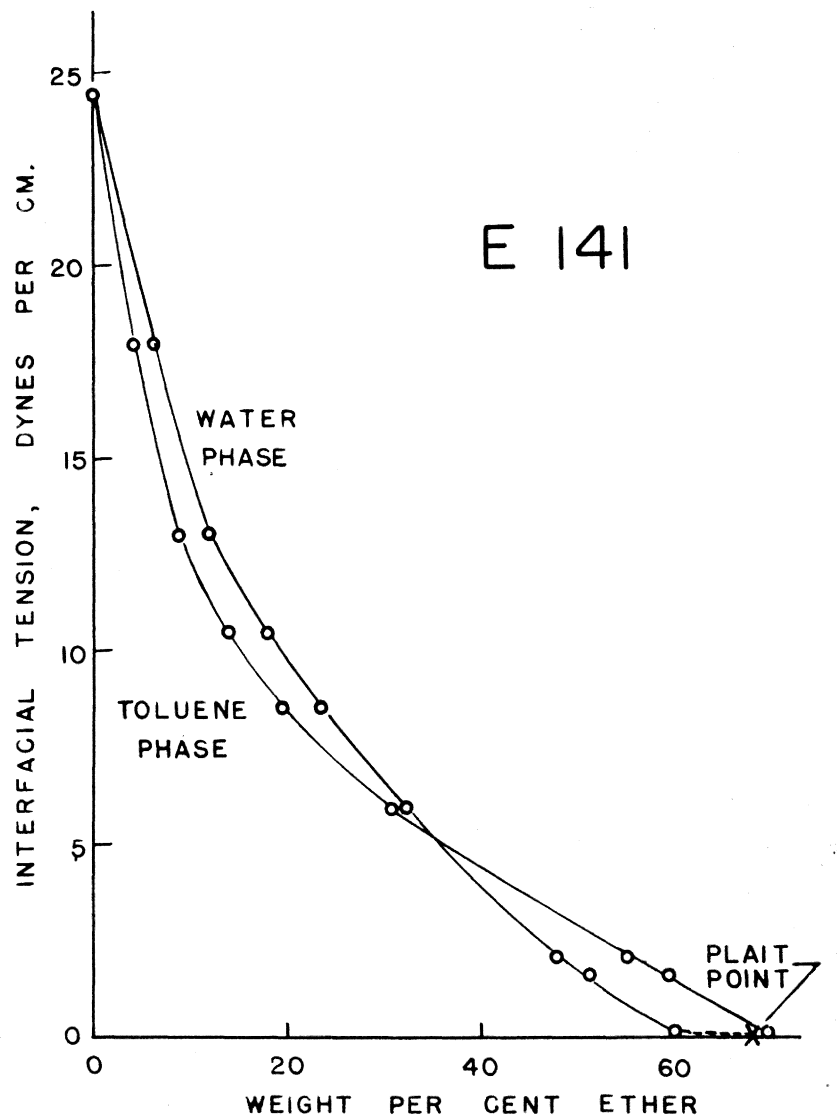
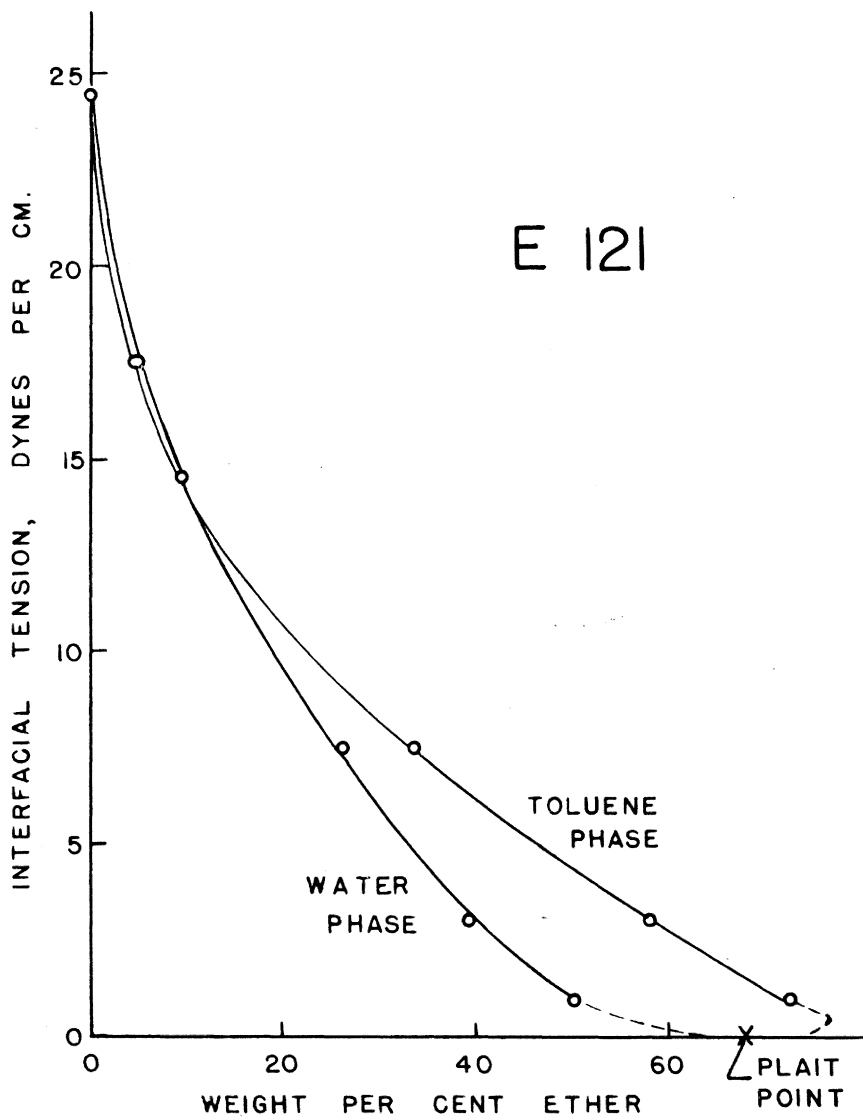


FIGURE II. VARIATION OF INTERFACIAL TENSION WITH CONCENTRATION OF ETHER FOR SYSTEMS OF GLYCOL ETHERS - TOLUENE-WATER AT 30°C.

