

CORRELATION OF LIQUID-LIQUID  
PHASE EQUILIBRIA

By

EDWARD N. PENNINGTON

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Thesis and Abstract Approved:

*Charles R. Nickalls*  
\_\_\_\_\_  
Thesis Adviser

*Leonard Shuman*  
\_\_\_\_\_  
Faculty Representative

*D. G. M. Zutoch*  
\_\_\_\_\_  
Dean of the Graduate School

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## ABSTRACT

The lack of design data for liquid-liquid extraction is hindering the development of this separation process. Experimental difficulties involved in determination of the required data make a method of predicting this data very desirable. It is the purpose of this paper to present and prove a method of predicting ternary liquid-liquid phase equilibrium data and show that the method may be extended to predict multicomponent phase equilibrium data.

Mutual solubility data for thirteen hydrocarbon-solvent binary systems and ternary phase equilibrium data for two hydrocarbon-solvent systems are given.

A correlation for determining component distribution in multicomponent systems is developed and charts of partition coefficients for twelve hydrocarbons in furfural and five hydrocarbons in aniline are presented.

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## I. INTRODUCTION

The separation of solutions into their various components is one of the major problems confronting the chemical engineer. There are in general use many means of effecting these separations. Prominent among these are the various methods of distillation, adsorption, absorption, evaporation, and solvent extraction. In choosing a method to be employed for a given separation consideration must be given to the chemical and physical properties of the components in the solution and the type of separation desired. The various methods of separation which depend upon vaporization of the more volatile components of a solution to effect the desired separation have always dominated the field of industrial separations. But in the current day of specialization the other methods are finding a place of increasing importance in satisfying the demand for special products and pure chemicals.

This is especially true in the field of petroleum refining where the distillations methods have been developed from an art to a science and have been employed on a grandiose scale. But with the ever increasing demand for higher quality motor fuels, more specialized aviation fuels, and pure paraffins, naphthenes, and aromatics as well as pure hydrocarbon chemicals methods, other than distillation, must be introduced and developed. This is not to say that the distillation methods are becoming obsolete and must be replaced, but rather that these methods are approaching the limits of application and must be supplemented with other methods. For example fractional distillation is employed to separate solutions of hydrocarbons into other solutions of narrower boiling range or perhaps even into individual components. However the

separation obtainable is limited by the closeness of boiling points of the various components and the formation of azeotropes or constant boiling mixtures. These limitations may be avoided in some cases by use of some other separation method. One of the most promising of these other methods is liquid-liquid extraction which separates the components of a solution as to relative solubilities in a solvent.

Liquid-liquid extraction is relatively new as an engineering practice in the process industries and is seldom used for precise separations. Until recent years its application has been an art and research has been limited. In order to develop liquid-liquid extraction which separates the components of a solution by distribution of the components between two liquid phases a large amount of phase equilibrium data is required. The limited research in the field of equilibrium studies has yielded a relatively small amount of data as shown by the bibliography in the appendix. This tabulation of literature references is only for solvent-hydrocarbon systems in which the hydrocarbon has five or more carbon atoms but is essentially complete.

The experimental determination of component distribution between phases for ternary or higher systems is either very difficult or impossible. Detailed discussions of experimental difficulties and methods are given by Treybal (17), Bogin (2), Hand (10), and McDonald (15). Because of experimental difficulties a convenient means of predicting the component distribution is very desirable even though the resulting data is only a close approximation. This problem has been studied by the rather unsatisfactory methods of empirical extrapolation and interpolation of existing data. Treybal has reviewed the work done by these methods (17). A more fundamental approach to the problem is possible

through the concepts of thermodynamics. The work done from this approach also has been summarized by Treybal. But the amount of data actually available is very small.

It is the purpose of this paper to present a method of predicting component distribution between two liquid phases in equilibrium and prove its applicability to hydrocarbon-solvent systems. This method is based on the thermodynamic concept of activity and utilizes mutual solubility data which is relatively easily determined by experimental means.

## II. THEORY

The equilibrium distribution of components between two phases is a condition of thermodynamic equilibrium. Therefore, the study of component distribution between two liquid phases under equilibrium conditions may be approached through the criteria for thermodynamic equilibria. These considerations require that when two immiscible phases are in equilibrium, the activity of a given component is the same in both phases (11) or

$$a_{iv} = a_{ih} \quad (1)$$

A more convenient function, activity coefficient, may be defined as the ratio of a component's activity to its mole fraction in the phase considered or

$$\gamma_{iv} = \frac{a_{iv}}{y_{iv}} \quad (2)$$

and

$$\gamma_{ih} = \frac{a_{ih}}{x_{ih}} \quad (3)$$

If equations (2) and (3) are combined with the identity, equation (1), an equilibrium relationship is derived,

$$\frac{y_{iv}}{x_{ih}} = \frac{\gamma_{ih}}{\gamma_{iv}} = K. \quad (4)$$

It will now be shown that the equilibrium relationship given by equation (4) is rigorous and fulfills the requirements of thermodynamic equilibria.

If the net work done on or by a system undergoing change at constant temperature and pressure is considered, a thermodynamic function may be

defined. This function was called "thermodynamic potential" by Gibbs (8) who was the first to apply it extensively. It was later called "free energy" by which name it is more generally known. Free energy is defined by the equation

$$F = H - TS. \quad (5)$$

Since enthalpy is defined as

$$H = E + PV \quad (6)$$

then

$$F = E + PV - TS \quad (7)$$

and differentiation gives

$$dF = dE + PdV + VdP - TdS - SdT. \quad (8)$$

If the process is assumed to be reversible and the work all due to expansion then (7)

$$TdS = dE + PdV. \quad (9)$$

Therefore

$$dF = VdP - SdT. \quad (10)$$

It readily follows that at constant temperature and pressure

$$dF = 0 \quad (11)$$

The derivation of the derivative of free energy is based on the assumption of a closed system and thus does not apply to systems of two or more phases (9). Since free energy is an extensive property its magnitude is also dependent on the amounts of the constituents of the system. And since a small change in free energy,  $dF$ , is a complete differential it may be expressed as

$$dF = \left(\frac{\partial F}{\partial T}\right)_{P, n_1, n_2, \dots} dT + \left(\frac{\partial F}{\partial P}\right)_{T, n_1, n_2, \dots} dP + \left(\frac{\partial F}{\partial n_1}\right)_{T, P, n_2, \dots} dn_1 + \left(\frac{\partial F}{\partial n_2}\right)_{T, P, n_1, \dots} dn_2 + \dots \quad (12)$$

where  $n_1, n_2, \dots$  are the numbers of moles of the various constituents making up the whole system. The quantities  $\frac{\partial F}{\partial n}$  are called partial molar free energy and is the quantity designated by Gibbs (g) as the chemical potential,  $\mu$ .

For an open system in equilibrium at constant temperature and pressure so that there is no net transfer of molecules between phases equation (12) reduces to

$$F = \mu_1 dn_1 + \mu_2 dn_2 + \dots = 0 \quad (13)$$

and

$$\sum \mu dn = 0. \quad (14)$$

Considering a binary system of components  $i$  and  $j$ , if a small quantity,  $dn_i$  moles, of component  $i$  is transferred from phase  $v$  to phase  $h$  it follows that

$$-\mu_{iv} dn_i + \mu_{ih} dn_i = 0 \quad (15)$$

and

$$\mu_{iv} = \mu_{ih} \quad (16)$$

That is, when two phases are in equilibrium at constant temperature and pressure the chemical potential of any component is the same in each phase.

If the temperature is held constant equation (10) reduces to

$$dF = VdP. \quad (17)$$

Then assuming for the moment that the material under consideration is an ideal gas,  $V = RT/P$  and therefore

$$dF = RTd \ln P. \quad (18)$$

In order to preserve this convenient form for cases in which the substance is not an ideal gas, Lewis (14) defines the function fugacity,

f, by the equation

$$dF = RTd \ln f. \quad (19)$$

For one mole of a pure substance the free energy and the chemical potential are identical; therefore equation (19) may be written

$$d\mathcal{U} = RTd \ln f. \quad (20)$$

This equation may be integrated at constant temperature between two states to give

$$\mathcal{U} - \mathcal{U}^{\circ} = RT \ln f/f^{\circ} \quad (21)$$

where the superscript denotes an arbitrarily chosen standard state. For the purpose of this paper the standard state is defined as the pure liquid component at the pressure under consideration, which is normally one atmosphere. Equation (21) defines the function activity,  $a = f/f^{\circ}$ . Also if equation (21) is combined with equation (16), it is shown that the activity of any component is the same in each phase provided the same standard state is used to define both phases. This proves the validity of equation (1). It shows that equation (4) is rigorous regardless of the number of components present and fulfills the thermodynamic requirements for equilibrium. It should be noted that the activity of a component in its standard state is unity.

In order to put the activity function in a more usable form, another function, activity coefficient, is defined as the ratio of activity to the molar concentration in a solution

$$\delta = a/x \quad (22)$$

Thus equation (21) may be written

$$\mathcal{U} - \mathcal{U}^{\circ} = RT \ln \delta x \quad (23)$$

or

$$\mathcal{U} - \mathcal{U}^{\circ} = RT \ln x + RT \ln \delta. \quad (23a)$$



This equation may be differentiated at constant temperature and pressure to give

$$d\mu = RTd \ln x + RTd \ln \gamma. \quad (24)$$

With a two component system in equilibrium at constant temperature and pressure equation (13) reduces to

$$dF = \mu_i dn_i + \mu_j dn_j \quad (25)$$

which may be integrated at constant composition to give

$$F = \mu_i n_i + \mu_j n_j. \quad (26)$$

This may be differentiated without restriction to constant composition to give

$$dF = \mu_i dn_i + n_i d\mu_i + \mu_j dn_j + n_j d\mu_j \quad (27)$$

Subtracting equation (25) from equation (27) gives

$$n_i d\mu_i + n_j d\mu_j = 0 \quad (28)$$

Also for a binary system

$$x_i + x_j = 1 \quad (29)$$

and differentiating

$$dx_i + dx_j = 0 \quad (30)$$

also

$$x_i \frac{dx_i}{x_i} + x_j \frac{dx_j}{x_j} = 0 \quad (31)$$

therefore

$$x_i d \ln x_i + x_j d \ln x_j = 0. \quad (32)$$

If equation (28) is divided by  $n_i + n_j$  it may be written

$$x_i d\mu_i + x_j d\mu_j = 0. \quad (33)$$

Substitution from equation (24) and division by RT gives

$$x_i d \ln x_i + x_i d \ln \gamma_i + x_j d \ln x_j + x_j d \ln \gamma_j = 0. \quad (34)$$

Subtract equation (32) from equation (34) to give

$$x_i d \ln \gamma_i + x_j d \ln \gamma_j = 0. \quad (35)$$

Or writing the equation in terms of partial differentials with respect to  $x_i$

$$x_i \left( \frac{\partial \ln \gamma_i}{\partial x_i} \right)_{T, P} + x_j \left( \frac{\partial \ln \gamma_j}{\partial x_i} \right)_{T, P} = 0 \quad (36)$$

This may be written in the form

$$\frac{\left( \frac{\partial \ln \gamma_i}{\partial x_i} \right)_{T, P}}{\left( \frac{\partial \ln \gamma_j}{\partial x_i} \right)_{T, P}} = - \frac{x_j}{x_i} \quad (36a)$$

to indicate that if the activity coefficients are plotted on a log scale versus the mole fraction of one of the components, the ratio of the slopes of the curves must be equal to the negative reciprocal of the mole fractions of the two components.

Equation (36) is of value in studying and evaluating experimental data but cannot be used to evaluate activity coefficients without being integrated. Several studies have been made to obtain convenient solutions to this equation. These studies are summarized by Carlson and Colburn (4) and are discussed and compared by Wohl (18). It has been found that the equations derived by van Laar (13) usually give values consistent with experimental liquid-liquid phase equilibria. These equations are also convenient to use. Therefore they were used in the present work to evaluate activity coefficients from mutual solubility data.

Equation (19) may be integrated for an ideal solution between two states to give

$$F - F^{\circ} = RT \ln x. \quad (37)$$

For  $n_i$  moles of component  $i$  and  $n_j$  moles of component  $j$  this becomes

$$n_i F_i = n_i RT \ln x_i + n_i F_i^{\circ} \quad (38)$$

$$n_j F_j = n_j RT \ln x_j + n_j F_j^{\circ} \quad (38a)$$

And the total free energy of an ideal solution is

$$F = n_i F_i + n_j F_j = n_i RT \ln x_i + n_j RT \ln x_j + n_i F_i^{\circ} + n_j F_j^{\circ}. \quad (39)$$

Similarly equation (23a) shows the total free energy for a nonideal solution to be

$$F = n_i F_i + n_j F_j = n_i RT \ln x_i + n_i RT \ln \gamma_i + n_j RT \ln x_j + n_j RT \ln \gamma_j + n_i F_i^{\circ} + n_j F_j^{\circ} \quad (40)$$

If equation (39) is subtracted from equation (40) the remainder is termed the excess free energy. That is it is the free energy of an actual solution which is in excess of the free energy of the same solution if it were ideal. Thus

$$F_E = n_i RT \ln \gamma_i + n_j RT \ln \gamma_j \quad (41)$$

Differentiation at constant temperature and pressure with respect to  $n_i$

$$\frac{\partial F_E}{\partial n_i} = RT \ln \gamma_i \quad (42)$$

or for an arbitrary amount of mixture,  $(n_i + n_j)$

$$\frac{\partial (n_i + n_j) F_E}{\partial n_i} = RT \ln \gamma_i. \quad (43)$$

Similarly

$$\frac{\partial (n_i + n_j) F_E}{\partial n_j} = RT \ln \gamma_j. \quad (44)$$

It is assumed that the excess free energy is a simple function of the molar concentrations such that

$$\frac{F_E}{2.3 RT} = x_i x_j a \quad (45)$$

where "a" is a constant. This equation may also be written for an arbitrary amount of mixture,  $(n_i + n_j)$

$$\frac{(n_i + n_j) F_E}{2.3 RT} = (n_i + n_j) \left( \frac{n_i}{n_i + n_j} \right) \left( \frac{n_j}{n_i + n_j} \right) a \quad (46)$$

This equation can be made more general by multiplying each  $n_i$  on the right hand side of the equality by  $q_i$  and each  $n_j$  by  $q_j$ .

These  $q$ -factors are interpreted by van Laar to be van der Waal's proper mole volumes (9). Thus equation (46) becomes

$$\frac{(n_i + n_j) F_E}{2.3 RT} = (q_i n_i + q_j n_j) \left( \frac{q_i n_i}{q_i n_i + q_j n_j} \right) \left( \frac{q_j n_j}{q_i n_i + q_j n_j} \right) a \quad (47)$$

Divide both sides by  $(n_i + n_j)$  and rearrange to give

$$\frac{F_E}{2.3 RT} = \left( x_i + \frac{q_j}{q_i} x_j \right) \left( \frac{x_i}{x_i + \frac{q_j}{q_i} x_j} \right) \left( \frac{x_j \frac{q_j}{q_i}}{x_i + \frac{q_j}{q_i} x_j} \right) q_i a \quad (48)$$

Define the products  $q_i a$  and  $q_j a$  as

$$q_i a = A \quad (49)$$

$$q_j a = B \quad (49a)$$

Then divide equation (49) by equation (49a) and

$$\frac{q_i}{q_j} = \frac{A}{B} \quad (50)$$

This ratio may be substituted in equation (48) to give

$$\begin{aligned} \frac{F_E}{2.3 RT} &= (x_i + \frac{B}{A} x_j) \left( \frac{x_i}{x_i + \frac{B}{A} x_j} \right) \left( \frac{x_j \frac{B}{A}}{x_i + \frac{B}{A} x_j} \right) A \\ &= \frac{B x_i x_j}{x_i + \frac{B}{A} x_j} \end{aligned} \quad (51)$$

Then combining with equation (42) to give the van Laar equations

$$\log \gamma_i = \frac{A x_j^2}{\left( x_j + \frac{A x_i}{B} \right)^2} \quad (52)$$

and similarly

$$\log \gamma_j = \frac{B x_i^2}{\left( x_i + \frac{B x_j}{A} \right)^2} \quad (52a)$$

That these equations are consistent with the Gibbs-Duhem equation may be shown by differentiation.

Elimination of  $\gamma$ 's between equation (4) and equations (52) and (52a) permits the evaluation of the constants A and B from mutual solubility data by the equations

$$A = \frac{\log (y_i/x_i)}{\left[ \frac{1}{1 + \frac{A}{B} \frac{x_i}{x_j}} \right]^2 - \left[ \frac{1}{1 + \frac{A}{B} \frac{y_i}{y_j}} \right]^2} \quad (53)$$

and

$$\frac{A}{B} = \frac{\left(\frac{x_i}{x_j} + \frac{y_i}{y_j}\right) \left[ \frac{\log (y_i/x_i)}{\log (x_j/y_i)} \right] - 2}{\left(\frac{x_i}{x_j} + \frac{y_i}{y_j}\right) - \frac{2 x_i y_i \log (y_i/x_i)}{x_j y_j \log (x_j/y_j)}} \quad (54)$$

As derived these equations are for binary mixtures. Similar equations for multicomponent mixtures are very complex and require a greater amount of data (18). However in hydrocarbon-solvent systems it may be assumed that the effect of the hydrocarbons on each other is negligible in comparison with the effect of the solvent. That is, it may be assumed that the hydrocarbons form perfect solutions in each other. On this basis, it may be stated that the activity coefficient of a hydrocarbon in a hydrocarbon-solvent mixture is a function of the solvent concentration only and is independent of any other hydrocarbon components present.

In approaching the study of phase equilibria attention should be given to the phase rule and its applications. The phase rule was deduced by Gibbs (8) from thermodynamics and its meaning depends upon the following definitions:

Phase.--A phase is any homogeneous, physically distinct part of a system which is separated from other parts of the system by definite bounding surfaces. Thus a liquid layer although it may be a solution of two or more components is a phase.

Component.--A component is an independently variable constituent of a system. The total number of components in a system is the smallest number of such constituents by means of which the composition of each phase of the system can be expressed. Thus

for the single phase system n-heptane dissolved in furfural there are two components. Also for the two phase system furfural saturated with n-heptane and n-heptane saturated with furural there are two components. But for the single phase system n-heptane and cyclohexane dissolved in furfural there are three components.

Degree of Freedom.--A degree of freedom is an independent variable of a system which must be fixed in order to completely define a system at equilibrium. These variables are limited to temperature, pressure, and concentration. The number of degrees of freedom of a given system is the number of such variables which must be specified to define the system.

Assuming that the equilibrium between any number of phases is influenced only by composition, temperature, and pressure, the total number of variables affecting the equilibrium is the sum of the concentration terms required to define the system plus two. Thus in a system of C components distributed among P phases, C - 1 concentration terms are required to define each phase and P(C - 1) concentration terms are required to define the system. Therefore the total number of variables is

$$P(C - 1) + 2.$$

However it has been pointed out that the equilibrium condition imposes P - 1 conditions that must be met by each component or a total of C(P - 1) conditions. Or that is C(P - 1) variables are automatically fixed. Therefore

$$P(C - 1) + 2 - C(P - 1) = C - P + 2 = F \quad (55)$$

where F is the total number of degrees of freedom.

For a system of two components distributed between two liquid phases in equilibrium the phase rule gives

$$F = 2 - 2 + 2 = 2.$$

And if the pressure is fixed at one atmosphere, the temperature alone will define the system completely. That is at a given temperature the composition of the two liquid layers are fixed.

For a system of three components distributed between two liquid phases in equilibrium the phase rule gives

$$F = 3 - 2 + 2 = 3.$$

Then at fixed temperature and pressure there remains one degree of freedom which must be the concentration of one component in one phase. This reasoning may be extended to give similar conclusions for increased number of components.



### III. EXPERIMENTAL WORK

The lack of liquid-liquid phase data in the literature necessitated the experimental determination of mutual solubility data for a number of hydrocarbon-solvent systems and a limited amount of ternary equilibrium data.

**Materials:** The Hydrocarbons used in the experimental work were all Phillips Pure Grade hydrocarbons. The furfural used was originally obtained as technical grade furfural from the Quaker Oats Company. This furfural was further purified by distillation with the heart cut only being used. The aniline was obtained as chemically pure from Baker and Company, Inc. It was freshly distilled each day with an eighty per cent heart cut being used.

**Determination of mutual solubilities:** The mutual solubilities of the hydrocarbon-solvent systems were determined by the cloud point temperature of synthetic samples. A more detailed discussion of the experimental method is given in the appendix.

The solubility data are limited to that which could be obtained at atmospheric pressure. In other words no data at temperatures above the boiling point of the mixture were determined. The solubility data obtained are presented in Figures 1 through 6.

**Determination of Ternary Equilibria:** A limited amount of ternary equilibria was determined by making a synthetic mixture of two hydrocarbons and a solvent such that two phases were formed. The mixture was well agitated at a constant temperature until equilibrium was reached. The phases were then allowed to settle

and were separated. Each phase was analyzed for the concentration of each component. The detailed procedure is explained in the appendix. The ternary equilibrium data determined are tabulated in Tables V and VI.

