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PREDICTION OF LIQUID-LIQUID PHASE EQUILIBRIUM DATA

BY

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ABSTRACT

This paper covers two methods for the prediction of liquid-liquid equilibrium data in ternary systems consisting of two hydrocarbons and a solvent and forming two liquid phases. One method is that of Pennington and Marwil (11) and the other is that described by Treybal (16), with some simplifying assumptions by the author. Both methods were applied to seven ternary systems in the present study. Five of the systems investigated were found to give good agreement with experimental results. The assumptions made in deriving the equations for the two methods of prediction did not hold for the other two systems and that is why these two systems showed disagreement between predicted and experimental results. As for comparison between the two methods of prediction, they both gave good results, when applicable. The method of Pennington and Marwil (11) is recommended, because it is the simpler of the two methods.

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INTRODUCTION

In liquid-extraction process evaluation and equipment design, the importance of having accurate liquid-liquid equilibrium data cannot be overemphasized. There is a great amount of data published on binary systems but very little on ternary and other more complex systems. It is, therefore, necessary to either have more experimental work done on these complex systems, which at present is a laborious task, or else find some means of predicting the equilibrium data required from properties of the substances involved, which are readily available in the literature. Several methods for predicting equilibrium data have been published. Most of the published material has been for the prediction of binary data, but some mention is made of ternary systems.

Some of the early work done on the prediction of equilibrium data was by Carlson & Colburn (1). They explained how vapor-liquid equilibrium data can be evaluated and extended when they are correlated in terms of activity coefficients. The equations proposed by van Laar (2), Margules (10), and Scatchard & Hamer (13), which express the activity coefficients of both components of a binary mixture as functions of the liquid composition and empirical constants, are capable of fitting most of the available vapor liquid data.

Both vapor-liquid and liquid-liquid equilibrium data are calculated from the binary van Laar equations 6 and 7, which

gives a means of finding the activity coefficients of the two components from empirical constants and the component concentrations, and equation 4, which states that the ratio of the concentration of a component in the light phase to its concentration in the heavy phase may be evaluated from the inverse ratio of the activity coefficients of the same component in the two phases. Taking equation 4, as an example, the concentrations x and y are defined as follows:

1. Vapor-Liquid Equilibrium data

x = mole fraction of the component in the liquid.

y = mole fraction of the component in the vapor in equilibrium with x .

2. Liquid-Liquid Equilibrium data

x = mole fraction of the component in the solvent phase.

y = mole fraction of the component in the hydrocarbon phase.

Carlson and Colburn (1) used these equations for the prediction of binary equilibrium data. They suggested that, when interpolating for the activity coefficients of a component in the presence of two others, a log-weighted average be used instead of a straight-weighted average. They mentioned briefly a graphical method for predicting ternary equilibrium data, but found that it was not a very satisfactory method.

Colburn, Schoenborn, and Shilling (3) did some experimental work on binary equilibrium systems. They used the equations of

Carlson & Colburn (1) to predict the equilibrium data for one of these systems, but these did not agree very well with their experimental results. The systems they used for their calculations gave van Laar constants that differed widely and the method of Carlson & Colburn (1) was derived for systems where the van Laar constants are nearly the same.

Treybal (15) explained how the method of Hildebrand (7) is used in predicting the usefulness of solvents in solvent extraction processes. This method is based on the departure from ideality of the two binary solutions of the distributed solute and the immiscible solvents, and utilizes the fact that the activity of the distributed solute must be the same at equilibrium in the two immiscible solutions. In his paper, he investigated the general reliability of the method and certain of its modifications when the activity coefficients were calculated from vapor-liquid equilibrium data of the two binary solutions. Treybal (15) gave reference to Carlson & Colburn (1) and used their suggestion for interpolation of the log of the activity coefficients when finding the activity coefficients of a component.

Colburn and Schoenborn (2) considered convenient means of determining the activity coefficients of, first, each of the components separately in a possible agent, and second, the estimation of the mutual effect of the components on their activity coefficients in the agent. The simplest method of

accomplishing the first objective is shown to be, in case of partially miscible agents, the application of mutual solubility data. The relationship of activity coefficients in ternary mixtures to binary data is explored and plots of activity coefficients of available ternary data are provided which give an indication of the trend of values from simple interpolation procedures. They used mutual solubility data of binary mixtures to calculate the van Laar constants and then predicted binary equilibrium and ternary equilibrium data.