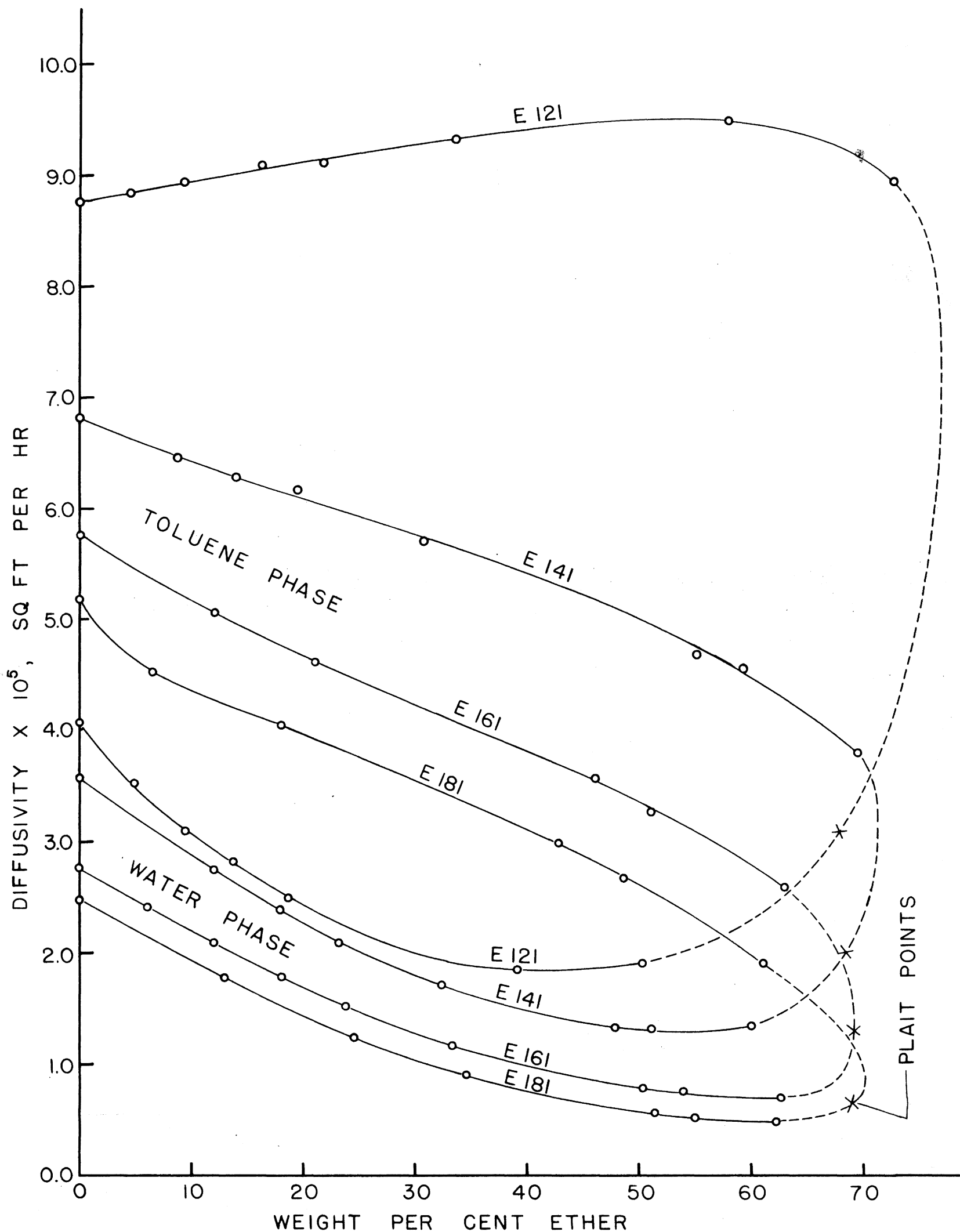


FIGURE 12. VARIATION OF DIFFUSIVITY WITH CONCENTRATION OF ETHER FOR SYSTEMS OF GLYCOL ETHERS-TOLUENE-WATER AT 30 °C

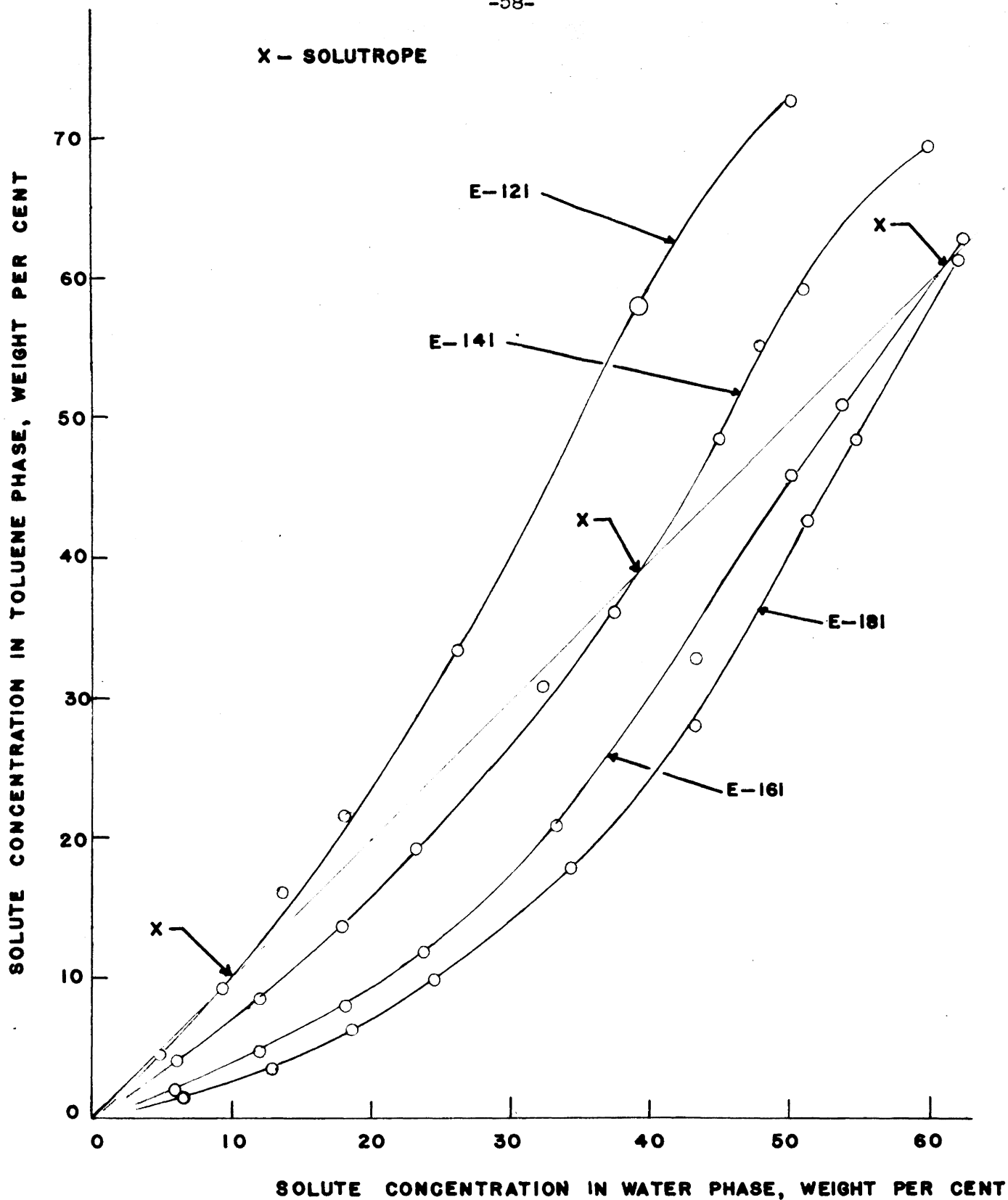


FIGURE 13. DISTRIBUTION OF SOLUTE BETWEEN TOLUENE AND WATER FOR TOLUENE-POLY GLYCOL ETHER-WATER SYSTEMS AT 30 °C

LD
5655
V855
1958
P874
c.2

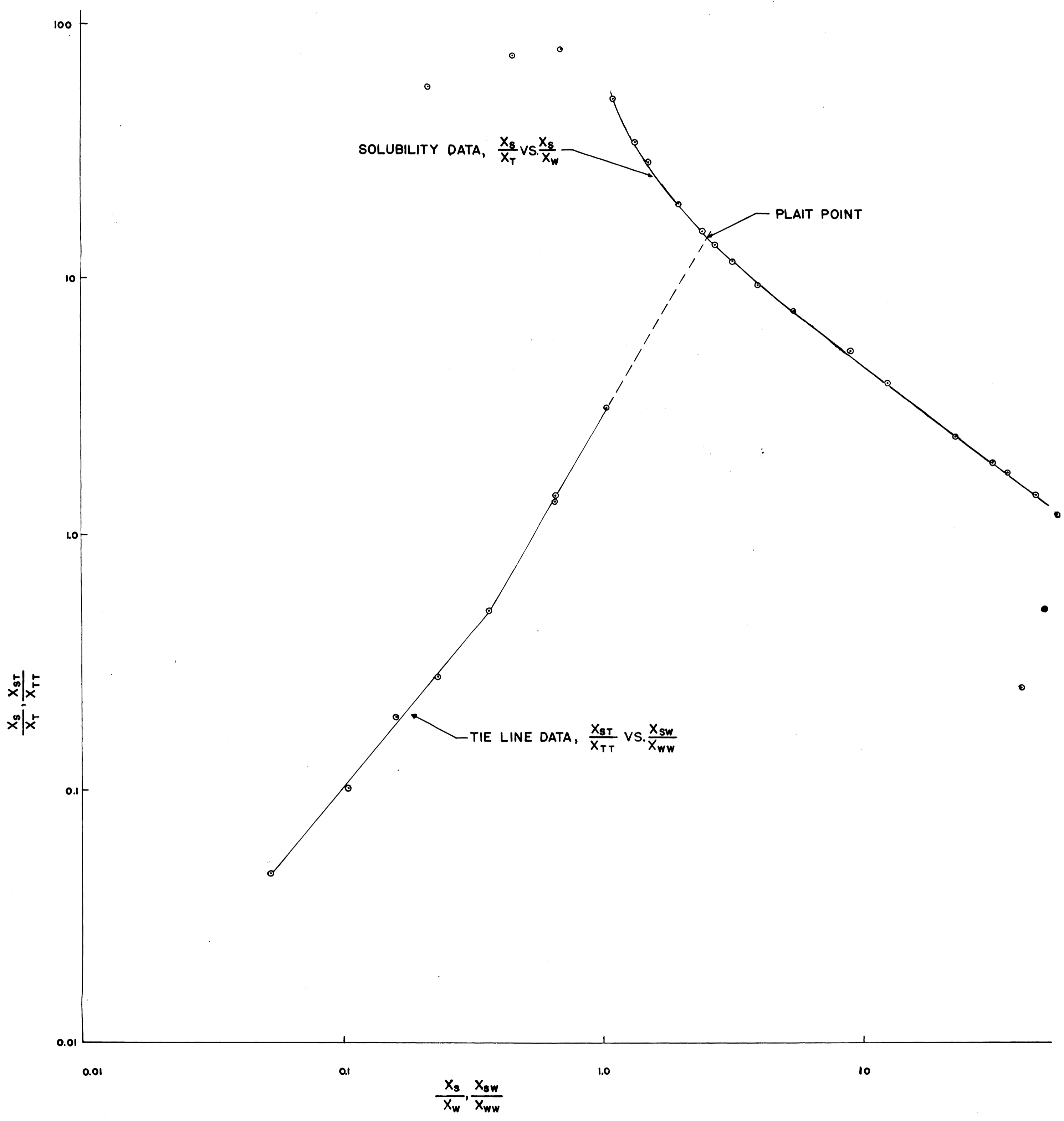


FIGURE 14. ESTIMATION OF PLAIT POINT FOR THE SYSTEM TOLUENE-ETHYLENE GLYCOL DIMETHYL ETHER-WATER AT 30 °C

LD
5655
V855
1958
P874
C.2

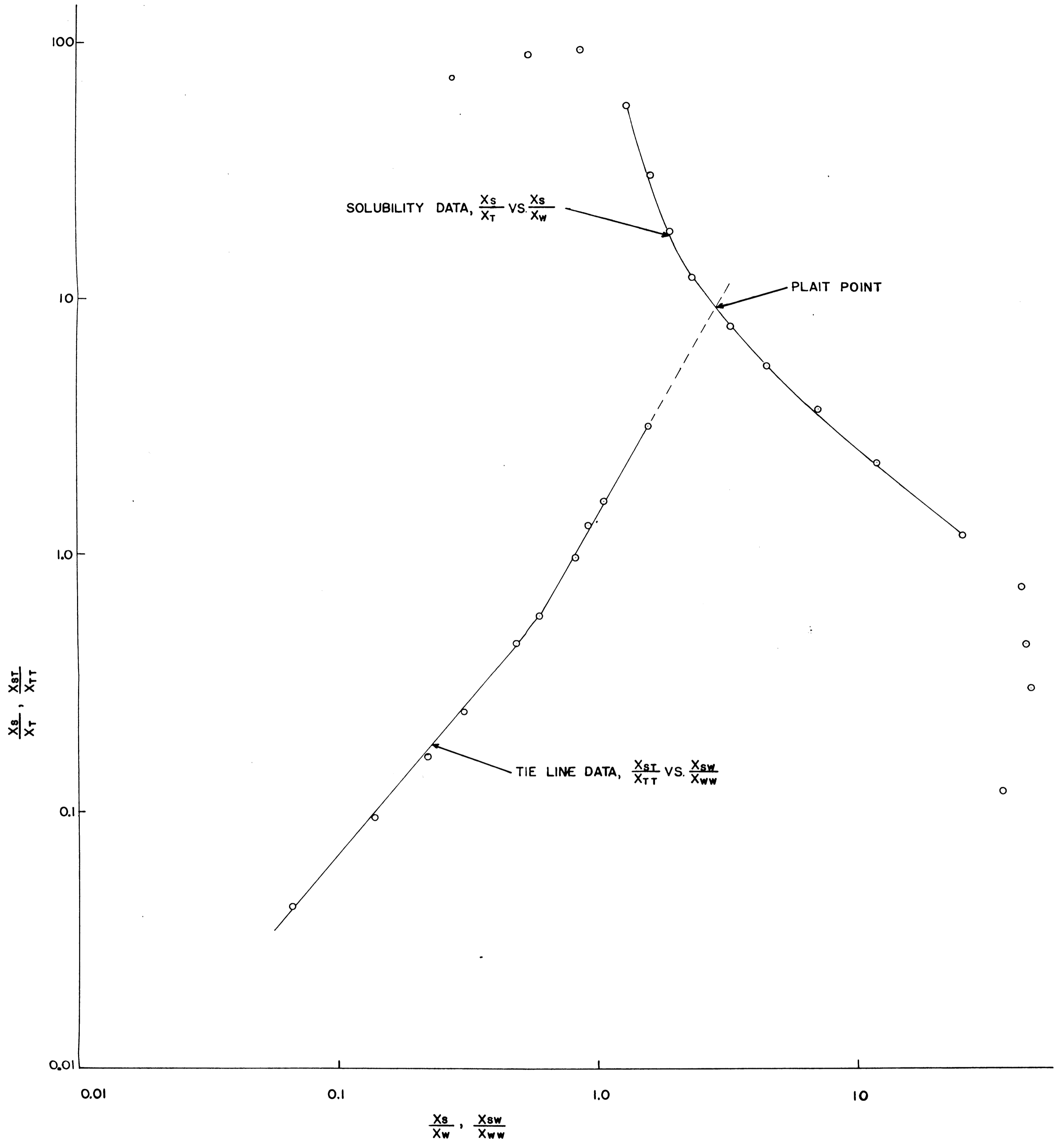


FIGURE 15. ESTIMATION OF PLAIT POINT FOR THE SYSTEM TOLUENE-DIETHYLENE GLYCOL DIMETHYL ETHER-WATER AT 30 °C

LD
5655
V855
1958
P874
c.2

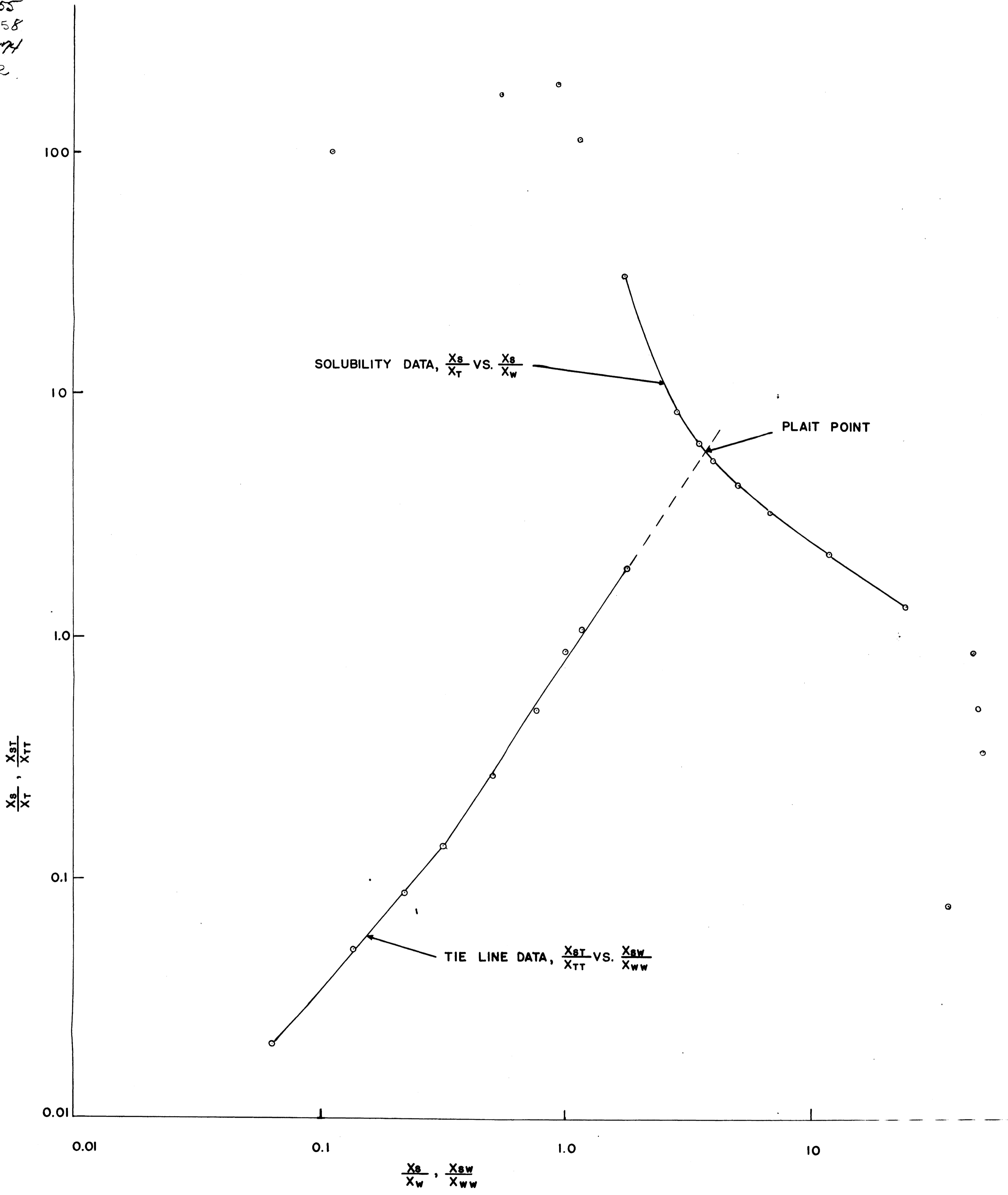


FIGURE 16. ESTIMATION OF PLAIT POINT FOR THE SYSTEM TOLUENE-
TRIETHYLENE GLYCOL DIMETHYL ETHER-WATER AT 30 °C

LD
5055
V855
1958
P874
e.2

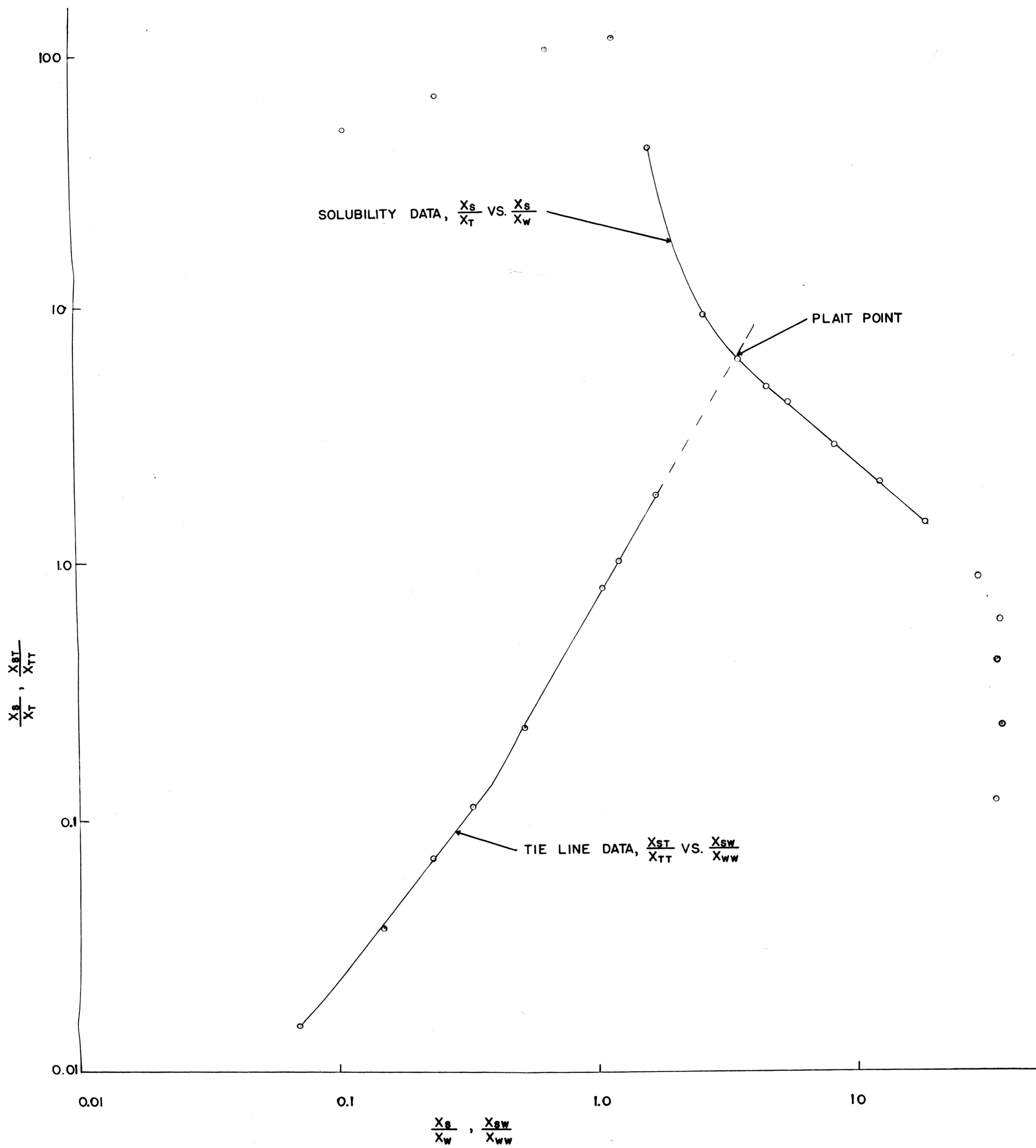


FIGURE 17. ESTIMATION OF PLAIT POINT FOR THE SYSTEM TOLUENE-TETRAETHYLENE GLYCOL DIMETHYL ETHER-WATER AT 30 °C

Extraction Data and Results. The data and results obtained from the extraction tests are presented in Table XI. The results of these tests are shown graphically in Figure 18.