\*

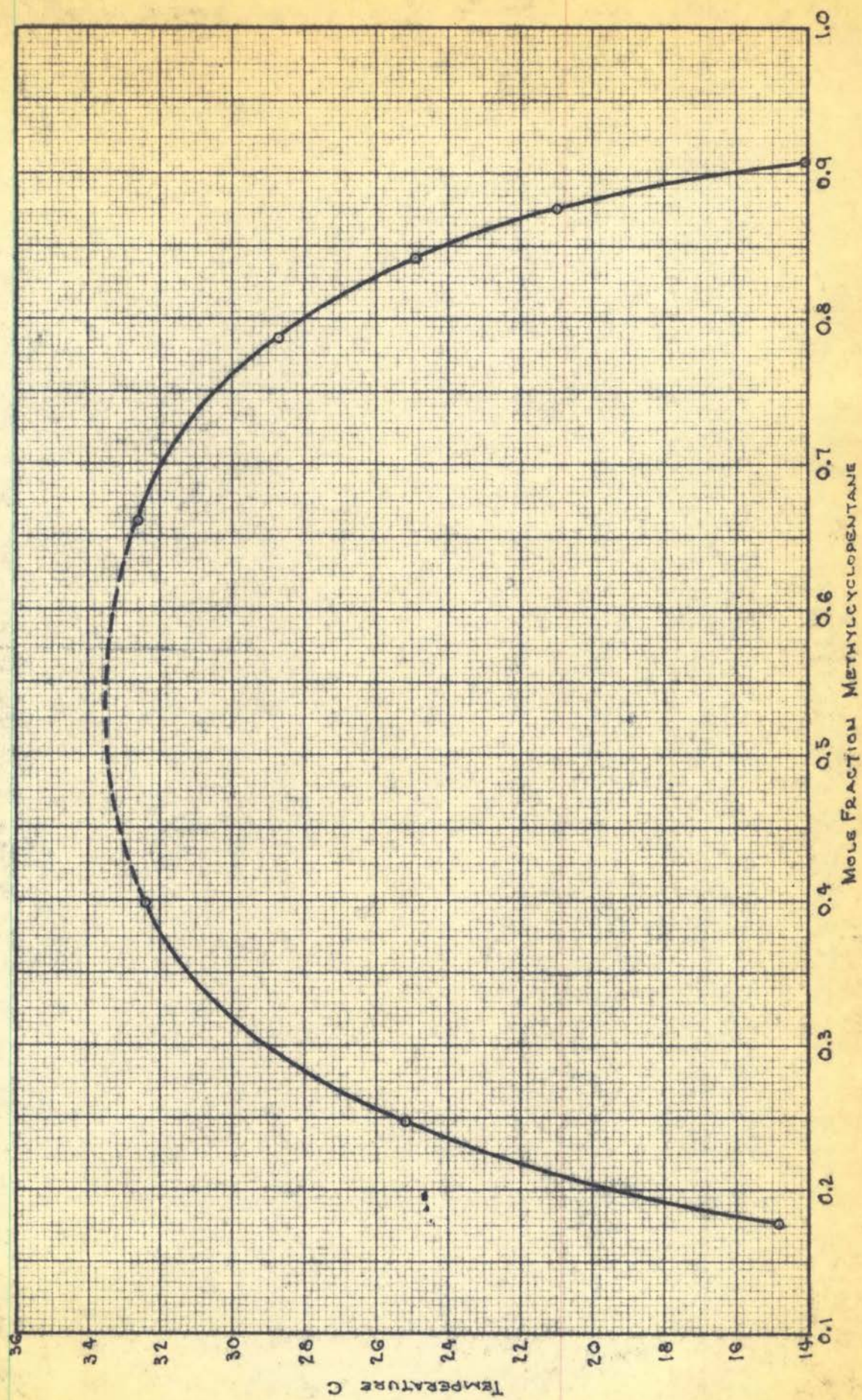


FIG. 1 MUTUAL SOLUBILITY METHYLCYCLOPENTANE - ANILINE

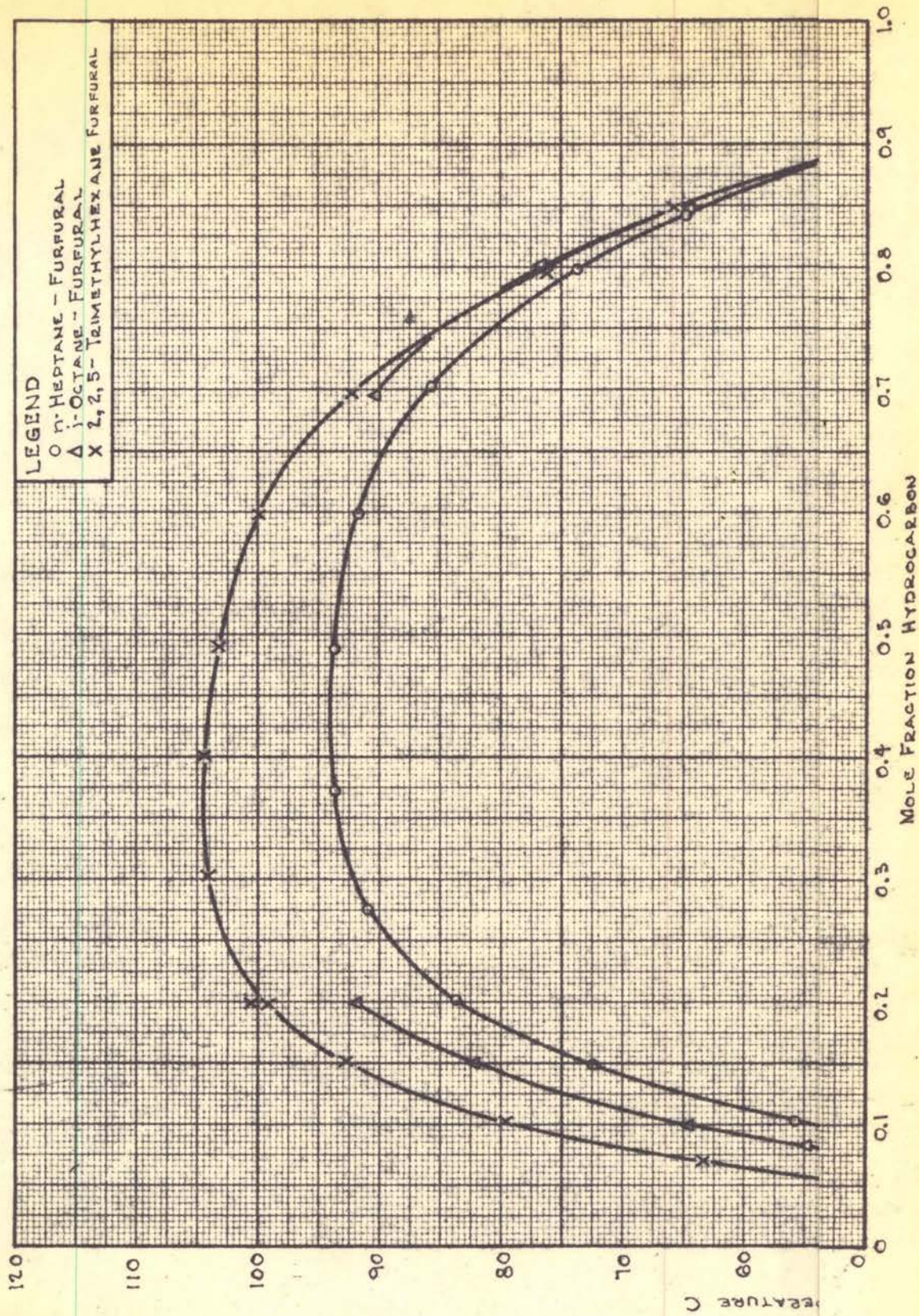


FIG. 2 MUTUAL SOLUBILITIES

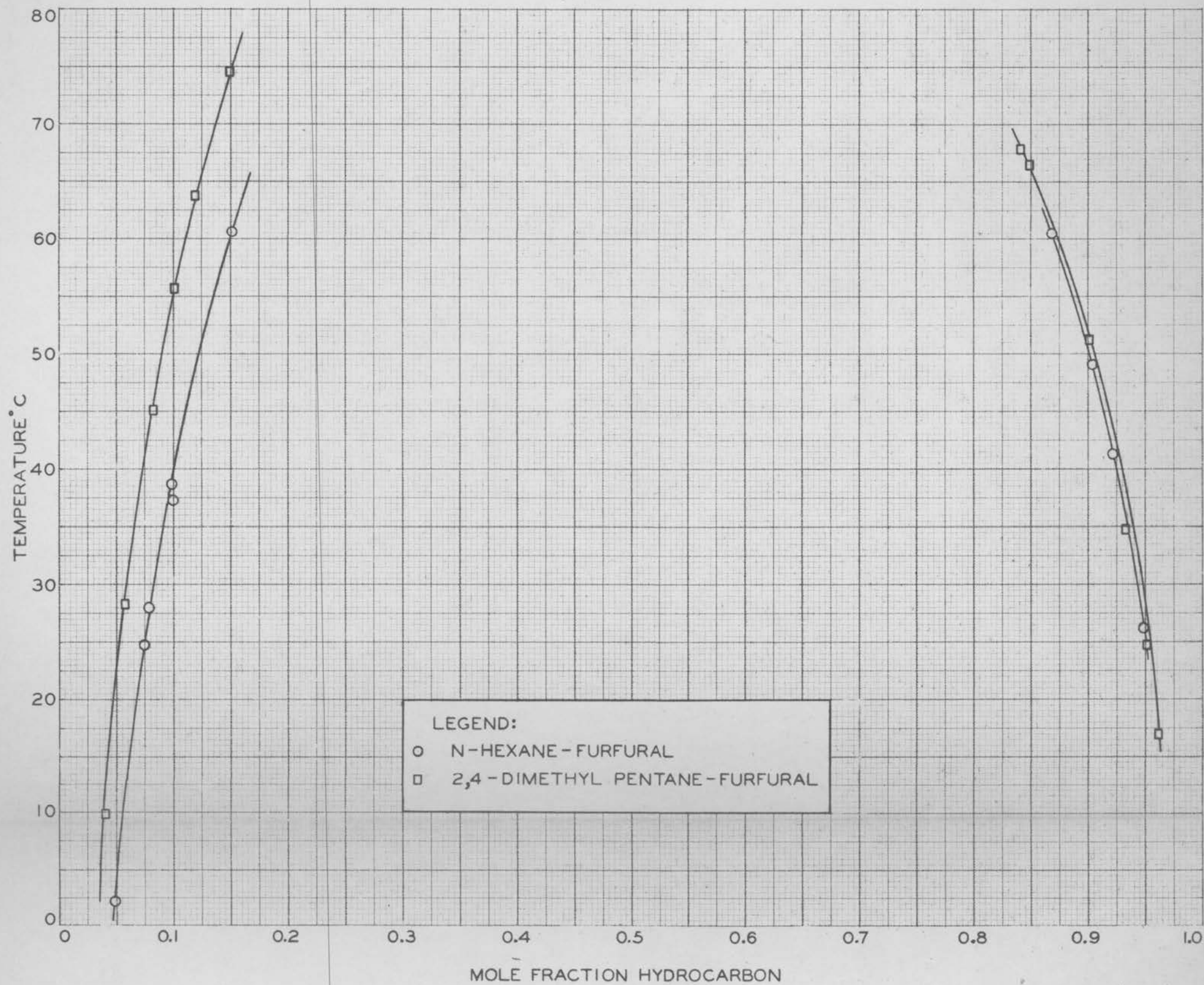


FIG. 3. MUTUAL SOLUBILITIES

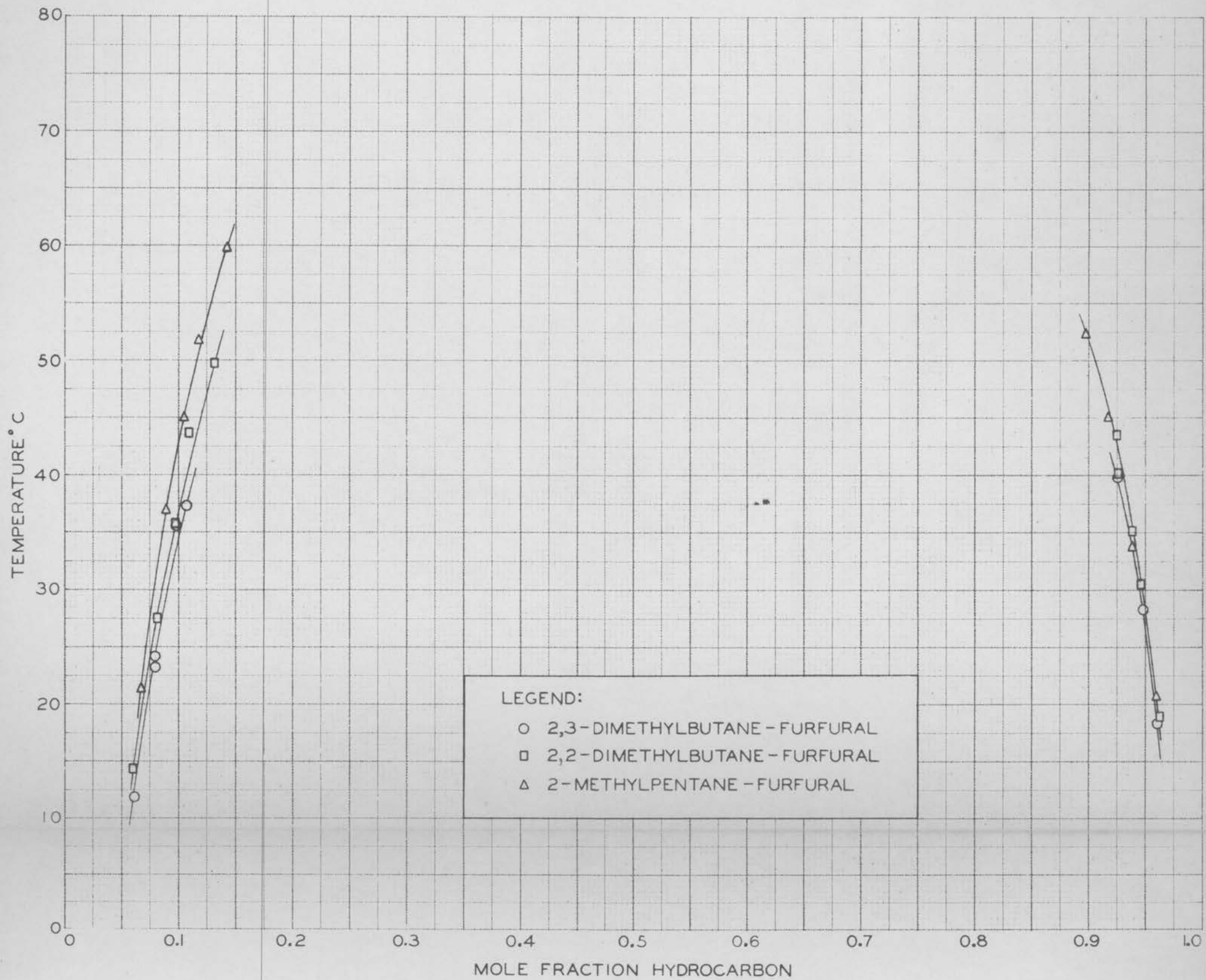


FIG. 4 MUTUAL SOLUBILITIES

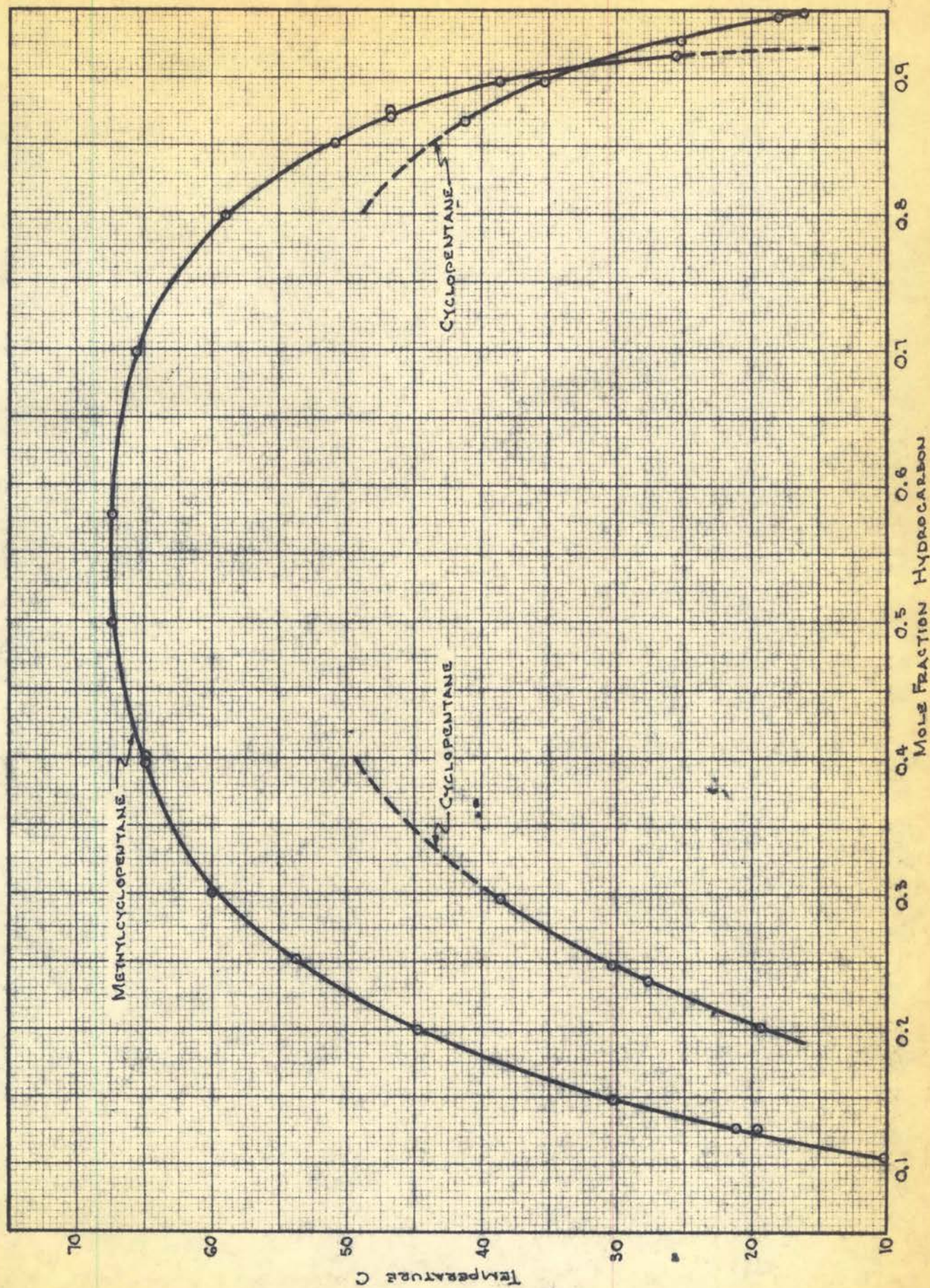


FIG. 5 MUTUAL SOLUBILITIES CYCLOPENTANE-FURFURAL  
METHYLCYCLOPENTANE-FURFURAL

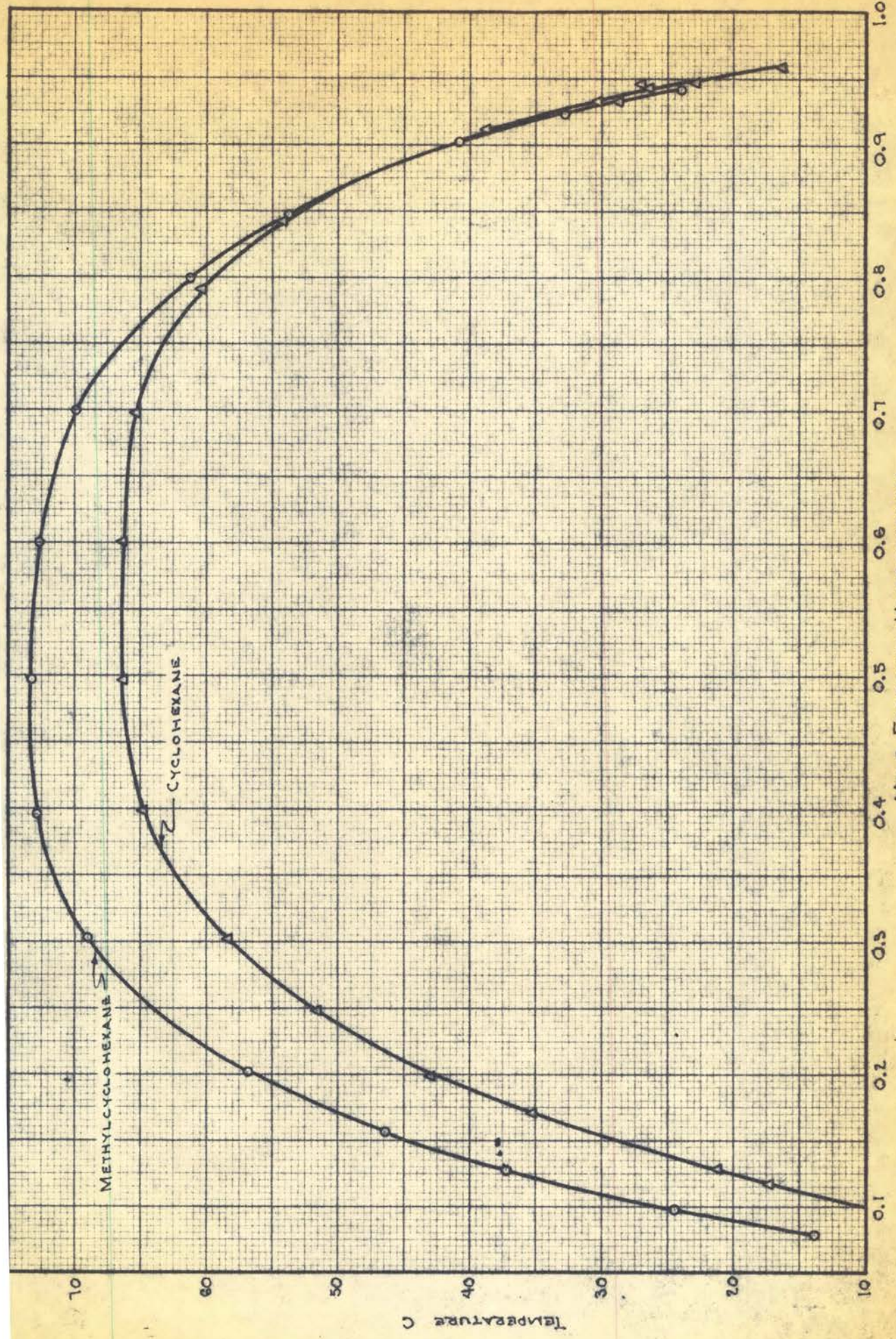


FIG. 6 MUTUAL SOLUBILITIES CYCLOHEXANE-FURFURAL  
METHYLCYCLOHEXANE-FURFURAL

METHYLCYCLOHEXANE

CYCLOHEXANE

TEMPERATURE C

MOLS FRACTION HYDROCARBON



#### IV. EVALUATION OF ACTIVITY COEFFICIENTS

The activity coefficients for a binary system may be evaluated by use of the van Laar equations and mutual solubility data as was demonstrated previously. The method will now be illustrated by a sample calculation of activity coefficients for the system n-hexane-furfural at 29.8° C.

The constants A and B can be determined from equations (53) and (54) if the concentrations in the two equilibrium phases at a specific temperature are known. The equations are:

$$\frac{A}{B} = \frac{\left(\frac{x_i}{x_j} + \frac{y_i}{y_j}\right) \left[\frac{\log(y_i/x_i)}{\log(x_j/y_j)}\right] - 2}{\left(\frac{x_i}{x_j} + \frac{y_i}{y_j}\right) - 2 \frac{x_i}{x_j} \frac{y_i}{y_j} \frac{\log(y_i/x_i)}{\log(x_j/y_j)}}$$

$$A = \frac{\log(y_i/x_i)}{\frac{1}{\left[1 + \frac{A}{B} \frac{x_i}{x_j}\right]^2} - \frac{1}{\left[1 + \frac{A}{B} \frac{y_i}{y_j}\right]^2}}$$

The solubility data for n-hexane-furfural from Figure 3, two points on isotherm of 29.8° C, are:

$$x_i = 0.083 \qquad y_i = 0.943$$

and  $x_i + x_j = 1.0 \qquad y_i + y_j = 1.0$

where n-hexane is component i.

The calculations are as follows:

$$x_i/x_j = 0.083/0.917 = 0.0905 \qquad y_i/y_j = 0.943/0.057 = 16.544$$

$$y_i/x_i = 0.943/0.083 = 11.361 \qquad x_j/y_j = 0.917/0.057 = 16.088$$

$$\log (y_i/x_i) = 1.05542$$

$$\log (x_j/y_j) = 1.20651$$

$$\log (y_i/x_i)/\log (x_j/y_j) = 0.8748$$

$$\frac{A}{B} = \frac{(0.0905 + 16.544) 0.8748 - 2}{(0.0905 + 16.544) - 2 \times 0.0905 \times 16.544 \times 0.8748}$$

$$= 0.8956$$

$$A = \frac{1.05542}{\frac{1}{(1 + 0.8956 \times 0.0905)^2} \frac{1}{(1 + 0.8956 \times 16.544)^2}} = 1.239$$

$$B = 1.239/0.8956 = 1.383$$

Solutions of these equations have been plotted by Colburn and Schoenborn (5) and the actual calculations are not necessary if the charts are available.

These values for A and B should be checked for accuracy by the Gibbs-Duhem relation

$$\frac{\gamma_{ih}}{\gamma_{iv}} = \frac{y_i}{x_i}$$

The activity coefficients are evaluated by equations (52) and (52a).

$$\log \gamma_i = \frac{A}{\left[1 + \frac{A x_i}{B x_j}\right]^2}$$

$$\log \gamma_j = \frac{B}{\left[1 + \frac{B x_j}{A x_i}\right]^2}$$

$x_i$	$x_j$	$x_i/x_j$	$\frac{A}{B} \times \frac{x_i}{x_j}$	$\left[1 + \frac{A}{B} \times \frac{x_i}{x_j}\right]^2$	$\log \gamma_{ih}$	$\gamma_{ih}$
0.083	0.917	0.0905	0.0810	1.1688	1.06006	11.48

$y_i$	$y_j$	$y_i/y_j$	$\frac{A}{B} \times \frac{y_i}{y_j}$	$\left[1 + \frac{A}{B} \times \frac{y_i}{y_j}\right]^2$	$\log \gamma_{iv}$	$\gamma_{iv}$
0.943	0.057	16.544	14.817	250.18	0.00495	1.012
			$\frac{\gamma_{ih}}{\gamma_{iv}} = \frac{11.48}{1.012} = 11.35$			
			$\frac{y_i}{x_i} = \frac{0.943}{0.083} = 11.36$			
$x_i$	$x_j$	$x_j/x_i$	$\frac{B}{A} \times \frac{x_j}{x_i}$	$\left[1 + \frac{B}{A} \times \frac{x_j}{x_i}\right]^2$	$\log \gamma_{jh}$	$\gamma_{jh}$
0.083	0.917	11.048	12.332	177.74	0.00778	1.018
$y_i$	$y_j$	$y_j/y_i$	$\frac{B}{A} \times \frac{y_j}{y_i}$	$\left[1 + \frac{B}{A} \times \frac{y_j}{y_i}\right]^2$	$\log \gamma_{iv}$	$\gamma_{iv}$
0.943	0.057	0.0604	0.06747	1.1396	1.21358	16.35
			$\frac{\gamma_{iv}}{\gamma_{jh}} = 16.06$			
			$\frac{x_j}{y_j} = 16.09$			

The activity coefficients at other concentrations may be calculated in the same manner.