Scheibel and Friedland (14) suggested a method for the prediction of vapor-liquid equilibrium data for non-ideal ternary systems. They classified the various non-ideal systems into three distinct classes based on the qualitative deviation from Raoult's law which are observed in the different binary systems. They used a graphical method for determining the activity coefficients and then, using Raoult's law corrected for non-ideal solutions, calculated the vapor in equilibrium with the liquid. This method involves trial and error calculations.

Pennington and Marwil (11) used solubility data of binary systems for predicting ternary equilibrium data in systems consisting of two hydrocarbons and a solvent. They used the van Laar equations for binary systems to calculate the activity coefficients. The activity coefficients in the ternary system were calculated from those of the binary systems with the aid of the following simplifying assumptions:

- (1) the activity coefficient of each hydrocarbon in the ternary is obtained from the corresponding hydrocarbon-solvent binary at the solvent concentration in the binary which the solvent possesses in the ternary system.
- (2) the activity coefficient of the solvent in the ternary is taken as the molal average of the activity coefficients of the solvent in the two binary hydrocarbon-solvent systems at the same solvent concentrations.

Their paper was analyzed in detail in the present study. A sample calculation showing their method of calculation is included in this report and Table VIII compares the equilibrium data of seven systems using their method of calculation, the method used by the author, and actual experimental results.

Treybal (16) summarizes the work done on the prediction of both binary and ternary equilibrium data. He gives an equation for calculating the activity coefficients for ternary systems in terms of the van Laar constants for the three components present in the system. The constants are defined in terms of the binary systems only.

Treybal (16) points out that none of the methods of prediction is capable of a high order of accuracy; nevertheless, they are useful. In trying to find a solvent to use in a given

system, the "selectivity" of the solvent is very important.

The selectivity of B for C is defined as follows:-

$$\beta = \frac{x_{CE}/x_{AB}}{x_{CA}/x_{AA}}$$

where the concentrations are those in the equilibrium layers.

For a satisfactory process, β must exceed unity; therefore, if the equilibrium concentrations for a given system can be predicted with some degree of accuracy, the selectivity of the solvent can be determined. This will indicate whether the solvent chosen will provide a successful extraction process. If this shows that the solvent is not a good one, it can be eliminated from any more consideration and a new one tried. Once a good solvent is found, experimental equilibrium data can be found so that accurate data will be used in the calculations thereafter.

Therefore, both of the methods for the prediction of equilibrium data discussed in this report are very useful tools. They eliminate the necessity of doing a great deal of experimental work, which is very tedious and time consuming.

PROCEDURE

The present investigation was undertaken to determine to what extent the assumptions of Pennington and Marwil (11) were consistent with a thermodynamic approach based on the ternary van Laar equations. It was assumed in the present study that the ternary van Laar constants would apply to the systems treated by Pennington and Marwil (11). It was further assumed that the two hydrocarbons of the ternary form an ideal and symmetrical binary system. This makes the van Laar constants for the two hydrocarbons essentially equal to zero and their ratio equal to one.

As in the method of Pennington and Marwil (11) the only data used in the present work to predict ternary equilibrium data was the solubility data of the binary systems. The procedure involves a trial and error calculation and is described in the sample calculations on page 18. The derivation of the equations used by Pennington and Marwil (11) and those used by the author follows.

DERIVATION OF EQUATIONS EMPLOYED IN PRESENT STUDY

Treybal (16) points out that deviations from ideality of real liquid solutions manifests itself by departure of the various characteristics such as partial pressure, fugacity, and activity, from the simple linear relationships that hold for ideal solutions. Of particular interest for this report is the activity coefficient γ .

Pennington and Marwil (11) note that, when two immiscible phases are in equilibrium, the activity of a given component is the same in both phases, or

$$a_{Av} = a_{Ah} \quad (1)$$

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

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

and

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

If equations 2 and 3 are combined with equation 1, the following equilibrium relationship is obtained:

$$\frac{\gamma_{Ah}}{\gamma_{Av}} = \frac{y_{Av}}{x_{Ah}} \quad (4)$$

Therefore, the ratio of the concentration of a component in the hydrocarbon phase to its concentration in the solvent phase may be evaluated from the inverse ratio of the activity coefficients of the same component in the two phases. From Gibbs' (5) concept of chemical potential, equation 4 can be proved to be rigorous and applies regardless of the number of components present.