Experiments are numbered with three values; the first is the experiment number, the second is the notebook number, and the third is the page number where the data are recorded.

Data and Results for Extraction Studies in a Horizontal Tube Extractor
for Transfer of Poly Glycol Ethers from Water to Toluene

Test No	Units	1-819-30	2-819-33	3-819-35	4-819-37	5-819-39	5-819-39	6-819-41	7-819-43	8-819-45	8-819-45
Solute		E-121	E-121	E-141	E-141	E-161	E-161	E-161	E-181	E-181	E-181
Temperature	°F										
Water phase		78.5	76	70	72	64	64	64	80	80	80
Solvent phase		78.5	76	76	77	66	66	66	76	76	76
Average flow rate	lb/hr										
Water phase		22.99	26.63	17.24	34.72	15.20	15.20	33.02	16.73	33.93	33.93
Solvent phase		33.83	18.98	25.65	22.88	26.50	26.50	21.38	19.55	18.86	18.86
Average phase density	lb/cu ft										
Water phase		61.79	61.88	62.47	62.45	62.83	62.83	62.84	62.90	62.91	62.91
Solvent phase		53.56	53.59	53.57	53.58	53.64	53.64	53.64	53.60	53.58	53.58
Entering solute concentration	wt %										
Water phase		13.19	9.10	14.40	14.35	15.13	15.13	15.18	14.69	14.70	14.70