The van Laar activity coefficient constants for the binary systems studied are given in Table I for the temperatures indicated. Plots of the activity coefficients for the systems n-hexane-furfural and isooctane-furfural at 29.8° C are shown in Figures 7 and 8.

TABLE I  
VAN LAAR ACTIVITY COEFFICIENT CONSTANTS

System	A	B	Temperature °C
Aniline with			
N-hexane (6)*	1.248	1.309	25
N-heptane (19)*	1.371	1.248	25
Methylcyclopentane	0.918	1.089	25
Cyclohexane (12)*	0.861	1.117	25
Methylcyclohexane (19)*	1.041	1.140	25
Furfural with			
N-hexane	1.119	1.203	50
	1.188	1.305	37.8
	1.239	1.116	29.8
2-methylpentane	1.208	1.326	37.8
2,2-dimethylbutane	1.181	1.333	37.8
2,3-dimethylbutane	1.169	1.322	37.8
N-heptane	1.334	1.365	29.8
	1.302	1.287	37.8
2,4-dimethylpentane	1.357	1.373	29.8
	1.307	1.301	37.8
Isooctane	1.306	1.173	50
	1.394	1.285	37.8
	1.446	1.371	29.8
2,2,5-Trimethylhexane	1.828	1.568	37.8
Cyclopentane	0.332	1.202	37.8
Methylcyclopentane	1.006	1.212	37.8
Cyclohexane	1.023	1.358	29.8
	0.983	1.265	37.8
Methylcyclohexane	1.177	1.382	25
	1.082	1.243	37.8

\*Calculated from data as indicated by references.

## V. PREDICTION OF COMPONENT DISTRIBUTION

The fact that component distribution between liquid phases in equilibrium can be predicted from activity coefficients has been demonstrated mathematically but must now be proved by comparison of calculated and experimental data. The method of calculating the predicted data is illustrated by the calculation of case 1 in Table VI.

The problem is to determine the composition of the heavy phase for the system isooctane-n-hexane-furfural when the light phase (hydrocarbon-rich phase) has a solvent-free composition of 0.841 mole fraction isooctane. The temperature is 29.8° C.

Solubilities for the system isooctane-furfural are presented in Figure 2 and for n-hexane-furfural in Figure 3.

The binary solubility data are

	Hydrocarbon Phase	Solvent Phase
Mole fraction furfural in isooctane	0.057	0.954
Mole fraction furfural in n-hexane	0.057	0.917

The van Laar constants and the activity coefficients are evaluated from this data as previously illustrated. The activity coefficients for these binary systems are shown in Figures 7 and 8.

The concentration of furfural in each of the two ternary phases is estimated by assuming it will be the weighted average of the concentration in the binary phases.

$$\begin{aligned} 0.841 \times 0.057 &= 0.048 \\ 0.159 \times 0.057 &= \frac{0.009}{0.057} \end{aligned}$$

estimated concentration of furfural in the hydrocarbon phase.

FIG.7 ACTIVITY COEFFICIENTS  
N-HEXANE - FURFURAL  
29.8°C

VAN LAAR CONSTANTS A=1.239 B=1.383.

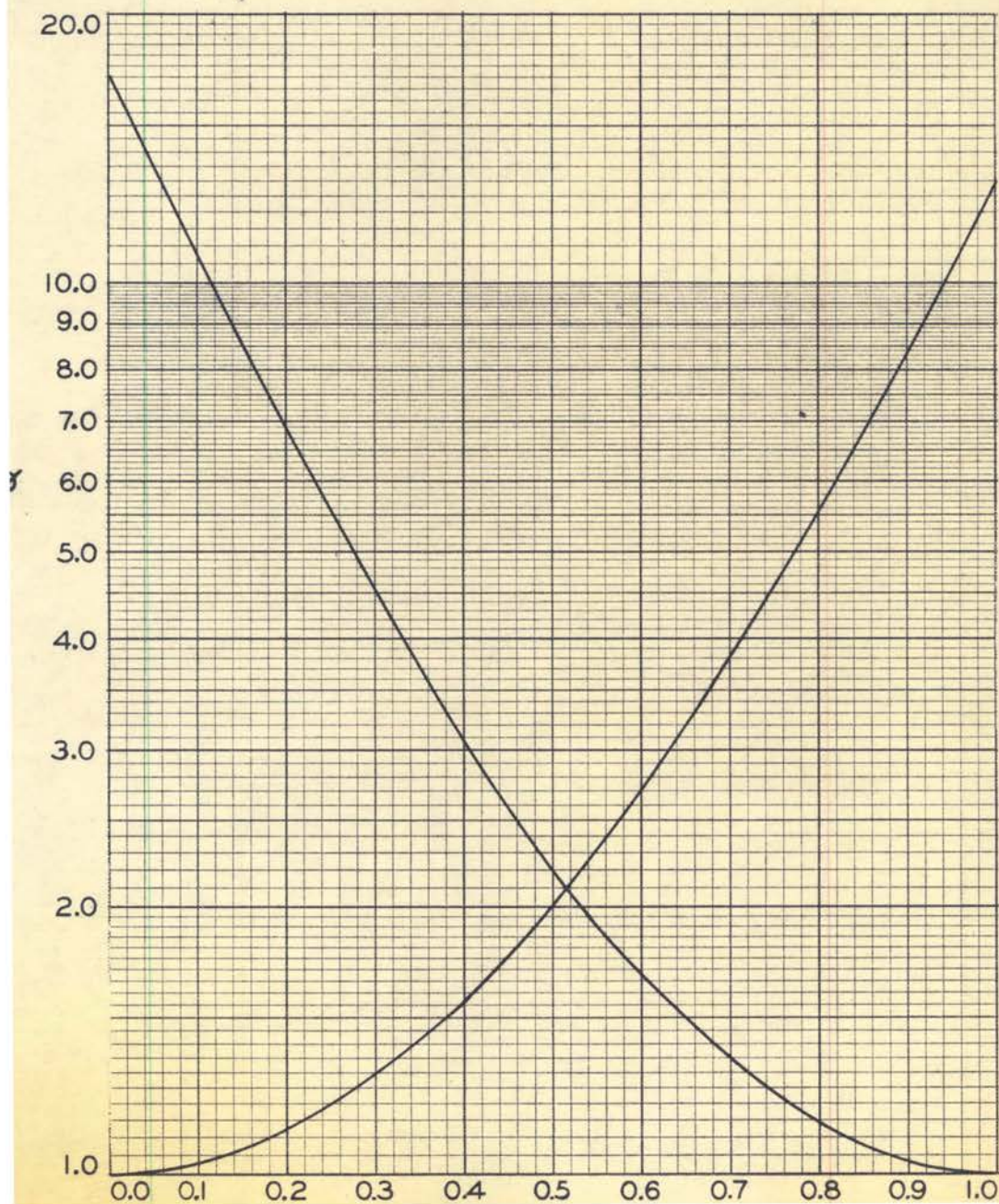
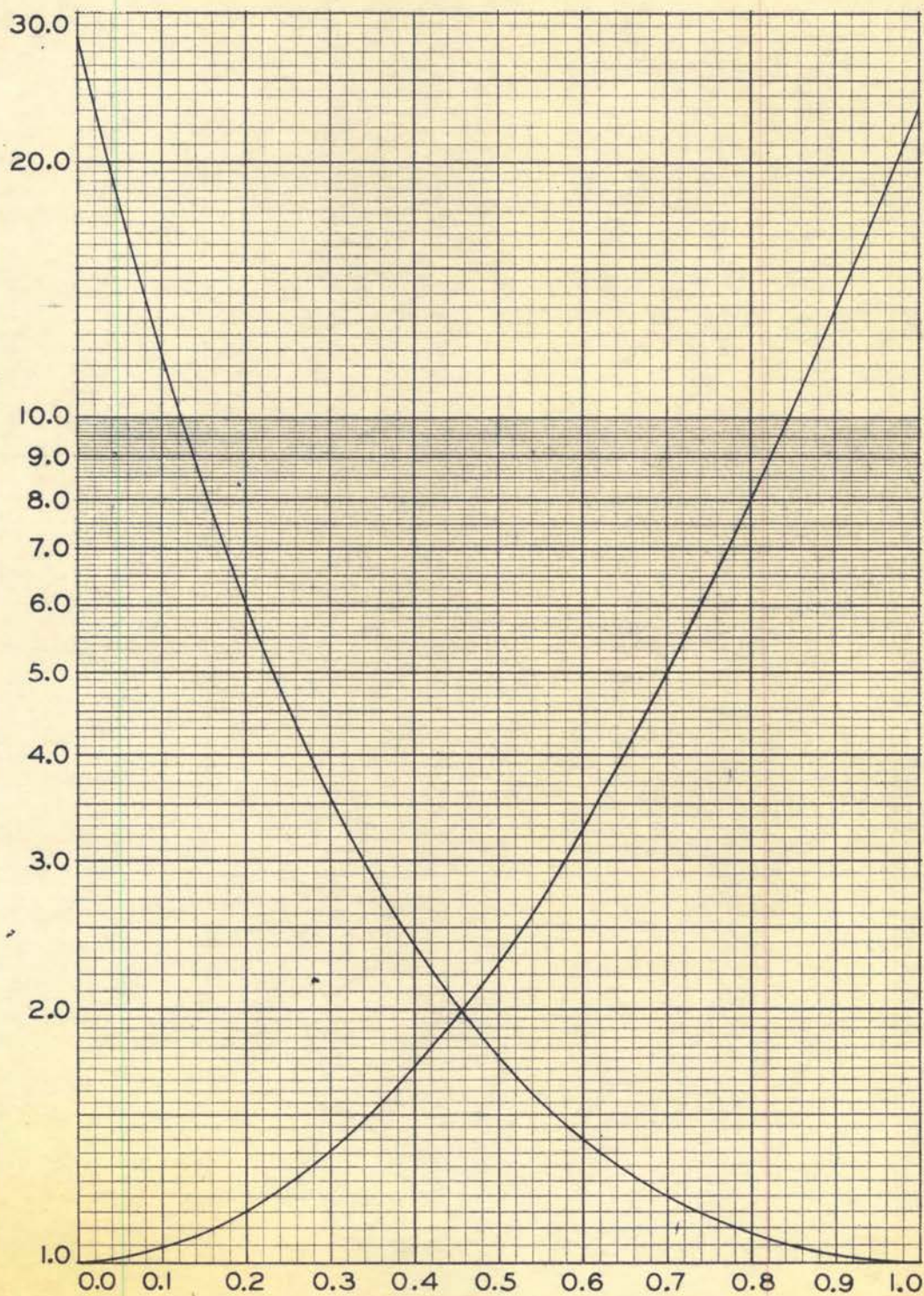


FIG.8 ACTIVITY COEFFICIENTS  
ISOOCTANE - FURFURAL  
29.8°C

VAN LAAR CONSTANTS  $A=1.446$   $B=1.371$



The activity coefficients for these solvent concentrations are read from the curves and the partition coefficients determined. Thus the activity coefficient of isooctane in 0.057 concentration furfural is 1.006 and in 0.948 concentration furfural is 17.51, and the partition coefficient is  $17.51/1.006 = 17.34$ . Therefore the concentration of isooctane in the heavy phase is

$$\frac{0.841 (1.000 - 0.057)}{17.34} = 0.046$$

And similarly for n-hexane the partition coefficient is  $13.36/1.013 = 13.19$ . And the concentration in the heavy phase is

$$\frac{0.159 (1.000 - 0.057)}{13.19} = 0.011$$

Therefore the heavy phase composition is:

<u>Component</u>	<u>mole fraction</u>
isooctane	0.046
n-hexane	0.011
furfural (by difference)	<u>0.943</u>
	1.000

The calculated concentration of furfural in the heavy phase deviates less than one per cent from the estimated concentration. Therefore a second approximation is not necessary.

The ternary phase equilibria which have been calculated in this manner are compared in Tables II through VI with experimental data. A study of the system n-hexane-methylcyclopentane-aniline presented in Table II reveals that the experimental data is not very consistent and the predicted values are well within the range of the apparent experimental error. The experimental separation between the two hydrocarbons is in some cases greater than the predicted separation and in others not as great.



The system n-heptane-methylcyclohexane-aniline as presented in Table III shows good agreement between the experimental and predicted values. With this system the predictions show a consistently smaller separation between the two hydrocarbons with the exception of Case 1 in which the experimental data are not in agreement with the rest of the data.

The data for the system n-heptane-cyclohexane-aniline compared in Table IV show very good agreement between experimental and predicted values. The predicted separation for this system is better than that obtained experimentally.

The predicted and experimental data for the system n-heptane-cyclohexane-furfural compared in Table V are in good agreement. Also with the exception of Cases 1 and 2 the predicted values are conservative.

Binary solubilities for various paraffin-furfural systems indicate that it would be possible to separate two paraffins of different molecular weights by extraction with furfural. To determine the possibilities of such a separation some experimental data were determined and compared with predicted values. The comparison in Table VI shows that the experimental separation is greater than the calculations predict.

These comparisons show that useable predictions of component distribution can be made from mutual solubility data by the method illustrated.

TABLE II

OF EXPERIMENTAL AND ESTIMATED CONCENTRATIONS FOR

HEXANE-METHYLCYCLOPENTANE-ANILINE AT 77°F

<u>Case 3</u>		<u>Case 4</u>		<u>Case 5</u>		<u>Case 6</u>		<u>Case 7</u>	
<u>Exp</u>	<u>Est</u>	<u>Exp</u>	<u>Est</u>	<u>Exp</u>	<u>Est</u>	<u>Exp</u>	<u>Est</u>	<u>Exp</u>	<u>Est</u>
0.621	0.621	0.472	0.472	0.310	0.310	0.155	0.155	0.086	0.086
0.522	0.464	0.385	0.334	0.240	0.211	0.166	0.103	0.032	0.057
0.139	0.104	0.090	0.117	0.104	0.131	0.120	0.145	0.130	0.151
0.885	0.856	0.870	0.831	0.846	0.805	0.831	0.779	0.784	0.768
	0.869		0.842		0.813		0.782		0.768

values.

benzene rich phase, solvent free basis.

benzene rich phase, solvent free basis.

benzene rich phase.

benzene rich phase.

benzene rich phase calculated from estimated values of  $x_j$  and  $y_j$ .

. Phy. Chem., 47, 444 (1943).

TABLE III

OF EXPERIMENTAL AND ESTIMATED CONCENTRATIONS FOR

HEPTANE-METHYLCYCLOHEXANE-ANILINE AT 77°F

<u>wt</u>	<u>Case 4</u>		<u>Case 5</u>		<u>Case 6</u>		<u>Case 7</u>		<u>Case 8</u>		<u>Case 9</u>	
	<u>Exp</u>	<u>Est</u>	<u>Exp</u>	<u>Est</u>	<u>Exp</u>	<u>Est</u>	<u>Exp</u>	<u>Est</u>	<u>Exp</u>	<u>Est</u>	<u>Exp</u>	<u>Est</u>
761	0.630	0.630	0.553	0.553	0.496	0.496	0.339	0.339	0.254	0.254	0.203	0.203
641	0.494	0.497	0.401	0.421	0.328	0.366	0.233	0.237	0.157	0.174	0.112	0.138
089	0.090	0.095	0.091	0.099	0.094	0.101	0.101	0.109	0.105	0.113	0.107	0.115
016	0.913	0.902	0.905	0.896	0.895	0.889	0.886	0.873	0.872	0.865	0.863	0.860
019		0.908		0.898		0.893		0.876		0.867		0.861

TABLE III (Continued)

COMPARISON OF EXPERIMENTAL AND ESTIMATED CONCENTRATIONS FOR

N-HEPTANE-METHYLCYCLOHEXANE-ANILINE AT 77°F

Columns headed Exp. are experimental values.

Columns headed Est. are estimated or predicted values.

$\frac{Y_i}{1-y_j}$  mole fraction heptane in hydrocarbon rich phase, solvent free basis.

$\frac{x_i}{1-x_j}$  mole fraction heptane in solvent rich phase, solvent free basis.

$y_j$  mole fraction aniline in hydrocarbon rich phase.

$x_j$  mole fraction aniline in solvent rich phase.

$x_j$  (Calc.) mole fraction aniline in solvent rich phase calculated from estimated values of  $x_j$  and  $y_j$ .

Experimental data from Varteressian and Fenske, Ind & Eng Chem 29, 271 (1937).

TABLE IV

COMPARISON OF EXPERIMENTAL AND ESTIMATED CONCENTRATIONS FOR

N-HEPTANE-CYCLOHEXANE-ANILINE AT 77°F

Concentrations	Case 1		Case 2		Case 3		Case 4	
	Exp	Est	Exp	Est	Exp	Est	Exp	Est
$\frac{y_i}{1-y_j}$	0.260	0.260	0.689	0.689	0.770	0.770	0.490	0.490
$\frac{x_i}{1-x_j}$	0.183	0.176	0.525	0.517	0.661	0.608	0.399	0.344
$y_j$	0.124	0.139	0.094	0.104	0.084	0.098	0.103	0.120
$x_j$	0.830	0.777	0.905	0.871	0.928	0.889	0.886	0.827
$x_j$ (Calc.)		0.784		0.880		0.898		0.837

Columns headed Exp. are experimental values.  
Columns headed Est. are estimated values.

$\frac{y_i}{1-y_j}$  mole fraction n-heptane in hydrocarbon rich phase, solvent free basis.

$\frac{x_i}{1-x_j}$  mole fraction n-heptane in solvent rich phase, solvent free basis.

$y_j$  mole fraction aniline in hydrocarbon rich phase.

$x_j$  mole fraction aniline in solvent rich phase.

$x_j$  (Calc.) mole fraction aniline in solvent rich phase calculated from estimated values of  $x_j$  and  $y_j$ .

Experimental data from Hunter and Brown, Ind. Eng. Chem. 39, 1343, (1947).

TABLE V

COMPARISON OF EXPERIMENTAL AND ESTIMATED CONCENTRATIONS FOR

N-HEPTANE-CYCLOHEXANE-FURFURAL AT 85.6°F

Concentrations	Case 1		Case 2		Case 3		Case 4		Case 5		Case 6	
	Exp	Est	Exp	Est	Exp	Est	Exp	Est	Exp	Est	Exp	Est
$\frac{y_i}{1-y_j}$	0.794	0.794	0.800	0.800	0.522	0.522	0.520	0.520	0.191	0.191	0.189	0.189
$\frac{x_i}{1-x_j}$	0.716	0.690	0.717	0.698	0.389	0.399	0.387	0.398	0.122	0.133	0.120	0.131
$y_j$	0.061	0.060	0.060	0.060	0.060	0.061	0.072	0.061	0.059	0.063	0.058	0.063
$x_j$	0.930	0.917	0.928	0.918	0.902	0.893	0.900	0.892	0.870	0.863	0.871	0.863
$x_j$ (Calc.)		0.919		0.919		0.894		0.894		0.862		0.862

Columns headed Exp. are experimental values.

Columns headed Est. are estimated or predicted values.

$\frac{y_i}{1-y_j}$	Mole fraction heptane in hydrocarbon rich phase, solvent free basis.
$\frac{x_i}{1-x_j}$	Mole fraction heptane in solvent rich phase, solvent free basis.
$y_j$	mole fraction furfural in hydrocarbon rich phase.
$x_j$	mole fraction furfural in solvent rich phase.
$x_j$ (Calc.)	mole fraction furfural in solvent rich phase calculated from estimated values of $x_j$ and $y_j$

TABLE VI

## COMPARISON OF EXPERIMENTAL AND ESTIMATED CONCENTRATIONS FOR

## ISOCTANE-N-HEXANE-FURFURAL SYSTEM AT 85.6°F

Concentrations	Case 1		Case 2		Case 3		Case 4		Case 5		Case 6	
	Exp	Est	Exp	Est	Exp	Est	Exp	Est	Exp	Est	Exp	Est
$\frac{y_i}{1-y_j}$	0.841	0.841	0.527	0.527	0.206	0.206	0.841	0.841	0.527	0.527	0.209	0.209
$\frac{x_i}{1-x_j}$	0.769	0.800	0.425	0.464	0.150	0.172	0.766	0.800	0.419	0.464	0.150	0.174
$y_j$	0.061	0.057	0.061	0.057	0.057	0.057	0.071	0.057	0.062	0.057	0.057	0.057
$x_j$	0.948	0.948	0.937	0.937	0.929	0.925	0.951	0.948	0.937	0.937	0.929	0.925
$x_j$ (Calc.)		0.942		0.933		0.923		0.942		0.933		0.923

Columns headed Exp. are experimental values.

Columns headed Est. are estimated values.

$\frac{y_i}{1-y_j}$	mole fraction isooctane in hydrocarbon rich phase, solvent free basis.
$\frac{x_i}{1-x_j}$	mole fraction isooctane in solvent rich phase, solvent free basis.
$y_j$	mole fraction furfural in hydrocarbon rich phase.
$x_j$	mole fraction furfural in solvent rich phase.
$x_j$ (Calc.)	mole fraction furfural in solvent rich phase cal- culated from estimated values of $x_j$ and $y_j$ .

## VI. CORRELATION OF PARTITION COEFFICIENTS

Since the comparison of predicted and experimental values of equilibrium concentrations has proven the acceptability of the assumption that paraffin and naphthene hydrocarbons form ideal solutions in each other, the method of prediction may be extended to multicomponent systems of these hydrocarbons. Holding the assumption of ideal hydrocarbon solutions as valid, the partition coefficient becomes a function of temperature and the concentration of the solvent in each of the phases and is independent of the concentrations of the hydrocarbon components. Therefore at constant temperature a system of "K" charts similar to vapor-liquid equilibria "K" charts can be plotted. These charts would be a plot of partition coefficient versus solvent concentration in one phase with solvent concentration in the equilibrium phase serving as parameter. Such a system of charts have been prepared and are shown in Figures 9 through 25. These charts may be used to determine component distribution between phases for multicomponent systems if the assumption of ideal hydrocarbon solutions can be shown to be acceptable. In general, for systems involving paraffins, olefins, and naphthenes, in admixture the charts will give good results. However, the present state of knowledge does not permit the prediction of the effect of aromatics on hydrocarbon-solvent systems.