Another relation involving the activity coefficient is the Gibbs-Duhem equation

$$\frac{\left[\frac{\partial \ln \gamma_A}{\partial x_A} \right]_{T, p}}{\left[\frac{\partial \ln \gamma_B}{\partial x_B} \right]_{T, p}} = - \frac{x_B}{x_A} \quad (5)$$

The van Laar (9) equations may be shown to be one of many possible solutions of the Gibbs-Duhem equation.

$$\log \gamma_A = \frac{A_{AB}}{\left[1 + \left(\frac{A_{AB} x_A / A_{BA} x_B}{A_{BA} x_B / A_{AB} x_A} \right) \right]^2} \quad (6)$$

$$\log \gamma_B = \frac{A_{BA}}{\left[1 + \left(\frac{A_{BA} x_B / A_{AB} x_A}{A_{AB} x_A / A_{BA} x_B} \right) \right]^2} \quad (7)$$

The constants, A_{AB} and A_{BA} , are calculated from the following equations:

$$A_{AB} = \frac{\log \frac{x_B}{x_A}}{\frac{1}{\left(1 + \frac{A_{AB} x_A}{A_{BA} x_B} \right)^2} - \frac{1}{\left(1 + \frac{A_{BA} x_B}{A_{AB} x_A} \right)^2}} \quad (8)$$

and

$$\frac{{}^A_{AB}}{{}^A_{BA}} = \frac{\left(\frac{x_{AA}}{x_{BA}} + \frac{x_{AB}}{x_{BB}} \right) \left[\frac{\log \frac{x_{AB}}{x_{AA}}}{\log \frac{x_{BA}}{x_{BB}}} - 2 \right]}{\frac{x_{AA}}{x_{BA}} + \frac{x_{AB}}{x_{BB}} - \frac{2x_{AA}x_{AB}}{x_{BA}x_{BB}} \frac{\log \frac{x_{AB}}{x_{AA}}}{\log \frac{x_{BA}}{x_{BB}}}} \quad (9)$$

Pennington and Marwil (11) employed equations 4, 6, 7, 8 and 9 in correlating binary systems from mutual solubility data.

Treybal (16) gives the following equations for nonideal ternary mixtures:

$$\log \gamma_C = \frac{x_A^2 {}^A_{CA} \left(\frac{{}^A_{AC}}{{}^A_{CA}} \right)^2 + x_B^2 {}^A_{CB} \left(\frac{{}^A_{BC}}{{}^A_{CB}} \right)^2 + x_A x_B \left(\frac{{}^A_{AC}}{{}^A_{CA}} \right) \left(\frac{{}^A_{BC}}{{}^A_{CB}} \right) \left[{}^A_{CA} + {}^A_{CB} - {}^A_{BA} \frac{{}^A_{CB}}{{}^A_{BC}} \right]}{\left[x_C + x_A \left(\frac{{}^A_{AC}}{{}^A_{CA}} \right) + x_B \left(\frac{{}^A_{BC}}{{}^A_{CB}} \right) \right]^2} \quad (10)$$

The expressions for $\log \gamma_A$ and $\log \gamma_B$ are obtained by rotating the subscripts throughout the equation. The constants are defined in terms of the binary system only:

$$\left. \begin{aligned} {}^A_{AB} &= \text{Limit of } \log \gamma_A \text{ as } x_A \rightarrow 0, x_B \rightarrow 1 \\ {}^A_{BA} &= \text{Limit of } \log \gamma_B \text{ as } x_B \rightarrow 0, x_A \rightarrow 1 \\ {}^A_{AC} &= \text{Limit of } \log \gamma_A \text{ as } x_A \rightarrow 0, x_C \rightarrow 1 \\ {}^A_{CA} &= \text{Limit of } \log \gamma_C \text{ as } x_C \rightarrow 0, x_A \rightarrow 1 \\ {}^A_{BC} &= \text{Limit of } \log \gamma_B \text{ as } x_B \rightarrow 0, x_C \rightarrow 1 \\ {}^A_{CB} &= \text{Limit of } \log \gamma_C \text{ as } x_C \rightarrow 0, x_B \rightarrow 1 \end{aligned} \right\} \begin{array}{l} \text{Binary A-B} \\ \text{Binary A-C} \\ \text{Binary B-C} \end{array} \quad (11)$$