Solvent phase		0.00	2.69	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.00
Entering solute concentration	lb/cu ft										
Water phase		8.150	5.631	8.996	8.962	9.506	9.506	9.539	9.240	9.248	9.248
Solvent phase		0.000	1.442	0.000	0.000	0.000	0.000	0.000	0.080	0.000	0.000
Leaving solute concentration	wt %										
Water phase		12.86	8.92	14.14	14.26	14.49	14.49	15.07	14.21	14.54	14.64
Solvent phase		0.82	2.91	0.16	0.77	0.22	0.15	0.15	0.70	0.29 *	0.11 *
Leaving solute concentration	lb/cu ft										
Water phase		7.946	5.520	8.833	8.905	9.104	9.104	9.470	8.938	9.147	9.210
Solvent phase		0.439	1.559	0.086	0.413	0.118	0.080	0.080	0.375	0.155	0.059
Change in concentration	wt %										
Water phase		0.33	0.18	0.26	0.09	0.64	0.64	0.11	0.48	0.16	0.06
Solvent phase		0.82	0.22	0.16	0.77	0.22	0.15	0.15	0.55	0.29 *	0.11 *
Rate of solute transfer	lb/hr										
Water phase		0.0759	0.0479	0.0448	0.0312	(0.0973)	(0.0973)	0.0363	(0.0803)	0.0543	0.0204
Solvent phase		(0.2774)	0.0418	0.0410	(0.1762)	0.0583	0.0398	0.0321	(0.1075)	----	----
Concentration in equilibrium with	lb/cu ft										