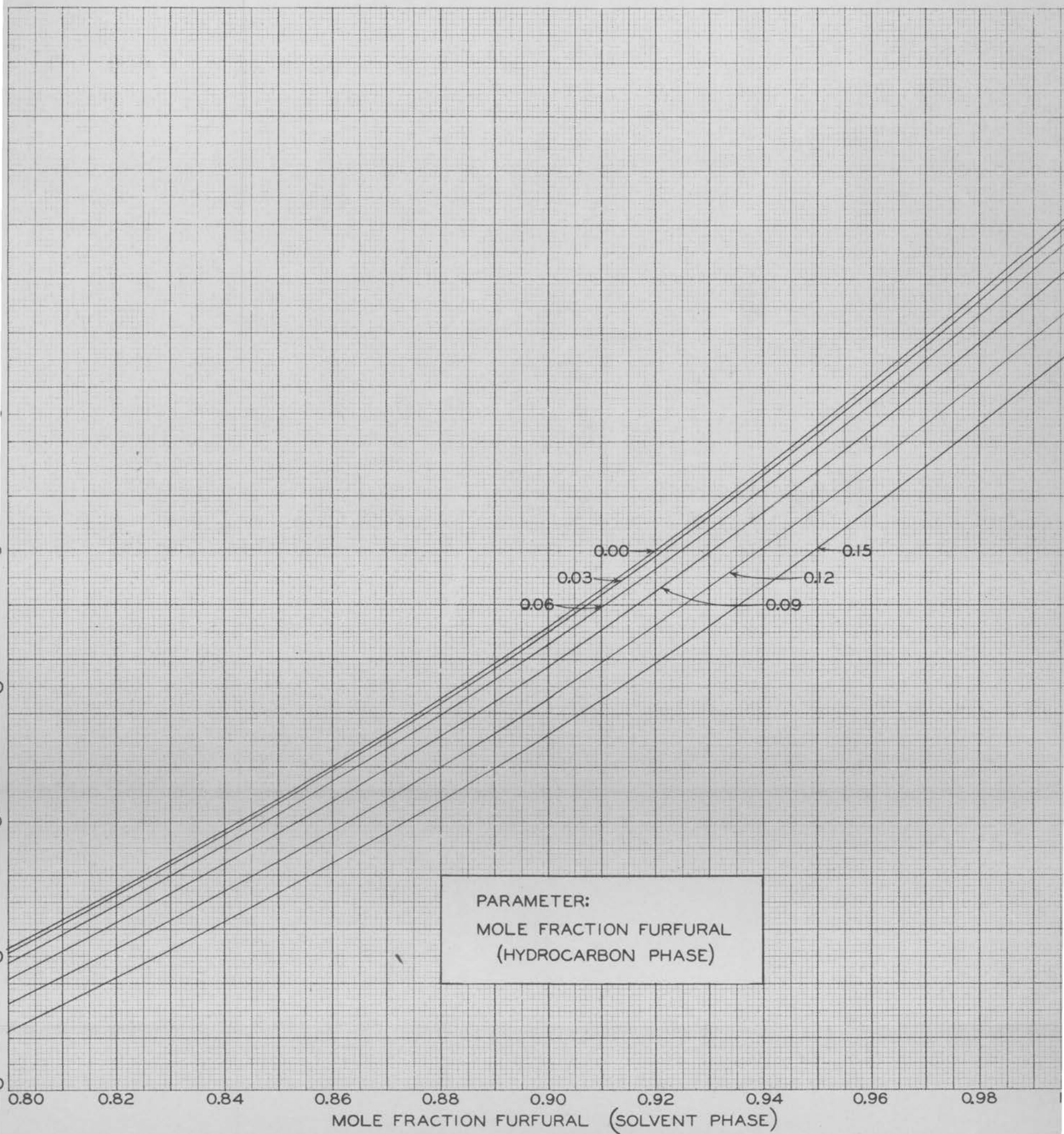


FIG. 9 PARTITION COEFFICIENTS CYCLOPENTANE-FURFURAL AT 37.8° C

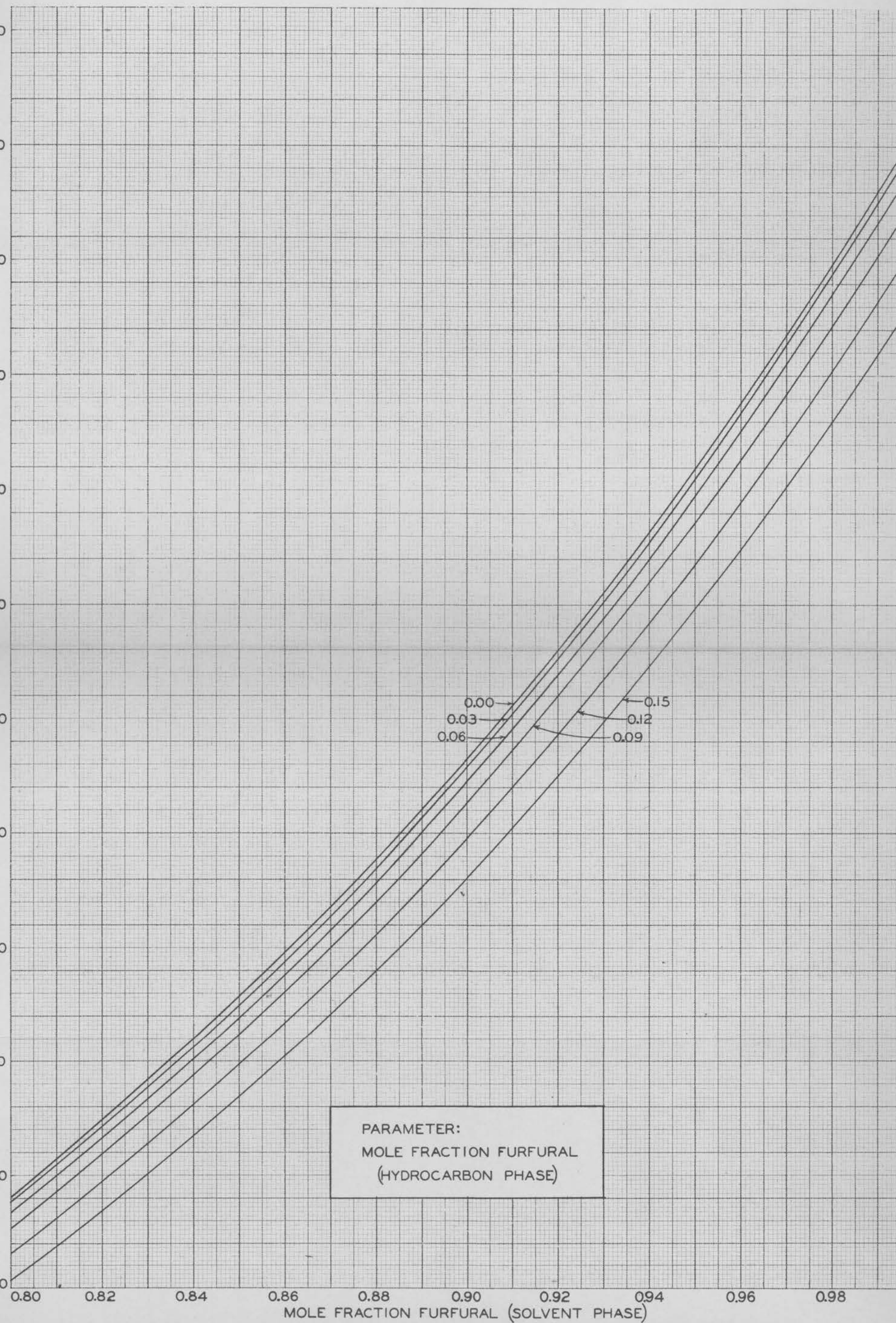
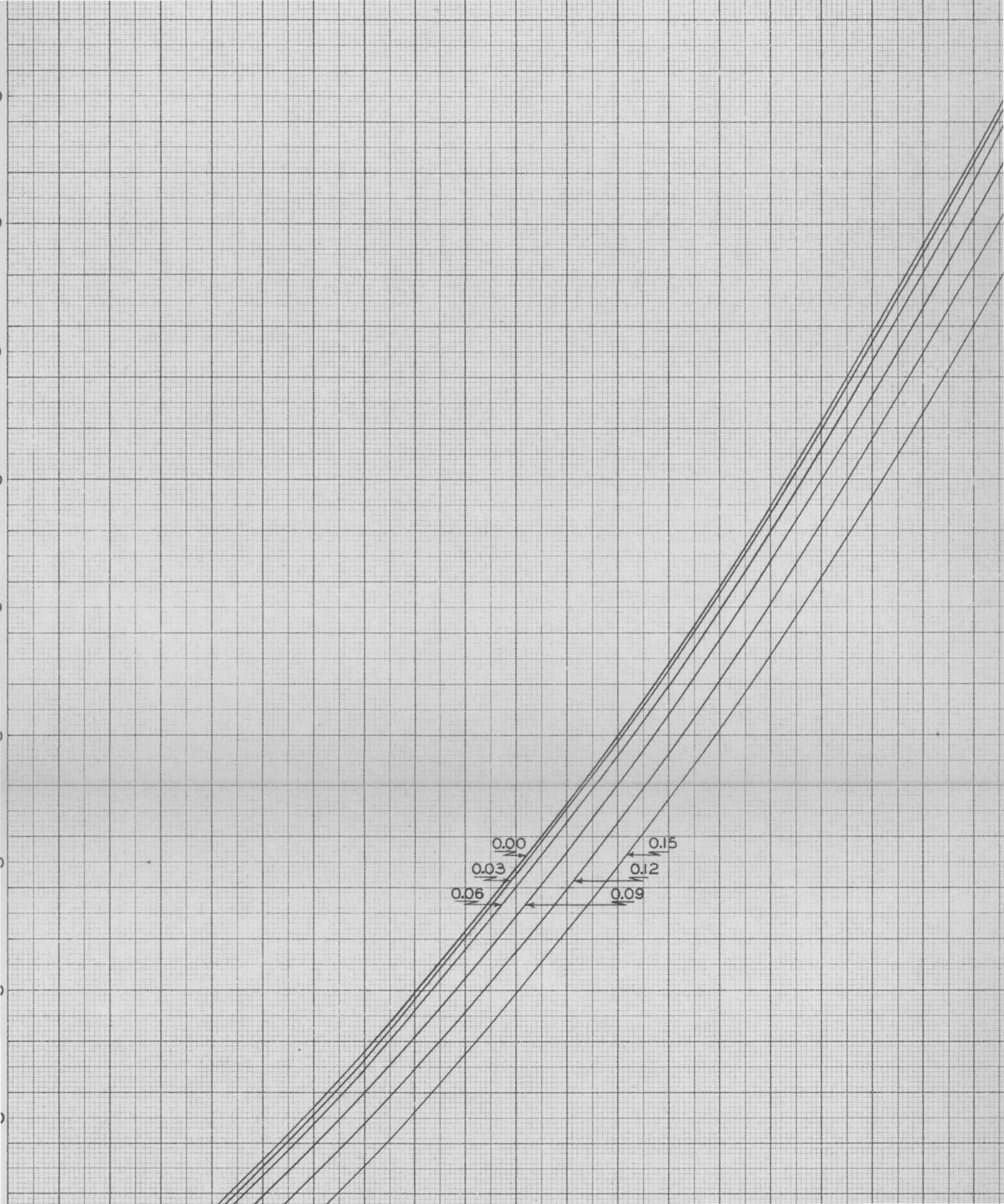


FIG.10 PARTITION COEFFICIENT CYCLOHEXANE-FURFURAL AT 37.8°C



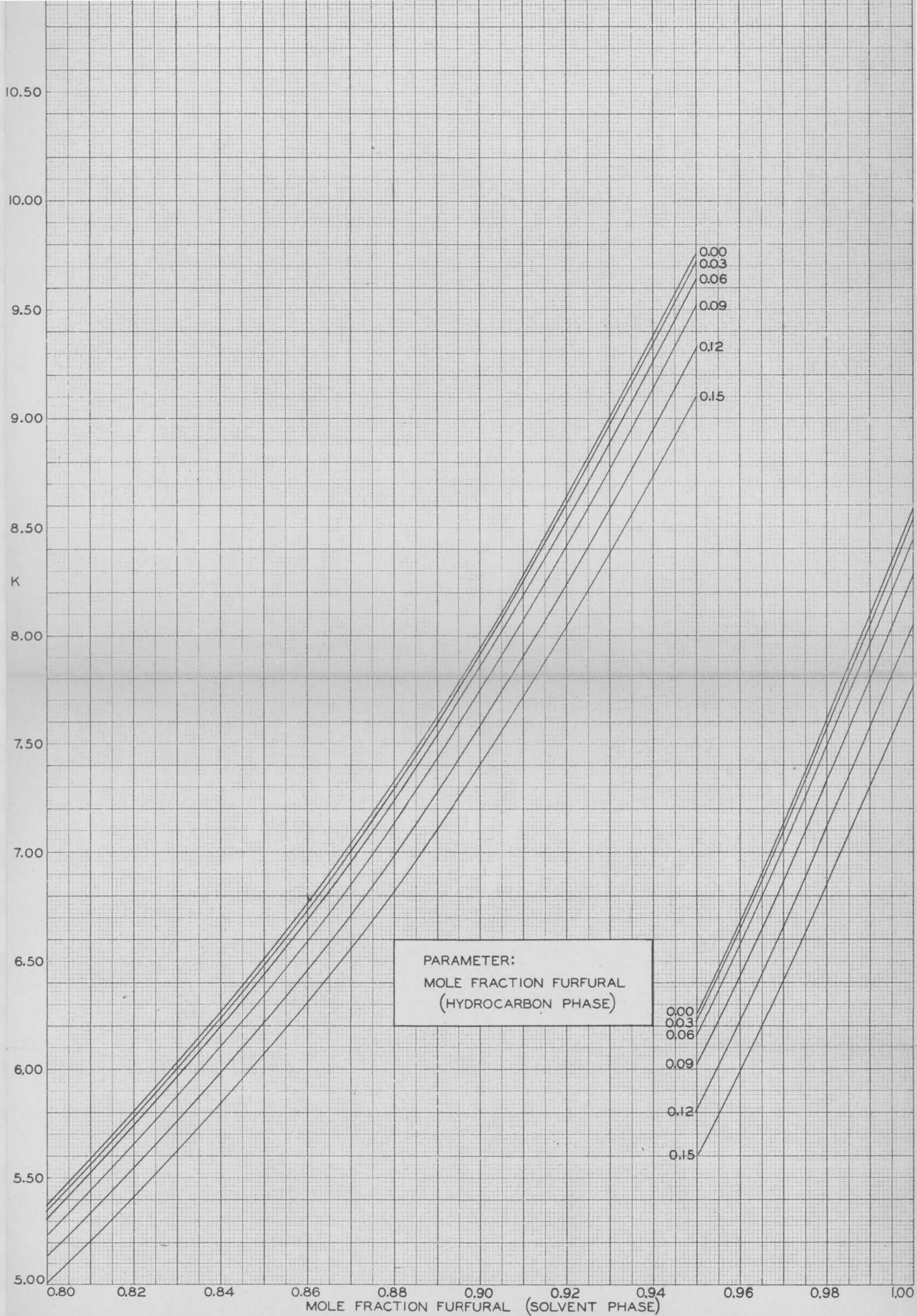


FIG.12 PARTITION COEFFICIENT METHYLCYCLOHEXANE - FURFURAL AT 37.8° C

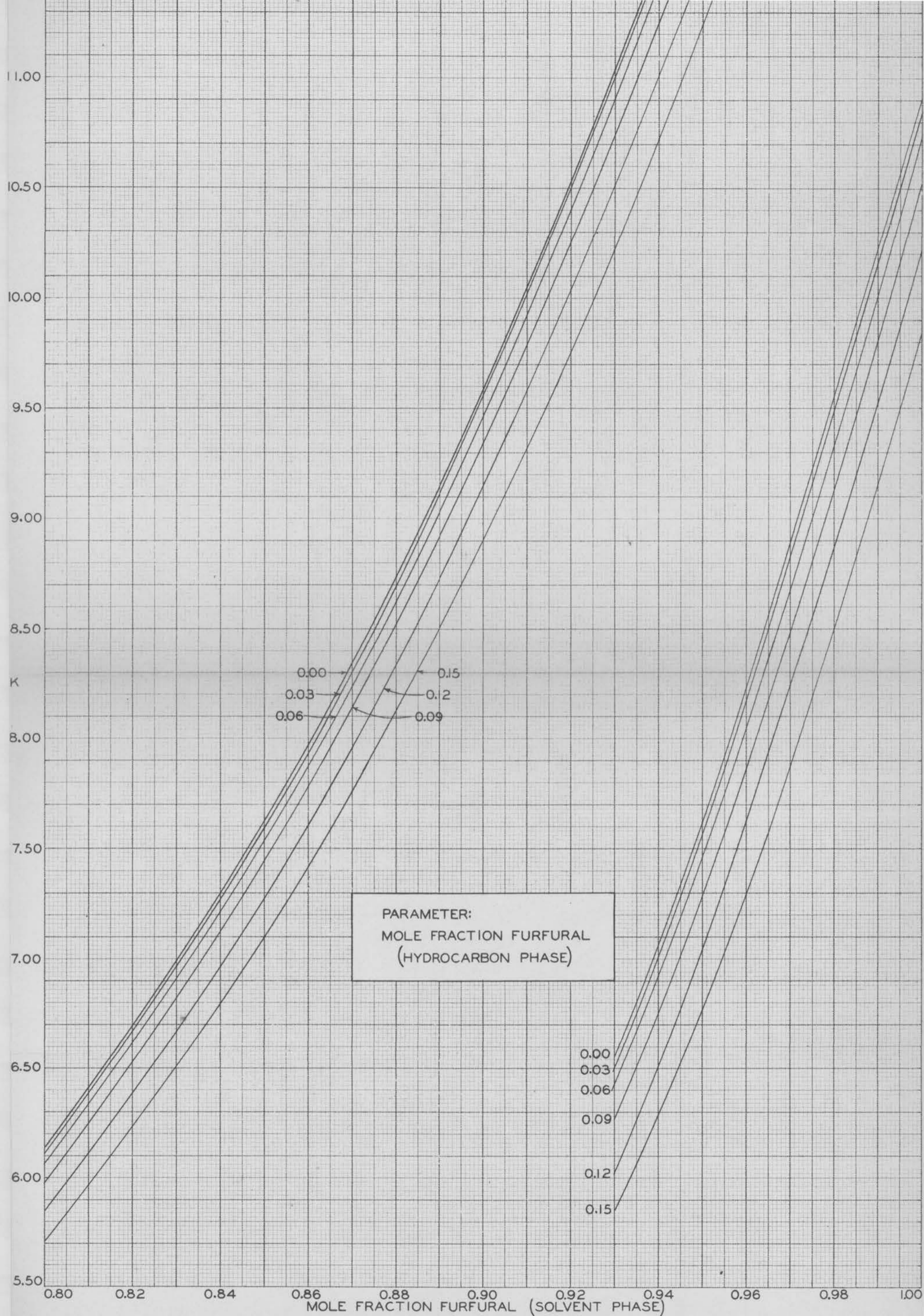


FIG.13 PARTITION COEFFICIENTS N-HEXANE-FURFURAL AT 37.8° C

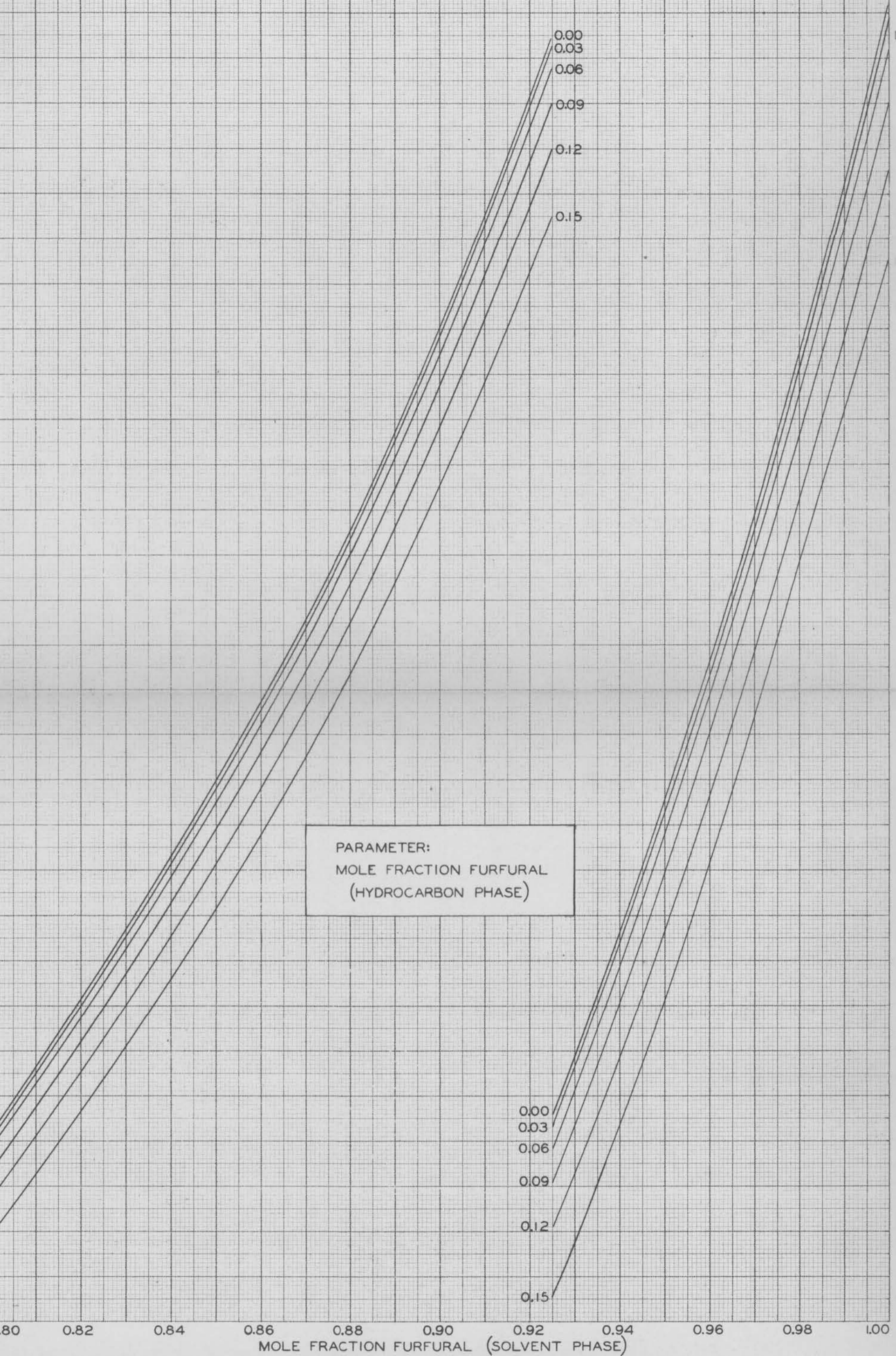
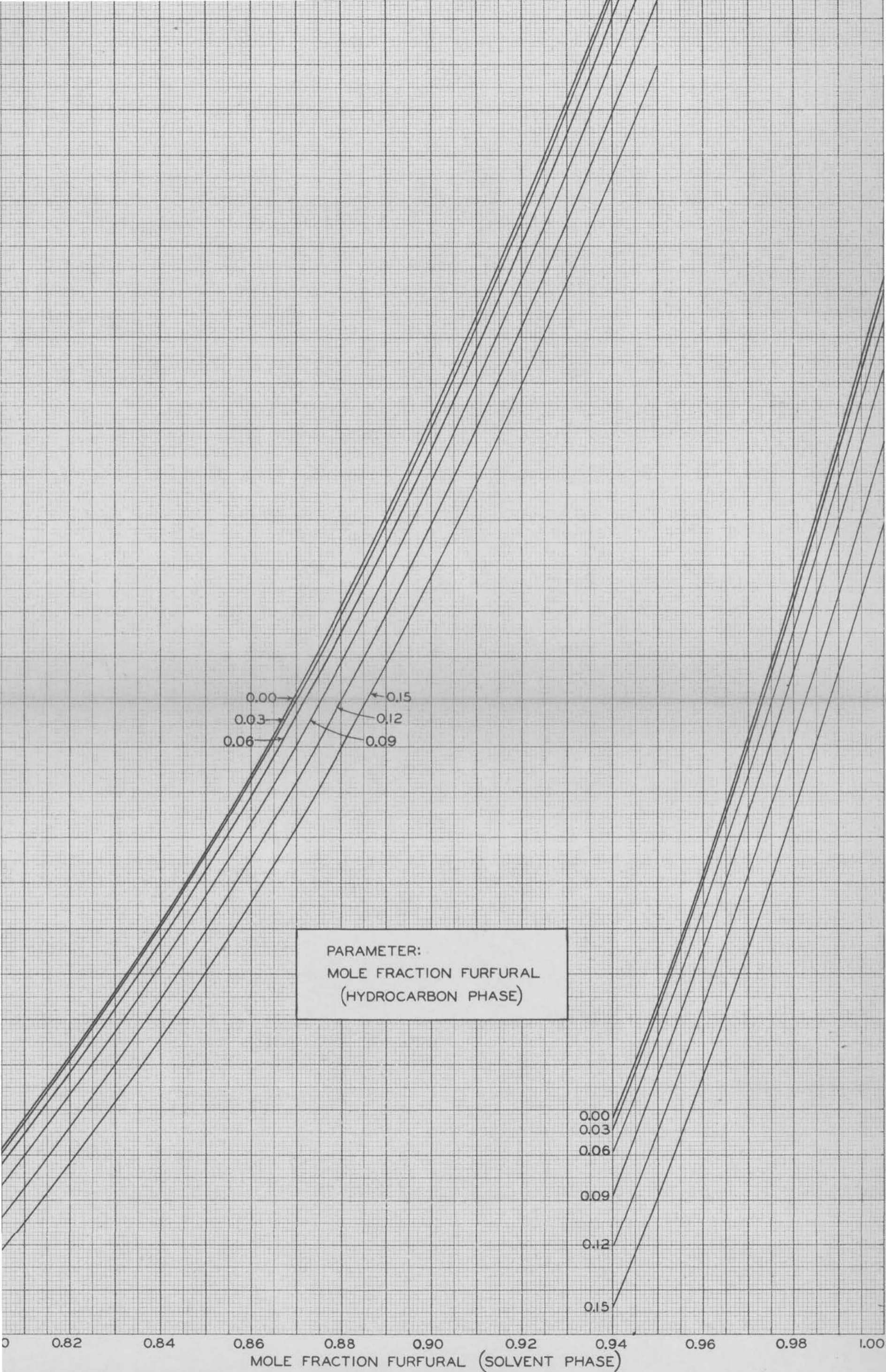
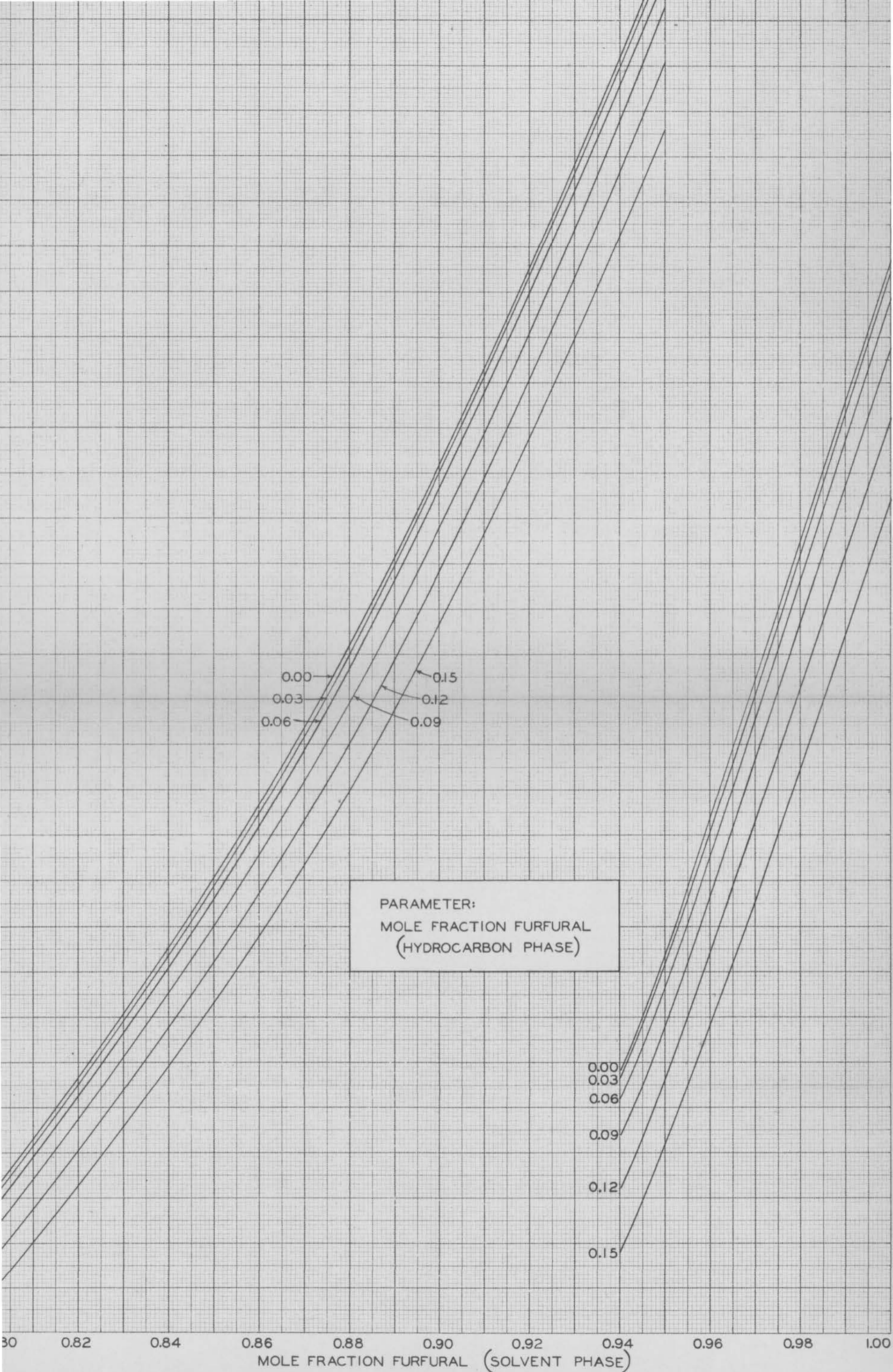