Entering water phase		0.000	1.912	0.000	0.000	0.000	0.000	0.000	0.654	0.000	0.000
Leaving water phase		0.615	2.061	0.137	0.747	0.062	0.430	0.430	2.292	1.145	0.466
Entering solvent phase		8.234	4.786	5.755	5.734	3.531	3.531	3.553	2.387	2.387	2.387
Leaving solvent phase		7.918	4.662	5.631	5.685	3.358	3.358	3.521	2.263	2.349	2.376
Average concentration difference	lb/cu ft										
Water phase		7.724	3.589	8.846	8.560	9.247	9.076	9.269	7.616	8.625	8.996
Solvent phase		7.856	3.223	5.650	5.503	3.385	3.404	3.497	2.097	2.290	2.352
Overall mass-transfer coefficient	ft/hr										
Water phase ^a		0.0098	0.0133	0.0051	0.0036	(0.0105)	(0.0107)	0.0039	(0.0105)	0.0063	0.0023
Water phase ^b		----	0.0116	0.0046	----	0.0063	0.0044	0.0035	(0.0141)	----	----
Solvent phase ^a		0.0097	0.0149	0.0079	0.0057	(0.0287)	(0.0286)	0.0104	(0.0383)	0.0237	0.0087
Solvent phase ^b		----	0.0130	0.0073	----	0.0172	0.0117	0.0092	(0.0513)	----	----

a Based on rate of solute transfer for water phase.
b Based on rate of solute transfer for solvent phase.
() Values were not used in calculations.
* Values calculated from water phase transfer rate.