FIG. 14 PARTITION COEFFICIENTS 2-METHYLPENTANE - FURFURAL AT 37.8°C



5.15 PARTITION COEFFICIENTS 2,2-DIMETHYLBUTANE-FURFURAL AT 37.8°C



G.16 PARTITION COEFFICIENTS 2,3-DIMETHYLBUTANE-FURFURAL AT 37.8°C



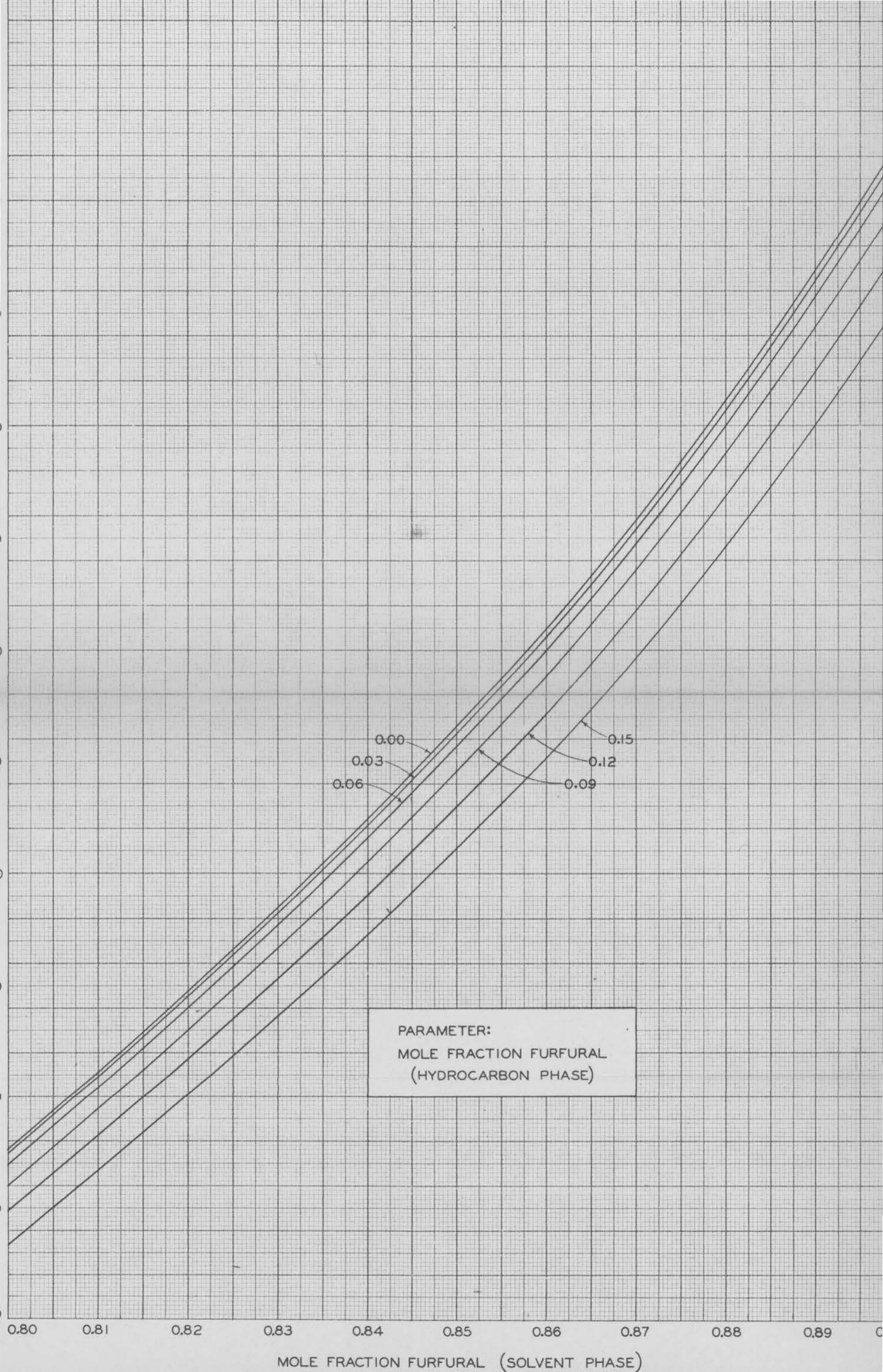


FIG. 17 PARTITION COEFFICIENTS N-HEPTANE-FURFURAL AT 37.8°C

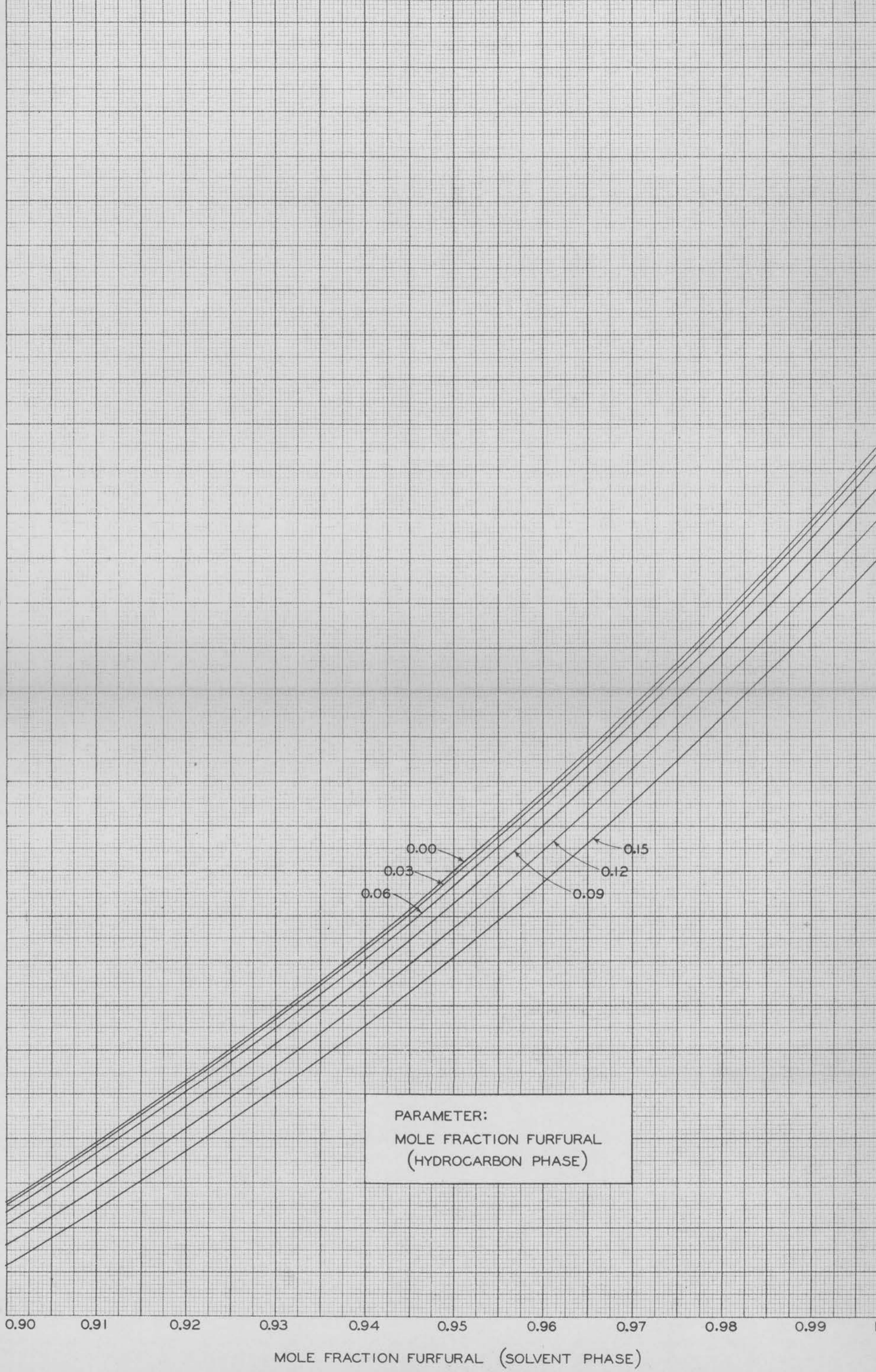


FIG.17 PARTITION COEFFICIENTS N-HEPTANE-FURFURAL AT 37.8°C

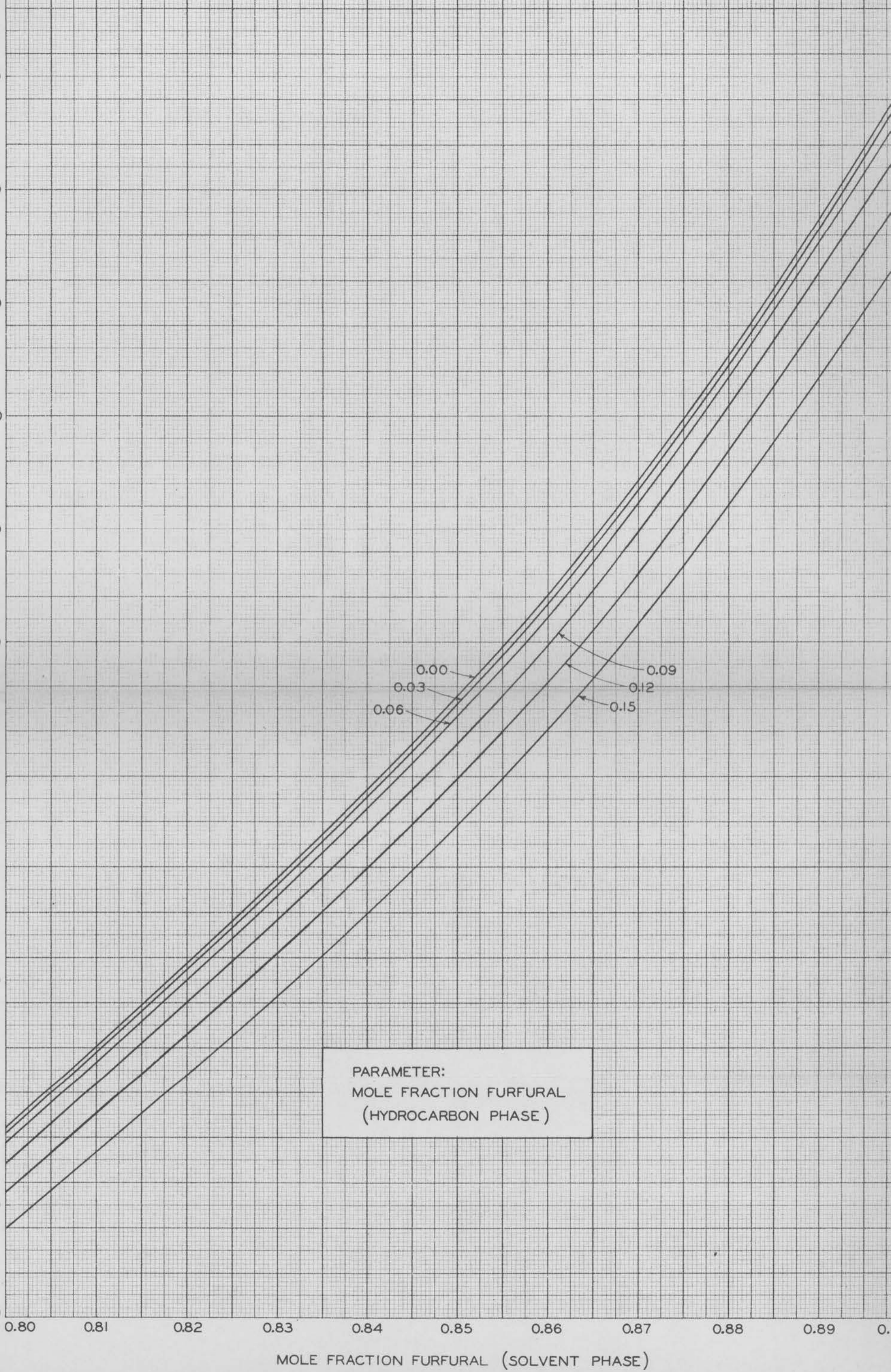


FIG. 18 PARTITION COEFFICIENTS 2,4-DIMETHYLPENTANE - FURFURAL AT 37.8

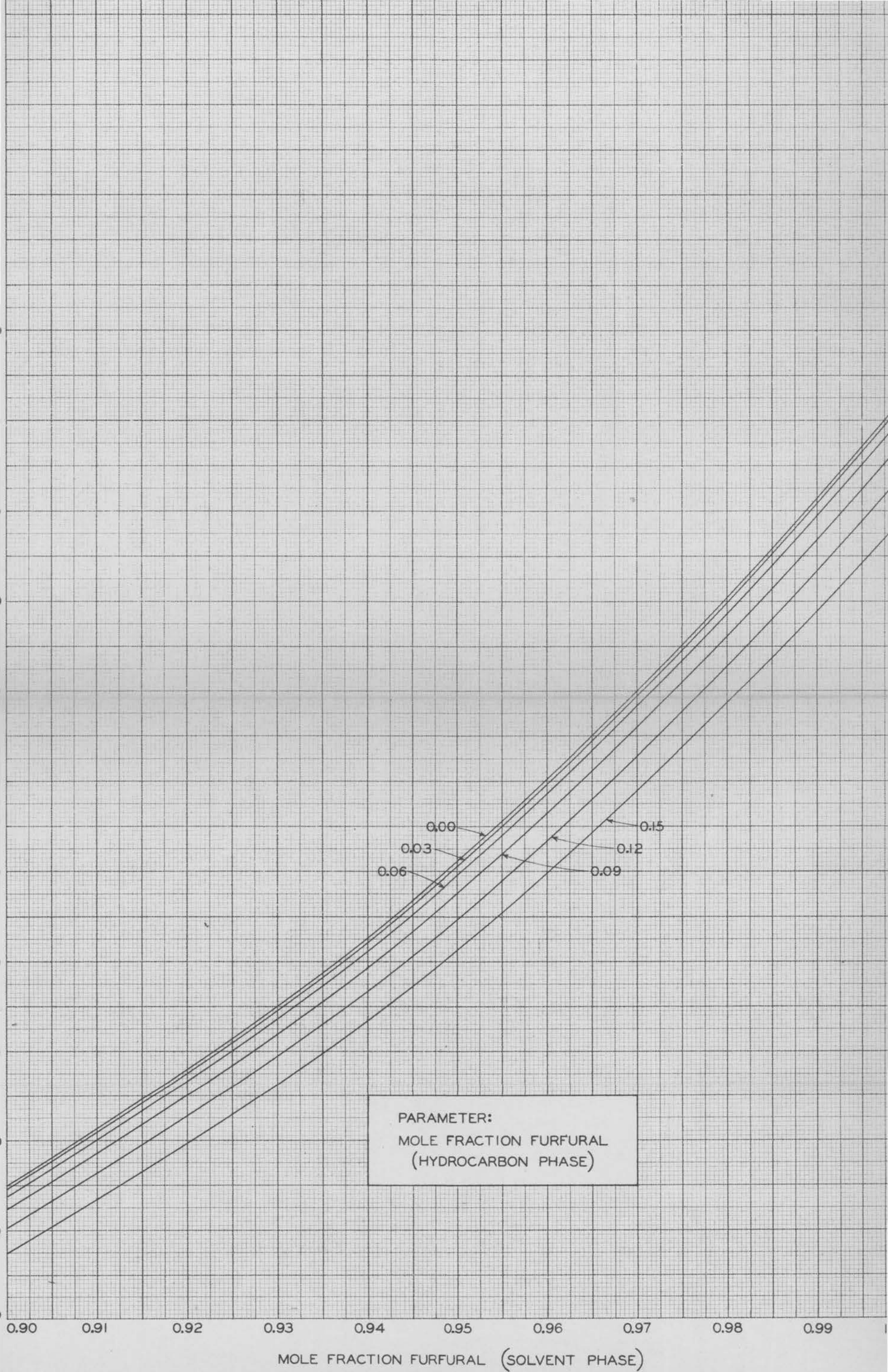


FIG.18 PARTITION COEFFICIENTS 2,4-DIMETHYLPENTANE - FURFURAL AT 37.5