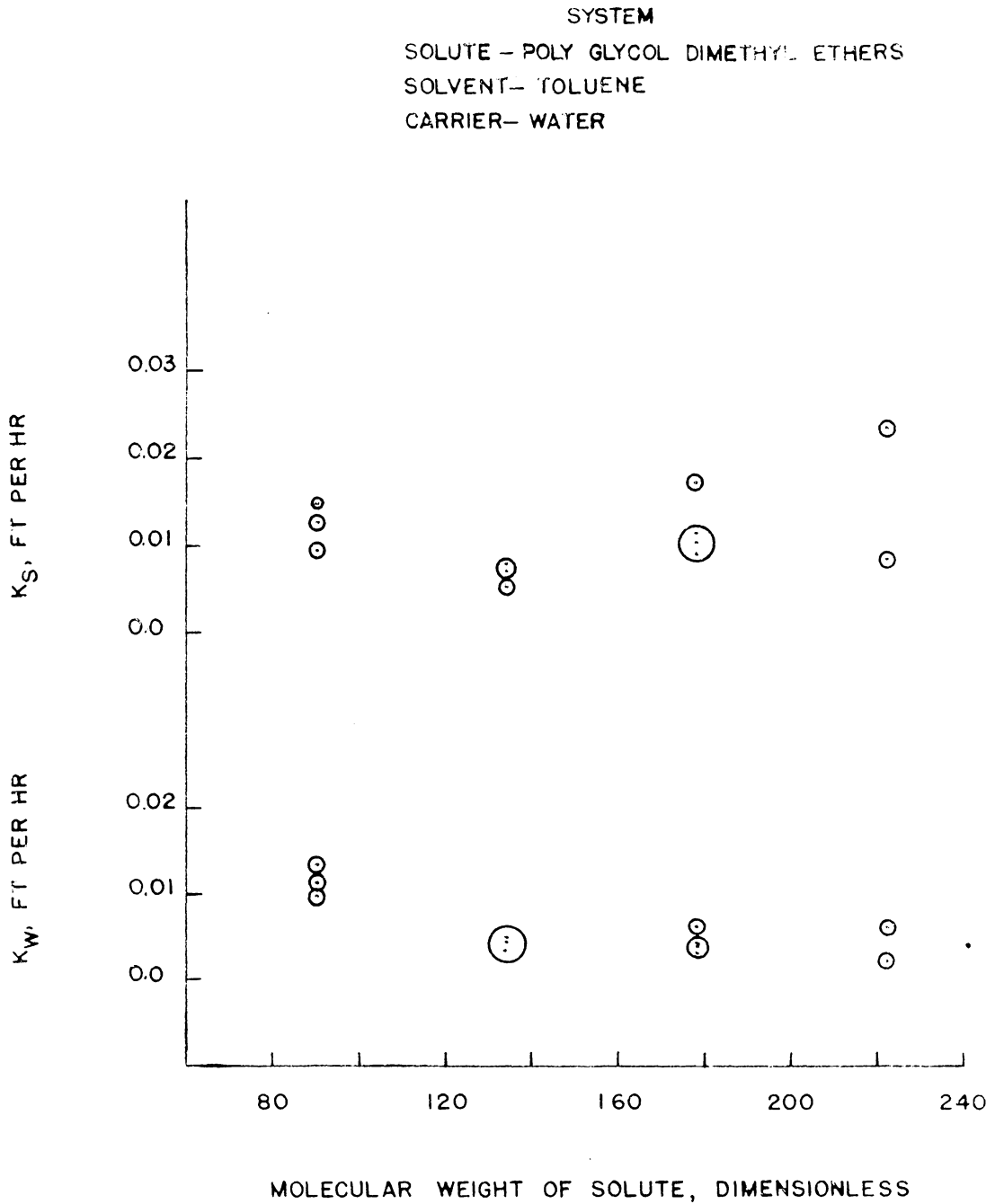


FIGURE 1. VARIATION OF OVERALL MASS-TRANSFER COEFFICIENTS WITH MOLECULAR WEIGHT OF SOLUTE AT 30 °C

Sample Calculations

This section contains a sample of each of the more complex calculations used in this investigation.

Physical Properties. The calculations used in the determination of the physical properties are presented by Landis⁽¹⁰⁾.

Rate of Solute Transfer. The rate of solute transfer was calculated from the change in concentration within the phase and the phase flow rate. The rates were calculated for solute leaving the water phase and for solute entering the solvent phase. The rates were calculated as follows:

$$N_w = G_w(C_{inlet} - C_{exit})_w$$

$$N_s = G_s(C_{exit} - C_{inlet})_s$$

where:

N_w, N_s = rate of solute transfer, lb/hr

G_w, G_s = weight rate of flow of solution,
lb/hr

C = solute concentration, weight fraction

w, s = refer to water and solvent phases,
respectively.

Substituting values from Test 3-819-35, Table XI,
page 64,

$$N_w = 17.24(14.40 - 14.14) = 0.0448 \text{ lb/hr}$$

$$N_s = 25.65(0.16 - 0.00) = 0.0410 \text{ lb/hr.}$$

Average Concentrational Driving Force. The driving force for each phase was calculated in the following manner.

$$(C_w - C_w^*)_{avg} = \frac{(C_w - C_w^*)_{inlet} + (C_w - C_w^*)_{exit}}{2}$$

$$(C_s^* - C_s)_{avg} = \frac{(C_s^* - C_s)_{inlet} + (C_s^* - C_s)_{exit}}{2}$$

where:

C_w = concentration of solute in water phase, lb/cu ft

C_w^* = concentration of solute in water phase in equilibrium with solvent phase concentration, lb/cu ft

C_s = concentration of solute in solvent phase, lb/cu ft

C_s^* = concentration of solute in solvent phase in equilibrium with water phase concentration, lb/cu ft

$(C_w - C_w^*)_{avg}$ = average concentrational driving force based on water phase, lb/cu ft

$(C_s^* - C_s)_{avg}$ = average concentrational driving force based on solvent phase, lb/cu ft.

Substituting values from Test 3-819-35, Table XI,
page 64,

$$(C_w - C_w^*)_{avg} = \frac{8.996 - 0.0 + 8.833 - 0.137}{2}$$

$$= 8.846 \text{ lb/cu ft}$$

$$(C_s^* - C_s)_{avg} = \frac{5.755 - 0.0 + 5.631 - 0.086}{2}$$

$$= 5.650 \text{ lb/cu ft.}$$

Interfacial Area. The area of the interface was
calculated as follows.

$$A = lw$$

where:

A = area of interface, sq ft

l = length of interface, ft

w = width of interface, ft

Substituting data from Figure 2, page 32,

$$A = 8(0.125) = 1.0 \text{ sq ft.}$$

Overall Mass-transfer Coefficients. The overall mass-transfer coefficients were calculated based on both the water and solvent phase driving forces. The equations used were:

$$K_s = \frac{N}{A(C_s^* - C_s)_{avg}}$$

$$K_w = \frac{N}{A(C_w - C_w^*)_{avg}}$$

where:

K_s, K_w = overall mass-transfer coefficients, ft/hr

N = rate of solute transfer, lb/hr

$(C_s^* - C_s)_{avg}$ = average concentrational driving force, lb/cu ft

$(C_w - C_w^*)_{avg}$ = average concentrational driving force, lb/cu ft

w, s = refer to water and solvent phases,

Substituting values from Test 3-819-35, Table XI, page 64,

$$K_s = \frac{0.0410}{1(5.650)} = 0.0073 \text{ ft/hr}$$

$$K_w = \frac{0.0448}{1(8.846)} = 0.0051 \text{ ft/hr.}$$

IV. DISCUSSION

A discussion of the results obtained, the limitations encountered, and the recommendations for future work are presented in this section.

Discussion of Results

A discussion of the results obtained in this investigation is presented in the following paragraphs.