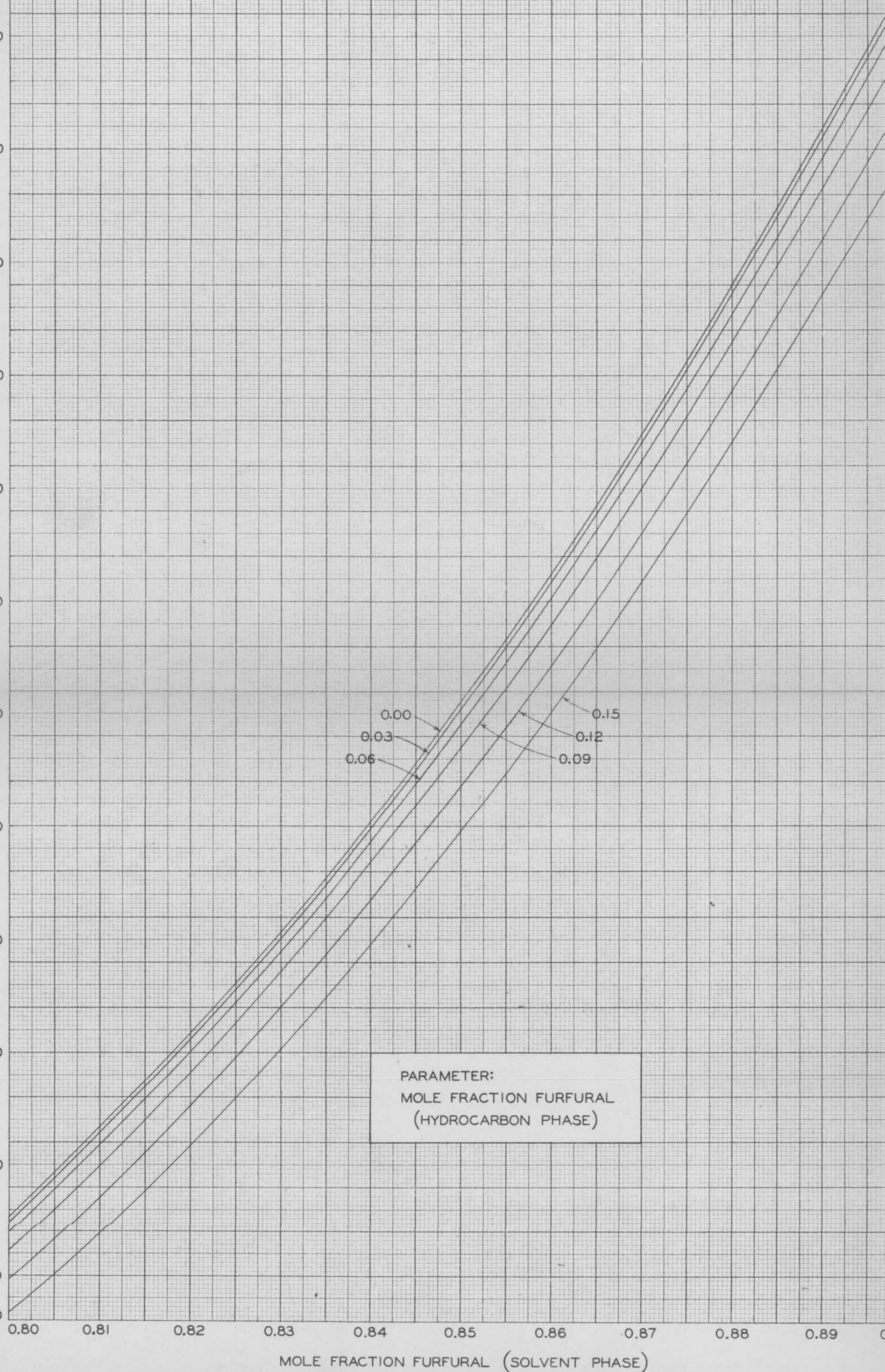


FIG.19 PARTITION COEFFICIENTS ISOCTANE-FURFURAL AT 37.8°C

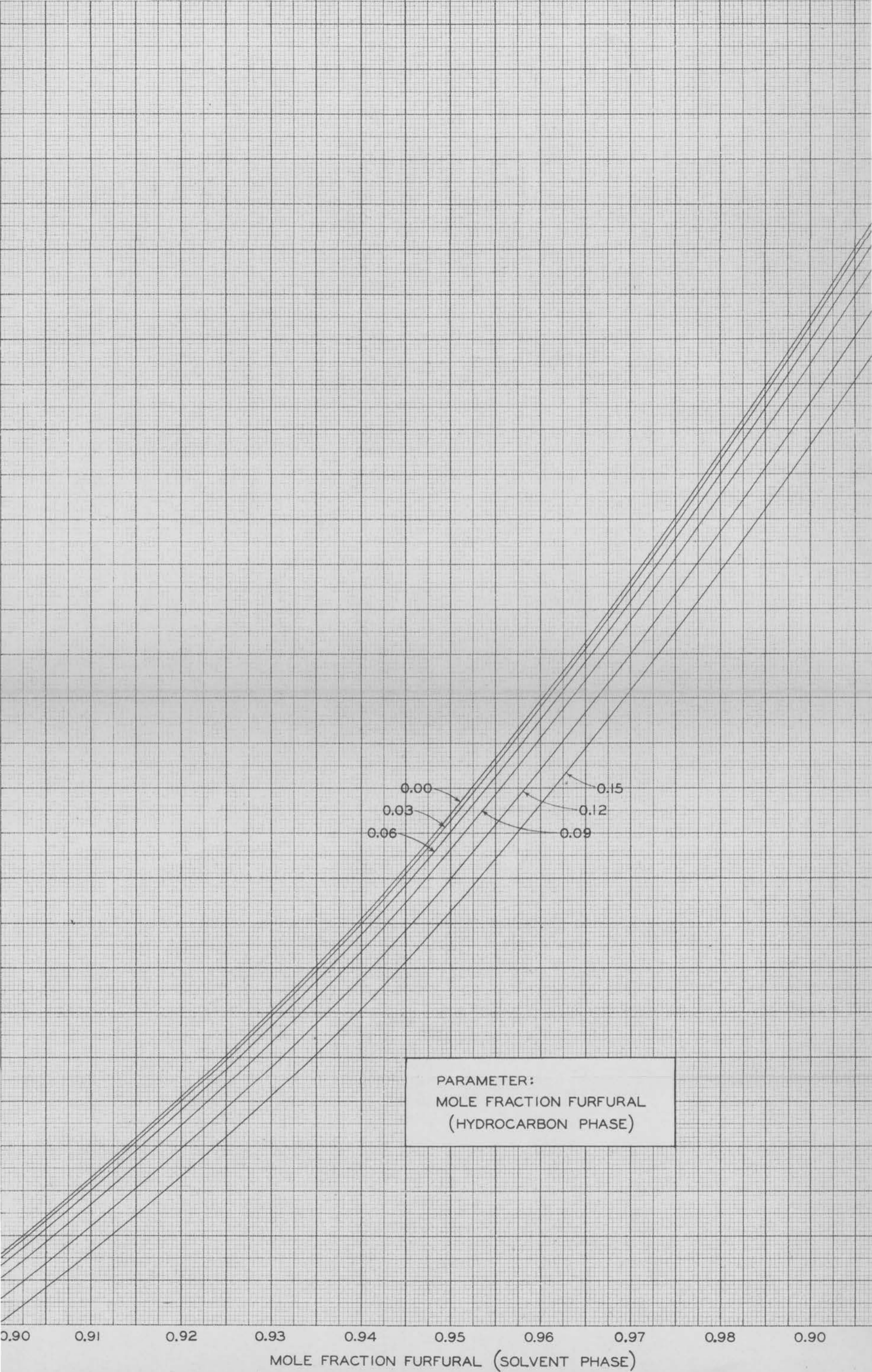
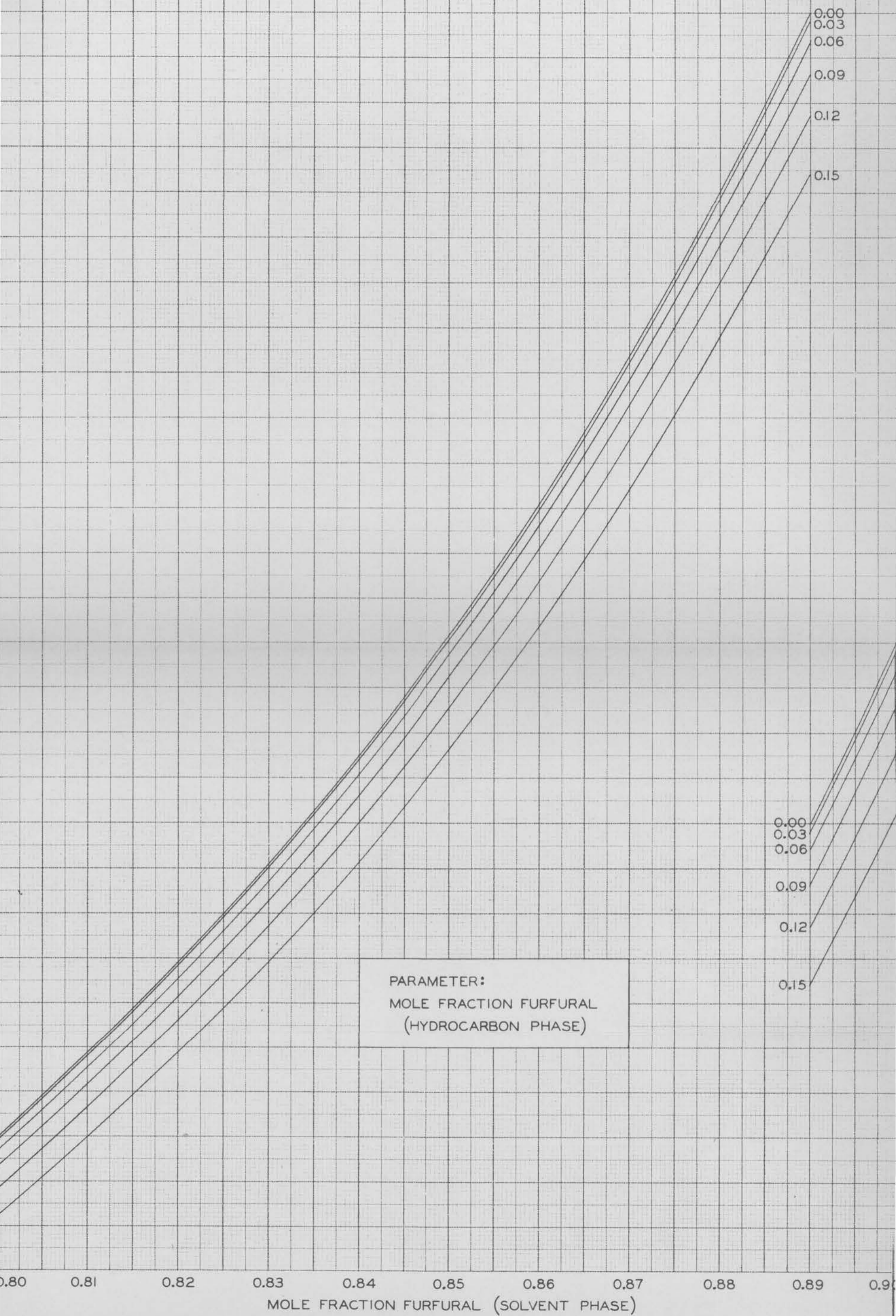
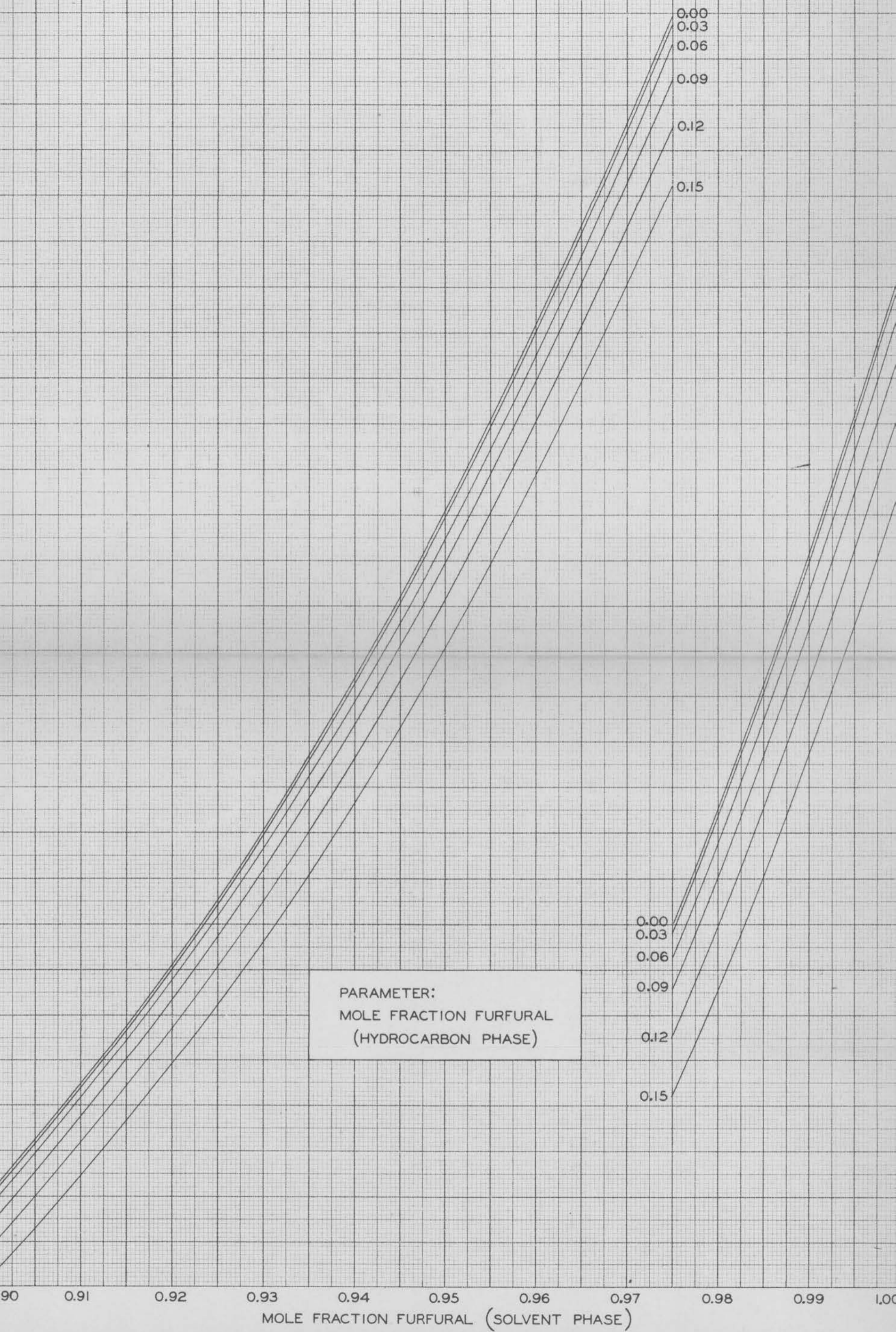


FIG.19 PARTITION COEFFICIENTS ISOCTANE-FURFURAL AT 37.8°C







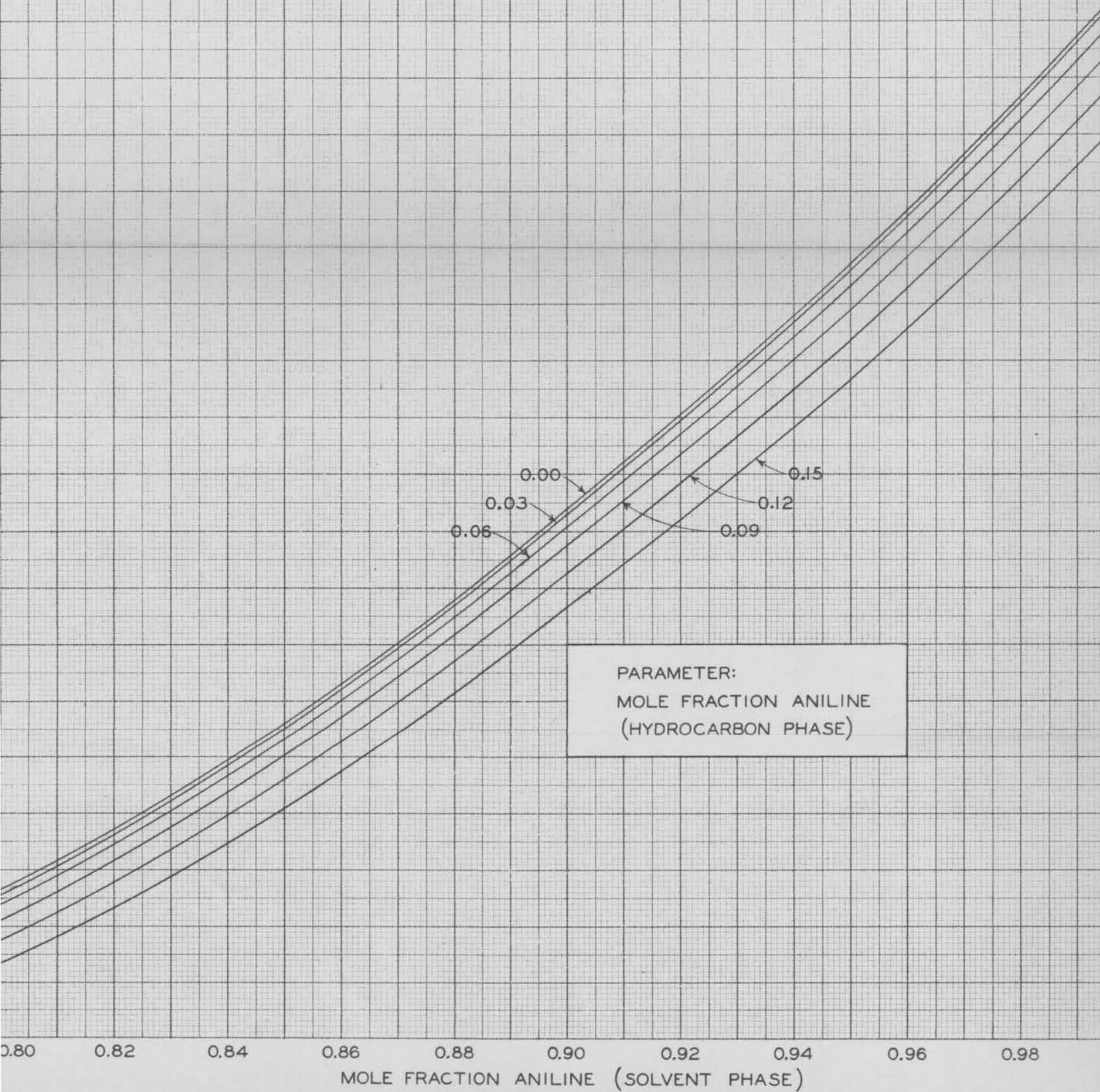


FIG. 21 PARTITION COEFFICIENTS CYCLOHEXANE-ANILINE AT 25°C

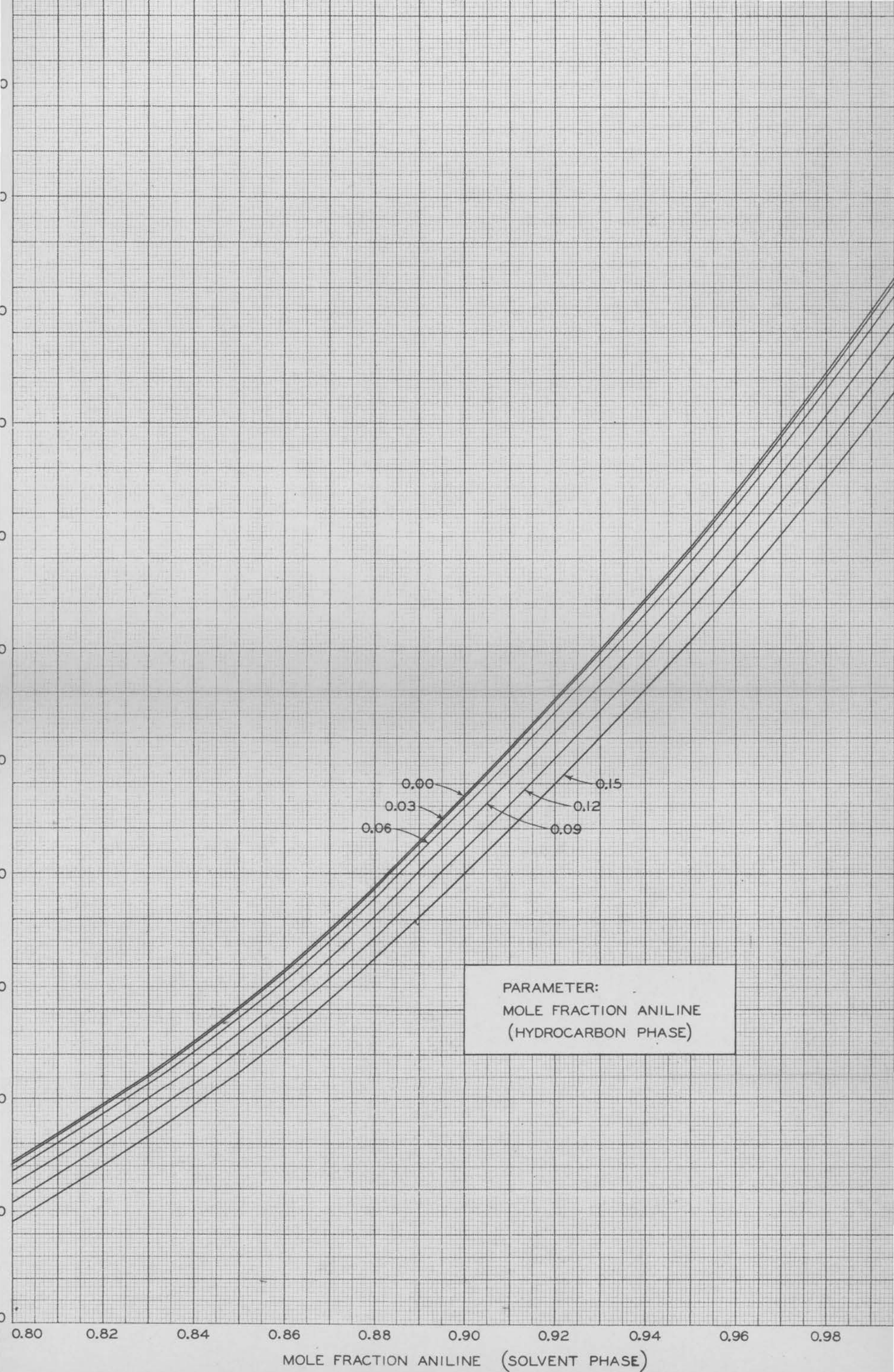


FIG.22 PARTITION COEFFICIENTS METHYLCYCLOPENTANE-ANILINE AT 25°

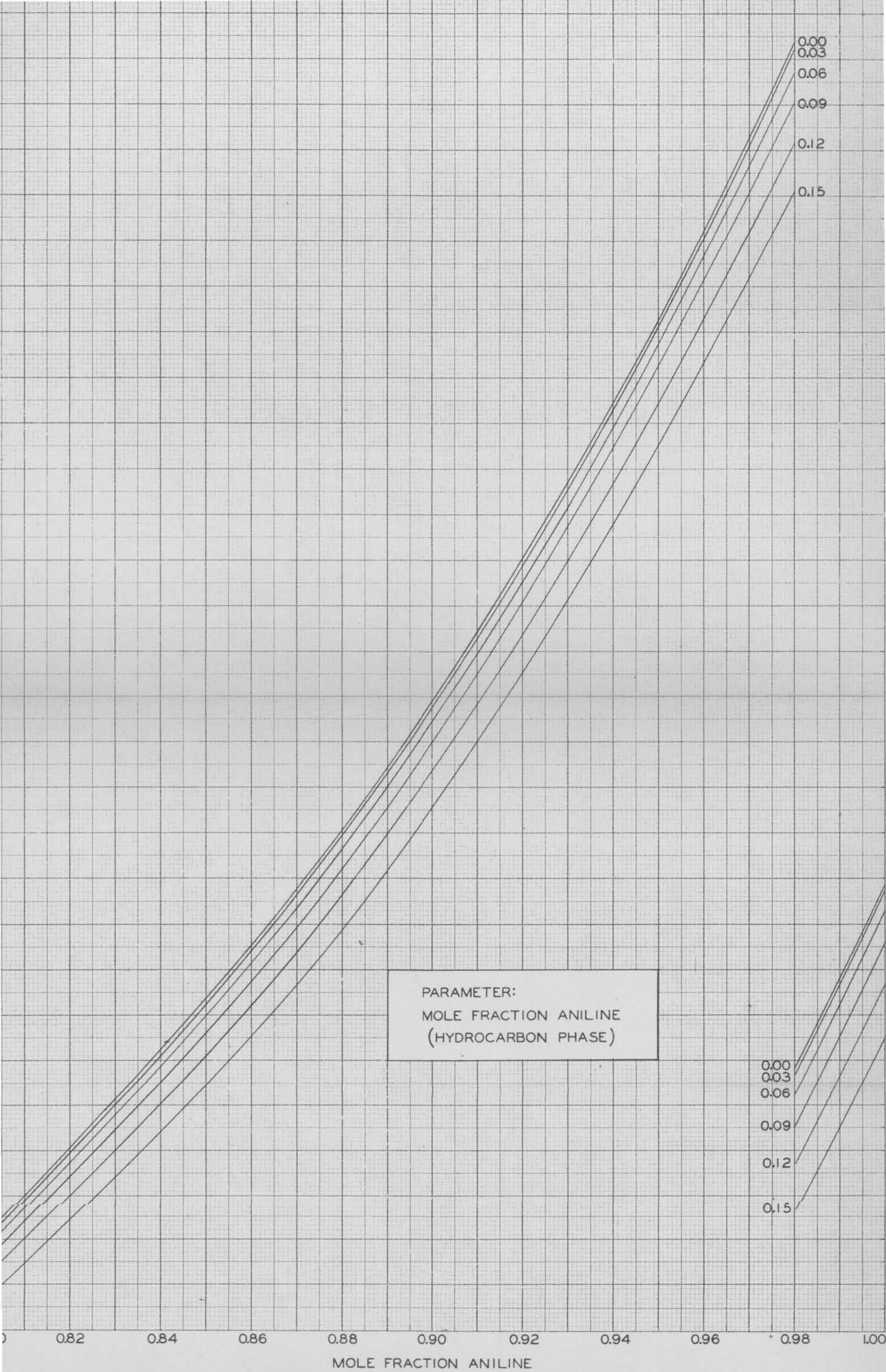
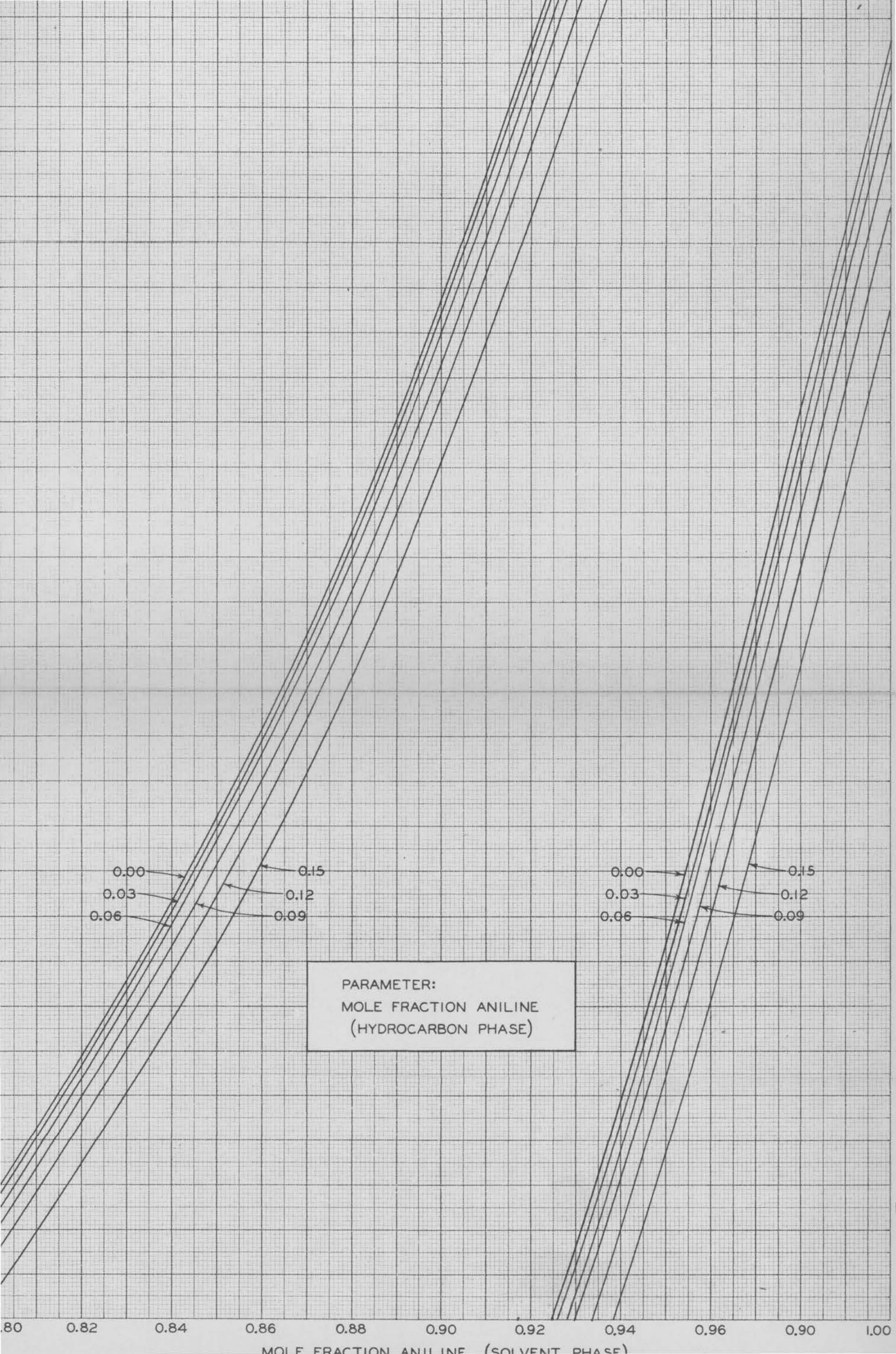


FIG. 23 PARTITION COEFFICIENTS METHYLCYCLOHEXANE - ANILINE AT 25°C



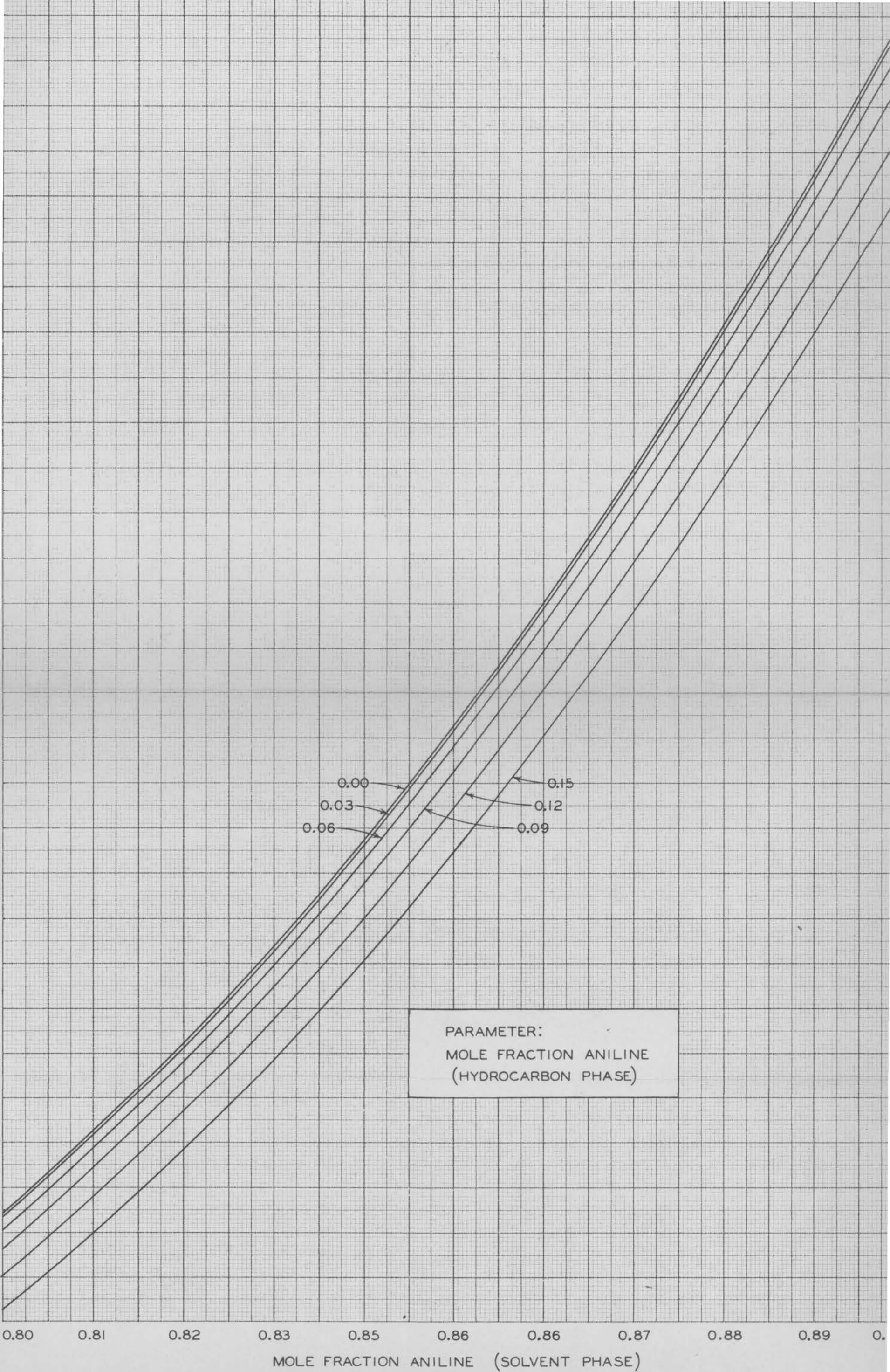


FIG. 25 PARTITION COEFFICIENTS N-HEPTANE - ANILINE AT 25°C

PART I

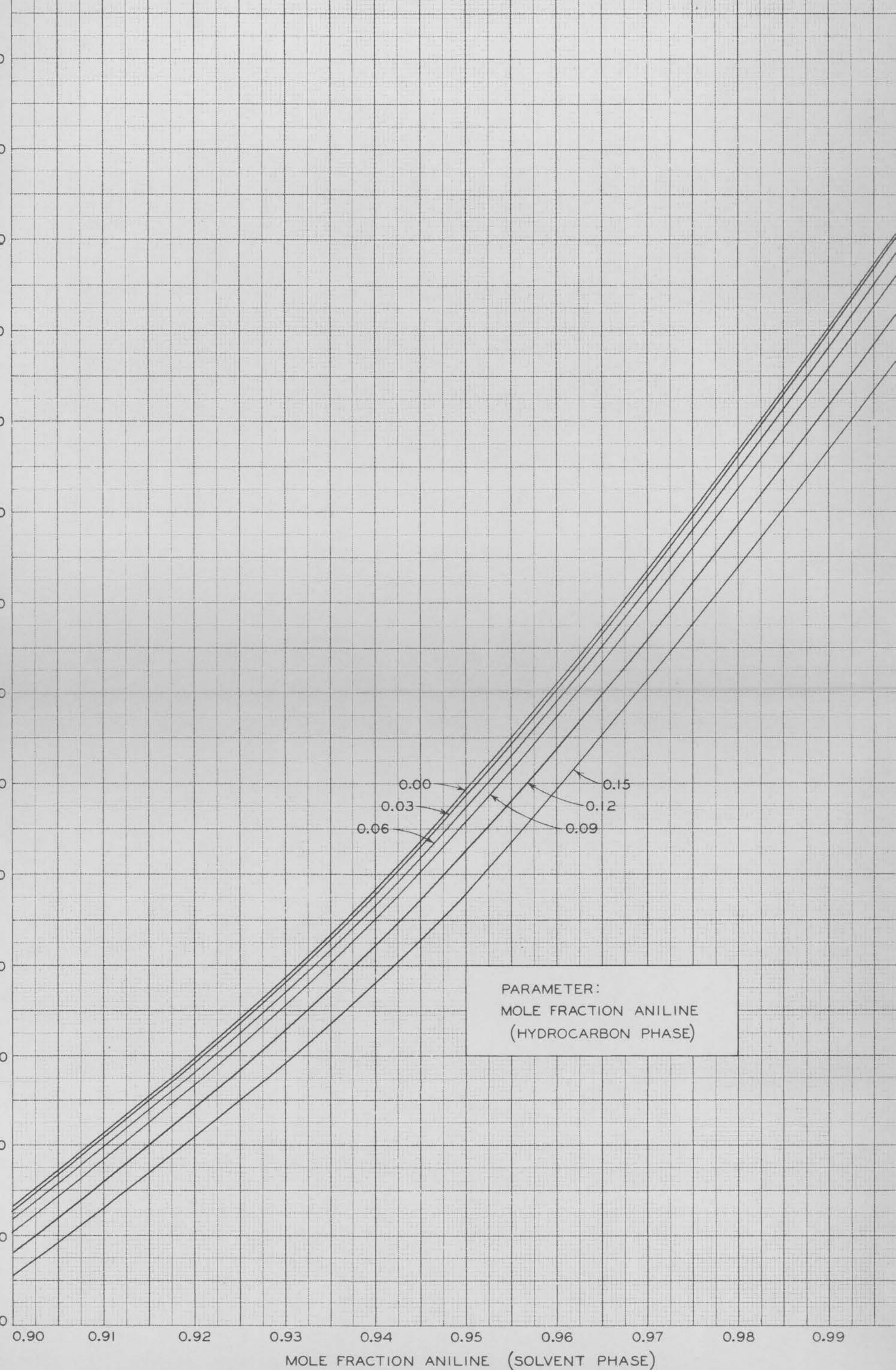


FIG. 25 PARTITION COEFFICIENTS N-HEPTANE - ANILINE AT 25°C

## VII. DISCUSSION OF RESULTS

The comparison of predicted and experimental equilibrium data has shown that reasonably accurate ternary equilibrium data can be calculated from experimental mutual solubility data of binary systems. These calculations are based on the assumption that two hydrocarbons form ideal solutions in each other. It is reasonable to assume that this assumption may be extended to multicomponent systems. This was done in making the "K-charts" for this series of systems. It is thought that these charts will be of value in the study of multicomponent extraction as well as in process design.

A study of this nature can never be complete; it is a continuing and even growing process. Each new development suggests the need for further study. In addition to extending this study to other solvents and other hydrocarbons, there are other related problems to be investigated. One is the effect that aromatics would have on solvent-hydrocarbon systems. Since solutions of aromatics and other hydrocarbons deviate appreciably from ideal solutions, it is possible that the presence of aromatics in a hydrocarbon mixture would cause an appreciable change in the component distribution.

In an extraction process it is frequently desirable to reduce the solubility of the hydrocarbons in the solvent. This has been done by the addition of water to the system (16). For this reason a study of the effect of water on the activity coefficients of solvent-hydrocarbon systems would be desirable.

Some study has been made of the effect of temperature on component distribution (1, 2) but more work needs to be done. Since there may be some economic advantage to operating extraction processes at temperatures higher than those considered in this paper, a combined study of the effect of water and temperature on component distribution may be desirable.



## NOMENCLATURE

A	Constant in van Laar equations
a	Activity, also a constant
B	Constant in van Laar equations
C	Number of components, phase rule
E	External energy
F	Gibbs free energy, also degrees of freedom, phase rule
f	Fugacity
H	Enthalpy
K	Partition coefficient
n	Number of moles of a component
P	Pressure, also number of phases, phase rule
q	Arbitrary factor sometimes defined as mole volume
R	Gas constant
S	Entropy
T	Absolute temperature
V	Volume
x	Mole fraction in solvent phase or in solution if only one phase is present
y	Mole fraction in hydrocarbon phase
$\gamma$	Activity coefficient
$\mu$	Chemical potential

## Subscripts and superscripts

E	Denotes excess free energy
h	Pertains to solvent phase
i	Indicates component i
j	Indicates component j
v	Pertains to hydrocarbon phase
1,2,3	Components 1,2,3, etc.
o	Indicates an arbitrary standard state

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## APPENDIX

## A. Experimental methods and data

1. Mutual solubility data: Solubility data for binary systems were determined by the cloud point temperature of synthetic samples. The synthetic samples were made in 20 mm test tubes by weighing in a predetermined amount of solvent, and then weighing in a predetermined amount of the hydrocarbon. A cork equipped with a thermometer and auger-type stirring rod was then inserted in the neck of the test tube. The test tube was placed in a glass jacket which was heated with a small burner. The mixture was agitated by means of a small electric motor. The mixture was heated while being agitated until one phase had been formed. The sample was then allowed to cool with agitation until a second phase appeared. The presence of a second phase is indicated by the turbidity of the mixture. The temperature at which the second phase appeared was noted and then checked by heating the sample and allowing it to cool a second time. Only the points which could be checked were accepted and recorded. The data determined are given in Tables VII through XIX.

2. Ternary equilibrium data: Equilibrium samples were mixed in a one liter separatory funnel by weighing a predetermined amount of each of the three components into the funnel. The sample was shaken well at frequent intervals and suspended in a constant temperature water bath between times. When the sample had attained the desired temperature, it was allowed to stand in the constant temperature bath until the phases had settled. The phases were then separated and analyzed.

A portion of the hydrocarbon phase was titrated to determine the concentration of furfural. The procedure for the titration is as follows: Determine the density of the mixture; then at the same temperature take a ten milliliter sample. Add ten millileters of methanol, five milliliters of 2 N hydroxylamine hydrochloride and five drops of methyl orange indicator. Titrate to a clear end point with a standardized potassium hydroxide solution. The potassium hydroxide solution used was standarized against a synthetic hydrocarbon furfural mixture in order to give greater accuracy and simplify calculations.

The remaining portion of the hydrocarbon phase was washed twice with sodium bisulphite solution and three times with water. The sample was then dried and analyzed by density. The composition-density data for the system isooctane-n-hexane are given in Table XXIII and are plotted in Figure 26. The plot of the density-composition data for the system n-heptane-cyclohexane, Figure 27, was received as private communication from G. H. Dale.

The solvent phase was distilled using a one liter kettle equipped with a short packed column. The hydrocarbon distilled over was collected in a graduate, measured and the density taken for material balance. The hydrocarbon was then washed and analyzed as explained previously. The data are given in Tables XX and XXI.

TABLE VII

## MUTUAL SOLUBILITY

## METHYLCYCLOPENTANE-ANILINE

	Molecular Weight								
Methylcyclopentane	84.156								
Aniline	93.064								
Weight Aniline	19.2280	7.6865	8.1725	4.1796	3.3065	2.5288	2.0674	1.4414	
Weight Methylcyclopentane	3.6954	2.2930	4.8907	7.4248	11.0210	12.1776	13.2616	14.0593	
Wt % Methylcyclopentane	16.12	22.98	37.44	63.98	76.92	82.8	86.51	90.70	
Mole % Methylcyclopentane	17.53	24.79	39.82	66.27	78.68	84.2	87.65	91.51	
Solution Temperature °C	14.8	25.2	32.4	32.6	28.7	24.9	21.0	11.8	

TABLE VIII

## MUTUAL SOLUBILITY

## 2-METHYLPENTANE-FURFURAL

	Molecular Weight								
2-Methylpentane	86.172								
Furfural	96.032								
Weight Furfural	18.5446	18.5759	18.0536	18.0436	17.9755	2.3430	1.1774	1.2026	0.5954
Weight 2-Methylpentane	1.2068	1.6492	2.1901	1.9292	2.6914	18.5966	11.6853	16.2286	12.4104
Wt. % 2-Methylpentane	6.11	8.15	10.82	9.66	13.02	88.81	90.85	93.10	95.42
Mole % 2-Methylpentane	6.76	9.00	11.91	10.65	14.30	89.84	91.71	93.77	95.87
Solution Temperature °C	21.5	37.0	52.0	45.1	60.0	52.5	45.2	34.0	20.8

TABLE IX  
MUTUAL SOLUBILITY

2,2-DIMETHYLBUTANE-FURFURAL

	Molecular Weight									
2,2-Dimethylbutane	86.172									
Furfural	96.032									
Weight Furfural	18.3631	18.3681	18.1206	1.1710	17.9346	1.1744	1.1898	0.5629	0.8950	
Weight 2,2-Dimethylbutane	1.0750	1.4628	1.7934	12.9410	1.9979	12.8752	16.2112	12.4614	13.8615	
Wt. % 2,2-Dimethylbutane	5.53	7.38	9.01	91.70	10.02	91.64	93.16	95.68	93.93	
Mole % 2,2-Dimethylbutane	6.13	8.15	9.93	92.49	11.05	92.43	93.82	96.11	94.52	
Solution Temperature °C	14.5	27.6	35.8	40.1	43.8	43.5	35.2	19.0	30.6	

TABLE X  
MUTUAL SOLUBILITY

2,3-DIMETHYLBUTANE-FURFURAL

	Molecular Weight									
2,3-Dimethylbutane	86.172									
Furfural	96.032									
Weight Furfural	18.5107	18.5014	18.3779	20.9173	20.8868	1.1910	0.6082	20.8646	1.1611	
Weight 2,3-Dimethylbutane	1.1048	1.8472	2.4844	2.2798	1.6248	19.1222	13.1266	1.6435	12.7997	
Wt % 2,3-Dimethylbutane	5.63	9.08	11.91	9.83	7.22	94.14	95.57	7.30	91.68	
Mole % 2,3-Dimethylbutane	6.24	10.01	13.09	10.83	7.98	94.71	96.01	8.07	92.47	
Solution Temperature °C	12.0	35.8	50.0	37.5	24.3	28.4	18.4	23.4	40.0	

TABLE XI  
MUTUAL SOLUBILITY  
N-HEXANE-FURFURAL

	Molecular Weight			
N-Hexane	86.172			
Furfural	96.032			
Weight Furfural	18.4635	18.4511	18.5564	17.8788
Weight N-hexane	0.8389	1.3432	1.4146	1.7748
Wt % N-hexane	4.35	6.79	7.08	9.03
Mole % N-hexane	4.82	7.51	7.83	9.96
Solution Temperature °C	2.2	24.8	28.0	37.4
Weight Furfural	17.2734	17.9772	2.3397	
Weight N-hexane	2.7552	1.7688	13.8448	
Wt % N-hexane	13.76	8.96	85.54	
Mole % N-hexane	15.09	9.88	86.83	
Solution Temperature °C	60.8	38.7	60.6	
Weight Furfural	2.2248	1.2152	1.7120	
Weight N-hexane	18.5570	12.6841	11.5846	
Wt % N-hexane	89.29	91.26	94.21	
Mole % N-hexane	90.29	92.09	94.78	
Solution Temperature °C	49.2	41.4	26.4	



TABLE XII

## MUTUAL SOLUBILITY

## 2,4-DIMETHYLPENTANE-FURFURAL

	Molecular Weight				
2,4-Dimethylpentane	100.198				
Furfural	96.032				
Weight Furfural	18.5121	18.5160	18.4797	18.5079	
Weight 2,4-Dimethylpentane	0.8062	1.1707	1.7224	2.1646	
Wt % 2,4-Dimethylpentane	4.17	5.95	8.53	10.47	
Mole % 2,4-Dimethylpentane	4.01	5.71	8.20	10.08	
Solution Temperature °C	9.9	28.3	45.2	55.8	
Weight Furfural	18.5286	3.5022	17.9202	2.3363	
Weight 2,4-Dimethylpentane	2.6134	19.1541	3.2862	13.7025	
Wt % 2,4-Dimethylpentane	12.36	84.54	15.50	85.43	
Mole % 2,4-Dimethylpentane	11.91	83.98	14.95	84.90	
Solution Temperature °C	64.0	68.0	74.7	66.6	
Weight Furfural	1.7435	1.1974	0.5879	0.7355	
Weight 2,4-Dimethylpentane	16.3607	17.0926	14.5239	14.4898	
Wt % 2,4-Dimethylpentane	90.37	93.45	96.11	95.17	
Mole % 2,4-Dimethylpentane	89.99	93.19	95.95	94.97	
Solution Temperature °C	51.3	34.8	17.0	24.8	

TABLE XIII

## MUTUAL SOLUBILITY

## N-HEPTANE-FURFURAL

	Molecular Weight					
N-heptane	100.198					
Furfural	93.032					
Weight Furfural	18.3399	17.8052	17.1760	14.9751	12.6740	
Weight N-heptane	1.0120	2.0972	4.4919	5.9306	7.8735	
Wt. % N-heptane	5.23	10.54	20.73	28.37	38.32	
Mole % N-heptane	5.02	10.14	20.04	27.51	37.32	
Solution Temperature °C	21.6	55.9	83.6	91.0	93.6	
Weight Furfural	10.3489	8.0779	4.6066	3.4470	2.2976	
Weight N-heptane	10.3406	12.5946	11.2557	14.3337	21.5900	
Wt % N-heptane	49.98	60.92	70.96	80.61	90.38	
Mole % N-heptane	48.92	59.91	70.07	79.94	90.00	
Solution Temperature °C	93.7	91.8	85.7	73.6	48.8	
Weight Furfural	1.1298	20.8578	18.1247	18.6563	1.1736	
Weight N-heptane	22.6770	1.1363	3.3309	1.5865	14.9664	
Wt % N-heptane	95.25	5.17	15.52	7.84	92.73	
Mole % N-heptane	95.06	4.96	14.97	7.53	92.44	
Solution Temperature °C	24.4	21.0	72.5	40.2	37.6	
Weight Furfural	2.3396	0.9408				
Weight N-heptane	13.0264	17.0203				
Wt % N-heptane	84.77	94.76				
Mole % N-heptane	84.22	94.55				
Solution Temperature °C	64.8	26.7				

TABLE XIV  
MUTUAL SOLUBILITY  
ISOOCTANE-FURFURAL

	Molecular Weight			
Isooctane	114.224			
Furfural	96.032			
Weight Furfural	18.3126	19.4299	17.7850	17.3176
Weight Isooctane	0.6482	1.3842	2.3353	5.1443
Wt % Isooctane	3.42	6.65	11.61	22.90
Mole % Isooctane	2.89	5.65	9.94	19.98
Solution Temperature °C	5.2	39.2	64.6	91.8
Weight Furfural	3.4872	3.4430	2.3035	0.8775
Weight Isooctane	9.5499	16.4064	24.6720	19.4167
Wt % Isooctane	73.25	82.65	91.46	95.68
Mole % Isooctane	69.72	80.03	90.00	94.90
Solution Temperature °C	90.4	76.5	49.6	25.2
Weight Furfural	20.9470	18.4578	17.3312	0.9657
Weight Isooctane	1.1691	1.9508	3.6376	13.4852
Wt % Isooctane	5.29	9.56	17.35	93.32
Mole % Isooctane	4.48	8.16	15.00	92.15
Solution Temperature °C	25.5	54.9	82.1	39.1