Preparation of Phase Diagrams. The phase diagrams for the systems used in this investigation were determined experimentally since the data were not available in the literature. The data were measured at 30 °C. Cloud-point titrations were used to determine the solubility data. The solubility curves were believed to be accurate within plus or minus 0.3 weight per cent of solute. Because of the slight solubility between toluene and water, the cloud point was difficult to obtain accurately along the solubility curve below 15 weight per cent of solute. For this reason the error might have been larger at the lower ends of the solubility curve.

The solute concentrations for the ends of the tie lines were obtained from the curves of refractive index versus solute concentration. The error in the determination of the refractive index was less than 0.01 per cent of the reading. The error in converting the refractive index to solute concentration was approximately plus or minus 0.1 weight per cent of solute.

Solute Transfer Rates. The overall mass-transfer coefficients based on the water phase driving force were calculated using the rate of solute transfer based on both the solvent and water phases. The coefficients based on the solvent phase driving force were calculated in a like manner. Both of the transfer rates were used because of the erratic variations between the rates. There was no way of determining which of the two rates was the more correct. Therefore, both were used since a range of coefficients would be of more use than average values.

The rates of transfer were calculated from the product of the change in concentration of the phase and the flow rate of the phase. The source of the variation appeared to be in the concentration. Four

to six samples were taken of the leaving streams, and these values were averaged to obtain the exit concentrations. A composite sample was also taken of the exiting streams for comparison with the averaged values. Three samples were taken of the entering feed and solvent streams, and these values were averaged to obtain the concentration of the entering streams.

The largest discrepancy and variation appeared in the concentration for the exiting solvent phase. The variation was as high as plus or minus 30 to 50 per cent in some instances. A possible source of error might have been the sampling procedure. If the sample lines were not drained sufficiently before taking a sample a nonrepresentative sample could have been obtained.

Another source of error might have been the conversion of refractive index to solute concentration. The solute concentrations in the extract stream were in the order of 0.1 to 0.8 weight per cent of solute. The calibration curves might have been in error in these regions of low solute concentrations. The percentage error in the determination of the solute

concentrations in these regions might have been as high as 50 per cent.

The refractive index-concentration curves were determined for the water phase saturated with toluene and the toluene phase saturated with water. It was possible that the feed and solvent used in the extraction tests were not completely saturated with toluene and water, respectively. This would have produced an error in the refractive index measurement. A check was made to determine if a phase was saturated with the other phase. The variation, between the refractive index of a sample from the extraction tests and that of the same sample saturated with the opposite phase, was found to be 0.00005 unit. Thus, an error of this type was negligible.

Overall Mass-transfer Coefficients. The overall mass-transfer coefficients based on the water phase, K_w , were found to vary between 0.0023 and 0.0133 foot per hour as the molecular weight of the solute was varied from 90 to 222. From Figure 18, page 65, there was no significant variation in K_w caused by increasing the molecular weight of the solute from 134 to 222. The coefficients for the system

containing ethylene glycol dimethyl ether as a solute were approximately 30 to 50 per cent higher than the coefficients for the other systems. Values of K_W obtained by Mote⁽¹³⁾, for acetone as the solute and essentially the same flow conditions, varied from approximately 0.05 to 0.10 foot per hour.

The overall mass-transfer coefficients based on the solvent phase, K_S , varied between 0.0057 and 0.0237 foot per hour for the four systems studied. As shown in Figure 18, page 65, the variation in K_S was much greater than that for K_W . This greater variation was caused by the erratic variation in the rates of solute transfer. However, no appreciable effect was found in the overall coefficients by using solutes with different molecular weights. Mote⁽¹³⁾, using acetone as the solute, found values of K_S varying from approximately 0.04 to 0.09 foot per hour.

The effect of molecular weight of solute on the overall mass-transfer coefficients might not have been of sufficient magnitude to produce any detectable effect in the coefficients found in this investigation. Application of the two-film concept to an extraction system of this type was

questionable. Although the flow rates appeared to be in the laminar range, the effect of the interface on the particle movement was unknown. Also, the entire phase represented a thick laminar zone, whereas the two-film theory described the transfer of material through thin laminar, transition zones into a turbulent zone.

By substitution of solutes of higher molecular weight the physical properties of the phases were expected to change. Since the physical properties of the phases would affect the amount of transfer, a change in the coefficients was expected. However, since the concentration of solute present in the extract stream was approximately 0.1 to 0.8 weight per cent of solute, the physical properties of the solvent phase, with the exception of diffusivity, were approximately those of the pure solvent, toluene. Therefore, the effect of physical properties of the phases on the transfer coefficients were negligible, and any changes in the transfer coefficients would probably be caused by the diffusivity of the solute.

Correlation of Coefficients. The data from this investigation were used to evaluate the overall

mass-transfer coefficients using the correlation equation proposed by Mote⁽¹³⁾. Since the physical properties, with the exception of diffusivity, were controlled by the solute concentration of the systems, these properties were considered to remain constant for this comparison. The evaluated solvent-phase coefficients were approximately 10 to 100 times greater than the experimentally determined values as shown in Table XII. Examination of Table XII indicated that all of the factors affecting the transfer coefficient had not been included, and that the proposed equation could not be used to determine the transfer coefficients for the systems used in this investigation.

Hand Plots. On examination of Figures 14, 15, 16, and 17, pages 59, 60, 61, and 62, a change in the slope for the curves connecting the tie line data was observed. The point at which the change in slope occurred corresponded to a point of inflection on the distribution curve. This change in slope was believed to represent a change in the mutual solubility of the toluene and water which was caused by the addition of the solute^(17a).

TABLE XII

Values of Physical Properties and Dimensionless Groups Used
To Evaluate Overall Mass-Transfer Coefficients

Solute		Acetone	E-121	E-141	E-161	E-181
d	ft	0.125	0.125	0.125	0.125	0.125
σ	dynes/cm	15.84	23.0	23.0	23.0	23.0
μ_s	cp	0.505	0.53	0.53	0.53	0.53
D_s	sq ft/hr	9.4×10^{-5}	8.77×10^{-5}	6.78×10^{-5}	5.76×10^{-5}	5.1×10^{-5}
$(d\sigma/\mu_s D_s)$	dimensionless	4.88×10^8	7.3×10^8	9.45×10^8	11.1×10^8	12.5×10^8
$(d\sigma/\mu_s D_s)^{0.7227}$	dimensionless	9.12×10^5	25×10^5	30.9×10^5	34.6×10^5	36.3×10^5
μ_w	cp	1.12	1.09	1.09	1.09	1.09
(μ_w/μ_s)	dimensionless	2.221	2.055	2.055	2.055	2.055
$(\mu_w/\mu_s)^{4.0592}$	dimensionless	25.1	18.6	18.6	18.6	18.6
ρ_s	lb/cu ft	53.20	53.52	53.52	53.52	53.52
$(\mu_s/\rho_s D_s)$	dimensionless	243.65	274	354	416	470
$(\mu_s/\rho_s D_s)^{5.4361}$	dimensionless	9.77×10^{12}	19×10^{12}	69.1×10^{12}	166×10^{12}	316×10^{12}
G_s	lb/hr-sq ft	3860	4180	4180	4180	4180
(dG_s/μ_s)	dimensionless	390.6	407	407	407	407
$(dG_s/\mu_s)^{0.4701}$	dimensionless	16.5	16.9	16.9	16.9	16.9
G_w	lb/hr-sq ft	3105	2810	2810	2810	2810
(dG_w/μ_w)	dimensionless	114.4	133.1	133.1	133.1	133.1
$(dG_w/\mu_w)^{0.3027}$	dimensionless	4.20	4.46	4.46	4.46	4.46
$(K_s d/D_s)$	dimensionless	42	181	312	2190	4360
K_s^a	ft/hr	0.0315	0.126	0.44	1.00	1.77
K_s^b	ft/hr	0.057	0.012	0.0065	0.013	0.016

a Values calculated from correlation equation.

b Values calculated from experimental results (average).