TABLE XV

## MUTUAL SOLUBILITY

## 2,2,5-TRIMETHYLHEXANE-FURFURAL

	Molecular Weight				
2,2,5-Trimethylhexane	128.250				
Furfural	96.032				
Weight Furfural	18.6424	18.4973	18.5564	18.3760	17.2329
Weight 2,2,5-Tri- methylhexane	0.6090	0.9255	1.3016	1.8400	2.6057
Wt % 2,2,5-Tri- methylhexane	3.34	4.77	6.55	9.10	13.13
Mole % 2,2,5-Tri- methylhexane	2.39	3.61	4.99	6.98	10.17
Solution Tempera- ture °C	14.8	33.5	48.6	63.5	79.6
Weight Furfural	15.0344	2.3679	1.7828	1.1530	0.6126
Weight 2,2,5-Tri- methylhexane	4.9920	12.4410	13.2518	13.8750	14.8534
Wt % 2,2,5-Tri- methylhexane	24.93	84.01	88.14	92.33	96.04
Mole % 2,2,5-Tri- methylhexane	19.91	79.73	84.77	90.01	94.78
Solution Tempera- ture °C	100.6	76.4	65.6	48.1	23.2
Weight Furfural	3.5278	0.9261	13.7379	11.5175	8.0725
Weight 2,2,5-Tri- methylhexane	10.7896	14.2404	7.8951	10.2508	10.7720
Wt % 2,2,5-Tri- methylhexane	75.36	93.89	36.50	47.09	57.16
Mole % 2,2,5-Tri- methylhexane	69.60	92.01	30.09	39.99	49.98
Solution Tempera- ture °C	92.2	38.5	104.1	104.4	103.4
Weight Furfural	5.7856	15.0252	0.7206	16.1314	
Weight 2,2,5-Tri- methylhexane	11.4934	4.9892	14.1388	3.8142	
Wt % 2,2,5-Tri- methylhexane	66.52	24.93	95.15	19.12	
Mole % 2,2,5-Tri- methylhexane	59.80	19.91	93.63	15.04	
Solution Tempera- ture °C	100.0	99.9	30.2	92.9	

TABLE XVI  
MUTUAL SOLUBILITY  
CYCLOHEXANE-FURFURAL

	Molecular Weight				
Cyclohexane	84.156				
Furfural	96.032				
Weight Furfural	18.3350	18.4816	17.2472	1.1943	1.1689
Weight Cyclohexane	2.3776	3.3201	5.0223	14.7066	18.2332
Wt % Cyclohexane	11.48	15.23	22.55	92.49	93.98
Mole % Cyclohexane	12.89	17.01	24.94	93.35	94.68
Solution Temperature °C	21.1	35.3	51.6	30.4	23.0
Weight Furfural	0.8522	2.3066	19.6042	16.2949	15.9133
Weight Cyclohexane	17.7524	10.8605	2.2706	3.5334	6.0270
Wt % Cyclohexane	95.42	82.48	10.38	17.82	27.47
Mole % Cyclohexane	95.96	84.31	11.68	19.84	30.18
Solution Temperature °C	16.3	54.3	17.2	43.0	58.2
Weight Furfural	12.0066	9.2799	1.2422	6.7400	4.5705
Weight Cyclohexane	6.9852	8.0150	18.1678	8.8654	9.2334
Wt % Cyclohexane	36.78	46.37	93.60	56.81	66.89
Mole % Cyclohexane	39.90	49.66	94.35	60.02	69.75
Solution Temperature °C	64.7	66.3	26.4	66.2	65.3
Weight Furfural	3.1604	1.5338	1.5006	1.2166	
Weight Cyclohexane	10.4798	14.0223	18.3223	18.7281	
Wt % Cyclohexane	76.83	90.14	92.43	93.90	
Mole % Cyclohexane	79.10	91.25	93.30	94.61	
Solution Temperature °C	60.2	38.7	28.7	27.0	

TABLE XVII

## MUTUAL SOLUBILITY

## CYCLOPENTANE-FURFURAL

	Molecular Weight									
Cyclopentane	70.130									
Furfural	96.032									
Weight Furfural	2.9041	2.2300	1.7595	1.2643	1.1951	21.3856	17.0191	16.1559	13.1660	
Weight Cyclopentane	13.9747	14.1789	16.5304	15.9134	15.8539	3.9258	3.8402	3.8961	4.0670	
Wt % Cyclopentane	82.79	86.41	90.38	92.64	92.99	15.51	18.41	19.43	23.60	
Mole % Cyclopentane	86.82	89.70	92.79	94.52	94.78	20.09	23.61	24.82	29.72	
Solution Temperature °C	41.4	35.3	25.2	18.0	16.2	19.3	27.7	30.4	38.2	

TABLE XVIII

## MUTUAL SOLUBILITY

## METHYLCYCLOHEXANE-FURFURAL

	Molecular Weight			
Methylcyclohexane	98.182			
Furfural	96.032			
Weight Furfural	17.3563	17.2630	2.3373	1.1842
Weight Methylcyclohexane	2.6086	3.2840	13.3847	14.4987
Wt % Methylcyclohexane	13.07	15.98	85.13	92.45
Mole % Methylcyclohexane	12.82	15.69	84.85	92.29
Solution Temperature °C	37.2	46.4	53.8	32.8
Weight Furfural	22.1923	20.9432	23.5489	16.4386
Weight Methylcyclohexane	1.9219	2.3012	6.1022	7.3029
Wt % Methylcyclohexane	7.97	9.90	20.58	30.76
Mole % Methylcyclohexane	7.81	9.70	20.22	30.29
Solution Temperature °C	13.9	24.5	56.8	69.0
Weight Furfural	12.1534	8.9818	6.3877	4.6822
Weight Methylcyclohexane	8.1090	9.0721	9.8001	11.1041
Wt % Methylcyclohexane	40.02	50.25	60.54	70.34
Mole % Methylcyclohexane	39.49	49.70	60.01	69.88
Solution Temperature °C	72.8	73.2	72.6	69.9
Weight Furfural	3.0147	1.4358	1.1829	0.8990
Weight Methylcyclohexane	12.2497	13.4799	14.5261	14.9849
Wt % Methylcyclohexane	80.25	90.38	92.47	94.34
Mole % Methylcyclohexane	79.90	90.19	92.31	94.22
Solution Temperature °C	61.3	40.8	32.8	24.0

TABLE XIX  
MUTUAL SOLUBILITY  
METHYLCYCLOPENTANE-FURFURAL

	Molecular Weight			
Methylcyclopentane	84.156			
Furfural	96.032			
Weight Furfural	18.4889	17.3405	2.3197	14.1745
Weight Methylcyclopentane	2.3353	5.1250	14.0362	8.1685
Wt % Methylcyclopentane	11.21	22.81	85.82	36.56
Mole % Methylcyclopentane	12.60	25.22	87.35	39.67
Solution Temperature °C	21.2	53.7	46.9	65.0
Weight Furfural	2.3307	18.5373	21.4782	18.3974
Weight Methylcyclopentane	11.8317	2.3545	2.2049	2.8002
Wt % Methylcyclopentane	83.54	11.27	9.31	13.21
Mole % Methylcyclopentane	85.28	12.66	10.49	14.80
Solution Temperature °C	50.8	19.6	10.2	30.3
Weight Furfural	23.7785	17.3241	14.4066	10.3369
Weight Methylcyclopentane	5.2020	6.5416	8.2417	8.9592
Wt % Methylcyclopentane	17.95	27.41	36.39	46.43
Mole % Methylcyclopentane	19.98	30.11	39.50	49.72
Solution Temperature °C	44.7	60.0	65.0	67.3
Weight Furfural	8.4873	5.9430	4.3776	3.0647
Weight Methylcyclopentane	10.1416	11.9737	15.1565	18.1592
Wt % Methylcyclopentane	54.44	66.83	77.59	85.56
Mole % Methylcyclopentane	57.69	69.68	79.80	87.12
Solution Temperature °C	67.3	65.6	59.0	46.9
Weight Furfural	2.4567	2.0439		
Weight Methylcyclopentane	18.9805	19.5167		
Wt % Methylcyclopentane	88.54	90.52		
Mole % Methylcyclopentane	89.81	91.59		
Solution Temperature °C	38.7	25.6		



TABLE XX  
 TERNARY EQUILIBRIA  
 N-HEPTANE-CYCLOHEXANE-FURFURAL

Sample	1	2	3	4	5	6
Charge:						
Total weight	696.3	717.1	475.4	695.0	712.6	465.7
Weight Furfural	598.5	598.9	357.5	597.7	594.2	348.5
Weight Cyclohexane	19.7	59.2	94.6	19.4	58.9	93.9
Weight N-heptane	78.1	59.0	23.3	77.9	59.5	23.3
Weight % Cyclohexane (Solv-free)	20.14	50.08	80.24	19.94	49.75	80.12
Solvent Phase:						
Total weight	640.0	655.2	397.5	639.9	649.8	387.2
Volume Hydrocarbon, ml	63.0	83.0	59.5	64.0	82.0	59.5
Density Hydrocarbon	0.7131	0.7414	0.7704	0.7118	0.7420	0.7708
Weight Hydrocarbon	44.9	61.5	45.9	45.6	60.8	45.9
Weight Furfural	595.4	592.3	349.4	594.3	589.0	342.1
Density Hydrocarbon	0.7044	0.7338	0.7629	0.7048	0.7340	0.7631
Wt % Cyclohexane (Solv-free)	25.5	57.5	86.1	25.4	57.7	86.4
Hydrocarbon Phase:						
Total weight	55.3	61.5	78.2	54.7	62.1	77.6
Density	0.7071	0.7332	0.7652	0.7057	0.7318	0.7662
ml KOH	23.88	25.42	26.20	25.10	25.80	25.96
Weight Furfural/ml HC	0.0431	0.0459	0.0473	0.0427	0.0466	0.0469
Weight Furfural	3.4	3.8	4.8	3.3	4.0	4.7
Weight Hydrocarbon	51.9	57.7	73.4	51.4	58.1	72.9
Density Hydrocarbon	0.6987	0.7215	0.7547	0.6982	0.7216	0.7550
Wt % Cyclohexane (Solv-free)	18.3	44.1	78.5	17.7	44.3	78.8

TABLE XXI  
 TERNARY EQUILIBRIA  
 ISOCTANE-N-HEXANE-FURFURAL

Sample	1	2	3	4	5	6
<b>Charge:</b>						
Total weight	702.3	649.1	596.7	701.0	649.5	595.5
Weight Furfural	603.7	551.2	497.7	600.4	552.9	496.7
Weight N-hexane	18.9	48.9	79.0	20.6	49.2	79.5
Weight Isooctane	79.7	49.0	20.0	80.0	47.4	19.3
Weight % N-hexane (Solv-free)	19.17	49.95	79.80	20.48	50.93	80.46
<b>Solvent Phase:</b>						
Total weight	636.5	582.8	528.2	633.9	584.7	527.6
Volume Hydrocarbon, ml	52.5	54.0	52.0	50.0	54.0	52.0
Density Hydrocarbon	0.6936	0.6833	0.6743	0.6925	0.6828	0.6745
Weight Hydrocarbon	36.4	36.8	35.1	34.6	36.9	35.1
Weight Furfural	599.8	545.1	492.0	599.9	546.5	492.6
Density Hydrocarbon	0.6861	0.6756	0.6666	0.6860	0.6754	0.6666
Wt % N-hexane (Solv-free)	21.2	54.8	83.7	21.5	55.4	83.7
<b>Hydrocarbon Phase:</b>						
Total weight	63.7	65.4	67.9	66.4	64.4	67.9
Density	0.6943	0.6848	0.6762	0.6952	0.6858	0.6766
Ml KOH	21.44	21.78	22.32	22.54	22.56	22.72
Weight Furfural/ml HC	0.0387	0.0393	0.0403	0.0407	0.0407	0.0410
Weight Furfural	3.5	3.8	4.0	4.2	3.8	4.1
Weight Hydrocarbon	60.2	61.6	63.9	62.2	60.6	63.8
Density Hydrocarbon	0.6882	0.6788	0.6685	0.6882	0.6788	0.6686
Wt % N-hexane (Solv-free)	14.5	44.6	77.7	14.5	44.6	77.3

TABLE XXII

## STANDARDIZATION OF POTASSIUM HYDROXIDE SOLUTION

<u>Weight Furfural</u>	<u>ml/KOH</u>	<u>gms furfural/ml KOH</u>
0.2912	16.12	0.01806
0.3179	17.62	0.01804
0.3579	19.84	0.01804
		<u>3/0.05414</u>
		0.01805

TABLE XXIII

## DENSITY VERSUS COMPOSITION

## ISOOCTANE-N-HEXANE

<u>Weight Isooctane</u>	<u>Weight N-hexane</u>	<u>Wt. % Isooctane</u>	<u>Density 20°C</u>
0.9670	18.7211	4.91	0.6631
2.0048	17.8773	10.08	0.6646
2.0029	17.6712	10.18	0.6650
2.9264	16.6776	14.93	0.6664
4.8895	14.8772	24.74	0.6691
7.1536	12.4937	36.41	0.6728
7.8415	11.8244	39.87	0.6745
9.3548	9.7805	50.19	0.6772
11.8824	7.8492	60.22	0.6807
13.8653	6.9848	66.50	0.6823
20.4404	3.8212	84.25	0.6878
18.6701	1.9678	90.47	0.6897
18.8100	0.9705	95.09	0.6912



FIG.26 DENSITY-COMPOSITION ISOCTANE - N-HEXANE AT 20°C

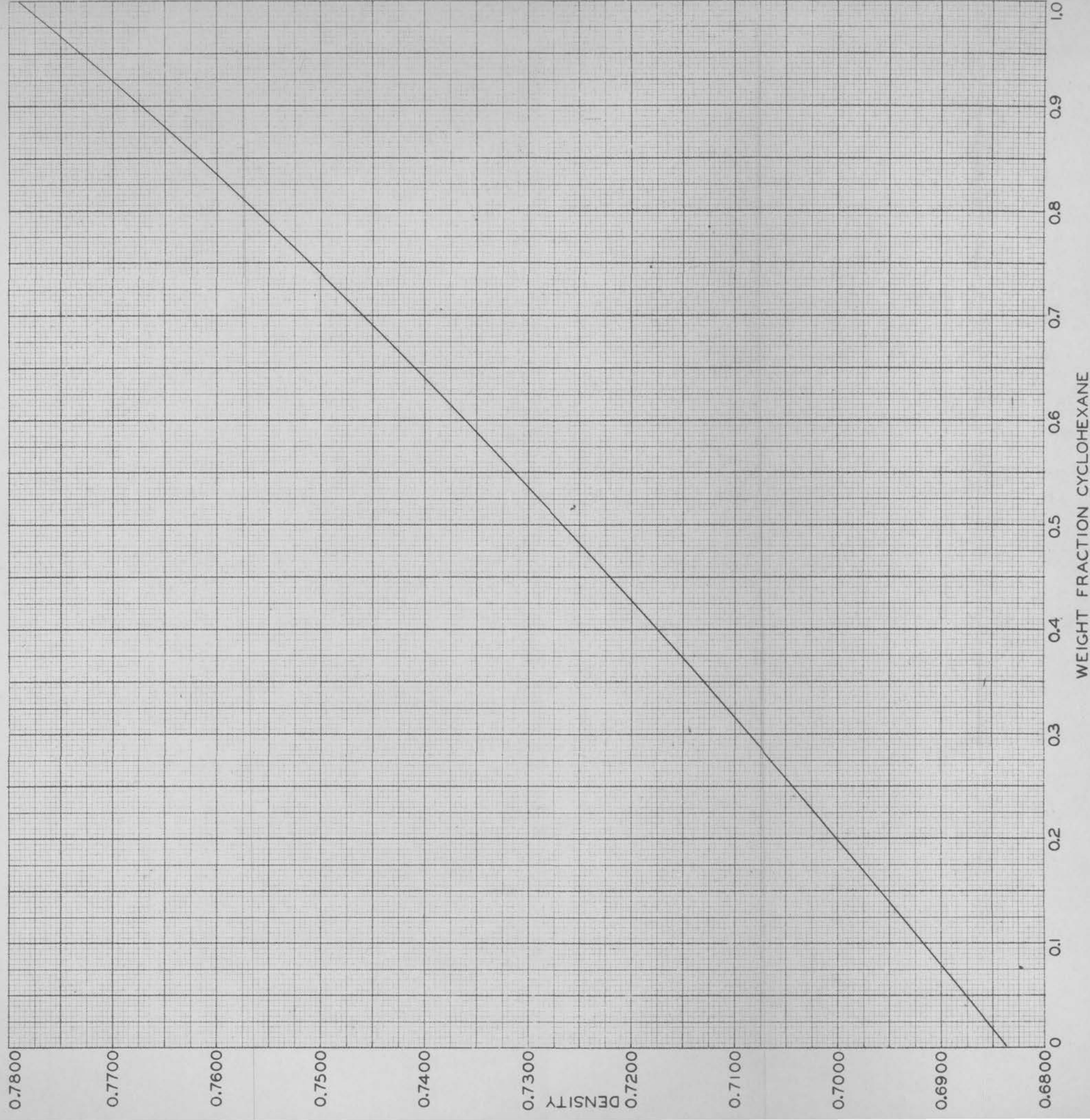


FIG. 27 DENSITY - COMPOSITION N-HEPTANE - CYCLOHEXANE AT 20°C

B. Literature Survey: A search of the literature was made for liquid-liquid phase data on solvent-hydrocarbon systems in which the hydrocarbons are  $C_5$  or heavier. The references found are listed in Table XXIV.

TABLE XXIV  
LITERATURE SURVEY

<u>Binary Systems</u>	Authors	Journal	Volume	Page	Year
Aniline n-hexane	Hildebrand, Keys	J Am Chem Soc	37	2126	1917
Tert-butyl alcohol benzene	Simonsen, et al	J Am Chem Soc	68	235	1946
Chlorex n-octane 2,2,4-Trimethyl- pentane	Tschamler, et al Ibid	Monatsch	80	572	1949
1,4-Dioxane benzene	Berndt, Lynch	J Am Chem Soc	66	282	1944
Ethylene chlorohydrin cyclohexane	Jasper, Pohrt	J Chem Ed	26	485	1949
Isopropanol cyclohexane toluene	Washburn et al Washburn et al	J Am Chem Soc J Am Chem Soc	62 61	1454 1694	1940 1939
Perfluoro-n-heptane benzene n-heptane 2,2,4-trimethyl- pentane	Hildebrand et al Ibid Ibid	J Am Chem Soc	72	4348	1950
Phenol n-hexane n-heptane benzene isopentane n-octane	Seidell Ibid Ibid Ibid Ibid	3rd Ed Vol 2		457 563 369 312 621	
<u>Ternary Systems with one hydrocarbon</u>					
Acetone-glycol benzene toluene Xylene	Trimble, Frazer Ibid Ibid	Ind Eng Chem	21	1063	1929
Formic acid-bromoform benzene	Avenarius, et al	J Gen Chem	16	1777	1940
Propylene glycol-sodium oleate benzene	Palit, McBain	Ind Eng Chem	38	741	1946

	Authors	Journal	Volume	Page	Year
Skellysolve B, 70% toluene	methanol + 30% glycol Smith, Funk	Trans AIChE	40	211	1944
Water					
Acetaldehyde					
benzene	Othmer, Tobias	Ind Eng Chem	34	690	1942
toluene	Ibid				
Acetic acid					
benzene	Hand	J Phy Chem	34	1961	1930
toluene	Ibid				
o-xylene	Scheibal, Karr	Ind Eng Chem	42	1048	1950
Acetone					
benzene	Briggs, Comings Seidell	Ind Eng Chem 3rd Ed	35	411	1943
heptane	Othmer et al	Ind Eng Chem	33	1240	1939
hexane	Treybal, Vondrak	Ind Eng Chem	41	1761	1949
toluene	Ibid				
xylene	Briggs, Comings Seidell	Ind Eng Chem 3rd Ed	35	411	1943
o-xylene	Othmer et al	Ind Eng Chem	33	1240	1939
Hartley	Hartley	J Soc Chem Ind	69	60	1950
Aniline					
toluene	Smith, Drexel	Ind Eng Chem	37	601	1945
n-Butanol					
benzene	Washburn et al	J Phys Chem	48	241	1944
Tert-Butyl alcohol					
benzene	Smith	Ind Eng Chem	42	1206	1950
Diethylamine					
toluene	Wehn, Franke	Ind Eng Chem	41	2853	1949
Ethanol					
benzene	Varteressian et al	Rubber Age	28	928	1936
cyclohexane	Washburn et al	J Am Chem Soc	53	3237	1931
cyclohexene	Vold, Washburn	J Am Chem Soc	54	4217	1932
hexane	Washburn et al	J Am Chem Soc	62	1454	1940
toluene	International Critical Tables				
m-xylene	Washburn et al	J Am Chem Soc	61	1694	1939
o-xylene	Miller, McPherson	J Phy Chem	12	706	1908
p-xylene	International Critical Tables				
Ibid	Ibid				
Furfural					
toluene	Knight	Trans AIChE	39	439	1943
Isopropanol					
benzene	Olsen, Washburn Smith	J Am Chem Soc Ind Eng Chem	57 42	303 1206	1935 1950
Methanol					
cyclohexane	Washburn, Spencer	J Am Chem Soc	56	361	1934
cyclohexene	Washburn, et al	J Am Chem Soc	53	3237	1931
styrene	Trogan	RubberAge	63	585	1948
toluene	McDonald	J Am Chem Soc	62	3183	1940



	Authors	Journal	Volume	Page	Year
xylene	Hartley	J Soc Chem Ind	69	60	1950
Methyl ethyl ketone					
heptane	Treybal, Vondrak	Ind Eng Chem	41	1761	1949
hexane	Ibid				
2,2,4-trimethyl- pentane	Moulton, Walkeg	Trans AIChE	40	695	1944
o-Phenylphenol					
cyclohexane	Galumbic, Weller	Anal Chem	22	1418	1950
Phosphate buffer, 0.5M					
cyclohexane	Ibid				
Pyridine					
benzene	International Critical Tables				
	Smith, et al	Ind Eng Chem	43	190	1951
Sodium arylsulfonates					
benzene	Booth, Everson	Ind Eng Chem	41	2627	1949
o-cresol	Ibid				
hexane	Ibid				

#### Ternary Systems with two hydrocarbons

Aniline					
cetane					
n-heptane	Hunter, Brown	Ind Eng Chem	39	1343	1947
benzene	Ibid				
cyclohexane	Ibid				
n-heptane					
cyclohexane	Ibid				
methyl- cyclohexane	Varteressian, et al	Rubber Age	29	270	1937
n-hexane					
methyl- cyclopentane	Darwent, Winkler	J Phy Chem	47	442	1943
neohexane					
cyclopentane	Serijan, et al	J Am Chem Soc	68	1763	1946
Furfural					
docosane					
diphenylhexane	Briggs, Comings	Ind Eng Chem	35	411	1943
Water					
toluene					
hydroformed naphtha	Arnold, Coghlan	Ind Eng Chem	42	177	1950

#### Quaternary Systems

Acetic acid (aqueous 97% and 98.1%)					
n-heptane-toluene	Othmer, Tobias	Ind Eng Chem	34	690	1942
Aniline					
Cyclohexane-cetane					
benzene	Brown	Ind Eng Chem	40	103	1948
n-heptane	Ibid				

	Authors	Journal	Volume	Page	Year
Water					
ammonia					
hydroformed naphtha					
toluene	Arnold, Coghlan	Ind Eng Chem	42	1217	1950
ethylene glycol					
hydroformed naphtha					
toluene	Ibid				

## VITA

Edward N. Pennington  
candidate for the degree of  
Master of Science

Thesis: CORRELATION OF LIQUID-LIQUID PHASE EQUILIBRIA

Major: Chemical Engineering

Minor: Industrial Engineering

Biographical and Other Items:

Born: December 24, 1917 at Ottawa, Kansas

Undergraduate Study: Southwest Baptist College, Bolivar,  
Missouri, 1936 - 1938; Carnegie Institute of Tech-  
nology, Pittsburgh, Pennsylvania, 1946 - 1948.

Graduate Study: O. A. M. C., 1948 - 1952

Experiences: Employed by Hall Brothers, Inc., 1938 - 1942;  
Army, Transportation Corps, 1942 - 1946; Employed by  
Phillips Petroleum Company, 1948 - present.

Member of American Chemical Society and American Institute of  
Chemical Engineers.

Date of Final Examination:

THESIS TITLE: CORRELATION OF LIQUID-LIQUID PHASE  
EQUILIBRIA

AUTHOR: Edward N. Pennington

THESIS ADVISER: C. L. Nickolls

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