Limitations

The limitations imposed on this investigation are presented in this section.

Horizontal Tube Extractor. A horizontal tube extractor, 1-1/2 inches in diameter, eight feet long, made of pyrex glass was used for the extraction studies.

Systems Investigated. The carrier solvent used was water, and the extracting solvent was toluene. The solutes used were ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether. The molecular weight of these solutes were 90, 134, 178, and 222, respectively.

Phase Flow Rates. The water phase flow rates varied from 15.20 to 34.72 pounds per hour. The solvent phase flow rates varied from 18.86 to 33.83 pounds per hour.

Feed Concentrations. The feed concentrations used in the extraction tests were 13.19 and 9.10 weight per cent of E-121 in water, 14.40 and 14.35 weight per cent of E-141 in water, 15.13 and 15.18

weight per cent of E-161 in water, and 14.69 and 14.70 weight per cent of E-181 in water.

Analysis of Samples. The samples were analyzed by measuring the refractive index with a dipping refractometer.

Phase Diagrams. The solubility data obtained for the phase diagrams were determined by cloud-point titrations.

Temperature. All solubility data, tie line data, physical properties and refractive indices were determined at 30 °C. The extraction tests were performed at temperatures between 17.7 and 26.6 °C. This was equivalent to making the assumption that the distribution curve applied over this temperature range.

Recommendations

Recommendations for future extraction studies are presented in this section.

Feed Concentrations. If the solutes used in this investigation are used in future studies, it is recommended that the feed concentrations be in the order of 25 to 30 weight per cent of solute in water. This should produce higher rates of solute transfer due to the larger driving forces. The higher concentrations which would result would be less sensitive to error in analysis and sampling. Also, wider variation in the physical properties of the phases would result.

Sampling. It is suggested that different techniques of sampling be investigated. With the present system it might be possible for stagnant areas to be present in the extraction tube.

Solubility Determinations. For the determination of solubility data for solute concentrations below 15 weight per cent, the cloud point is difficult to determine. It is recommended that when working in this region the volume of the samples be in the order

of 100 milliliters and that several determinations be made as checks.

Preparation of Feed and Solvent. When the feed solution is prepared a sufficient amount of solvent should be added to completely saturate the feed. Also, a sufficient quantity of carrier solvent should be added to the solvent phase to insure complete saturation. If possible, the feed and solvent solutions should be allowed to stand overnight to allow their temperature to reach that of the room.

Other Solutes. It is recommended that when future studies are made the type of solute should be varied as well as the molecular weight. That is, solutes of different molecular structure should be used.

Analytical Procedure. Because of the expense of the prisms used and the lengthy and tedious technique required for analysis by refractive index, it is recommended that other methods of analysis be investigated.

V. CONCLUSIONS

Preparation of phase diagrams for the systems toluene-ethylene glycol dimethyl ether-water, toluene-diethylene glycol dimethyl ether-water, toluene-triethylene glycol dimethyl ether-water, and toluene-tetraethylene glycol dimethyl ether-water at a temperature of 30 °C, led to the following conclusions.

1. All four systems had similar phase diagrams with the maximum solubility ranging from 69.9 to 76.7 weight per cent of solute.

2. Three of the systems exhibited solutropes, and the fourth system, containing tetraethylene glycol dimethyl ether, approached a solutrope at a solute concentration of approximately 64 per cent.

Extraction studies made for the transfer of a homologous series of poly glycol dimethyl ethers between water and toluene in a 1-1/2-inch diameter, horizontal tube extractor, eight feet long, for feed concentrations of 9.10 to 15.18 weight per cent of solute in water, water phase flow rates between 15.20 and 34.72 pounds per hour, and solvent phase flow rates

between 18.86 and 33.83 pounds per hour, led to the following conclusions.

1. The overall mass-transfer coefficients for the systems containing poly glycol dimethyl ethers as solutes were one-tenth as large as the values of the coefficients obtained for the systems containing acetone as the solute for similar conditions.

2. The values of the overall mass-transfer coefficients were not affected appreciably by changing the molecular weight of the solute from 90 to 222.

3. The equation proposed by Note⁽¹³⁾ for evaluation of the overall coefficients for mass transfer of acetone, based on the solvent phase, could not be used to determine the overall mass-transfer coefficients for the systems used in this investigation.

VI. SUMMARY

The purpose of this investigation was to determine the effect of a homologous series of solutes on the overall mass-transfer coefficients for liquid-liquid extraction. The solutes used were ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether. The carrier solvent was water, and the extracting solvent was toluene. The phase diagrams for these systems were determined at 30 °C.

The phase diagrams were found to be similar and to have maximum solubilities ranging from 69.9 to 76.7 weight per cent of solute. Three of the systems exhibited solutropes, and the system containing tetraethylene glycol dimethyl ether approached a solutrope at a solute concentration of approximately 64 per cent.

A countercurrent-flow, 1-1/2-inch diameter, horizontal, pyrex glass tube, eight feet long with an interfacial surface area of one square foot, was used for the extraction tests. The feed concentration ranged from 9.10 to 15.18 weight per cent of solute

in water. The flow rates of the water phase varied from 15.20 to 34.72 pounds per hour, and the solvent phase flow rates varied from 18.86 to 33.83 pounds per hour.

The overall mass-transfer coefficients based on the water phase were found to vary between 0.0098 and 0.0133, 0.0036 and 0.0051, 0.0035 and 0.0063, and 0.0023 and 0.0063, for the systems investigated. The solvent phase coefficients were found to vary between 0.0097 and 0.0149, 0.0057 and 0.0079, 0.0092 and 0.0172, and 0.0087 and 0.0237.

The overall coefficients were not affected appreciably by changing the molecular weight of the solute. Also, experimentally determined values of the overall coefficients based on the solvent phase did not agree with those values of the coefficients calculated by previously determined equations.

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ABSTRACT

OVERALL MASS-TRANSFER COEFFICIENTS FOR A
HOMOLOGOUS SERIES OF POLY GLYCOL
ETHERS BETWEEN TOLUENE AND WATER

by

Robert H. Pusey

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute
in candidacy for the degree of

MASTER OF SCIENCE

in

CHEMICAL ENGINEERING

July, 1958

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The purpose of this investigation was to determine the effect of a homologous series of solutes on the overall mass-transfer coefficients for liquid-liquid extraction. The solutes used were ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether. The carrier solvent was water, and the extracting solvent was toluene. The phase diagrams for these systems were determined at 30 °C.

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