Wohl (10) has shown that these equations are limited to those cases where

$$\frac{A_{CB}}{A_{BC}} = \left(\frac{A_{CA}}{A_{AC}} \right) \left(\frac{A_{AB}}{A_{BA}} \right) \quad (12)$$

As can be seen from the equations, the ternary data can be predicted from information on the binary systems alone.

To solve for the activity coefficient of the solvent C, it is assumed in the present study that hydrocarbons A and B form a system that is ideal and symmetrical. Therefore,

$$A_{AB} = A_{BA} = 0 \quad (13)$$

and

$$\frac{A_{AB}}{A_{BA}} = 1 \quad (14)$$

also

$$\frac{A_{CB}}{A_{BC}} = \frac{A_{CA}}{A_{AC}} \quad (15)$$

Substituting equations 13, 14 and 15, in equation 10 and rearranging terms gives:

$$\log \gamma_C = \frac{(x_A^2 + x_A x_B) A_{CA} \left(\frac{A_{AC}}{A_{CA}} \right)^2 + (x_B^2 + x_A x_B) A_{CB} \left(\frac{A_{BC}}{A_{CB}} \right)^2}{\left[x_C + (x_A + x_B) \frac{A_{AC}}{A_{CA}} \right]^2} \quad (16)$$

whence

$$\log \gamma_C = \frac{\left(\frac{A}{CA}\right)^2 (x_A + x_B) \left[x_A \frac{A}{CA} + x_B \frac{A}{CB} \right]}{\left[x_C + (x_A + x_B) \frac{A}{CA} \right]^2} \quad (17)$$

Letting $x_{A'} = x_{B'} = x_A + x_B = 1 - x_C$ and dividing numerator and

denominator by $\left(\frac{A}{CA}\right)^2$ gives:

$$\log \gamma_C = \frac{x_{A'} (x_{A'} + x_{B'})}{\left[x_{A'} + \frac{CA}{AC} x_C \right]^2} \quad (18)$$

Equation 18, can be written in the following form:

$$\log \gamma_C = \frac{x_A}{x_A + x_B} \frac{x_{A'} \frac{CA}{CA}}{\left[x_{A'} + \frac{CA}{AC} x_C \right]^2} + \frac{x_B}{x_A + x_B} \frac{x_{B'} \frac{2A}{CB}}{\left[x_{B'} + \frac{CA}{AC} x_C \right]^2} \quad (19)$$

this is equivalent to:

$$\log \gamma_C = \frac{x_A}{x_A + x_B} \log \gamma' + \frac{x_B}{x_A + x_B} \log \gamma'' \quad (19a)$$

where γ' is the activity coefficient of C in AC binary at mole fraction x_C and γ'' is the activity coefficient of C in BC binary at mole fraction x_C .

Equation 19 shows that when solving for the activity coefficient of the solvent, the log molal average should be used and not a straight molal average as in the method of Pennington and Marvil (11).

To solve for the activity coefficient of one of the hydrocarbons say A, B being the other hydrocarbon, and C the solvent, the same conditions holding as when solving for the activity coefficient of the solvent, the following equations result:

$$\log \gamma_A = \frac{x_C^2 \frac{A}{AC} \left(\frac{A}{A/C} \right)^2 + x_C x_B \frac{A}{AC} \left[\frac{A}{AC} - \frac{A}{BC} \right]}{\left[x_A + x_B + x_C \frac{A}{AC} \right]^2} \quad (20)$$

Letting $x_{A'} = x_A + x_B = 1 - x_C$ and dividing numerator and de-

nominator by $\left(\frac{A}{AC} \right)^2$ gives:

$$\log \gamma_A = \frac{x_C^2 \frac{A}{AC} + x_C x_B \frac{A}{CA} \left[\frac{A}{AC} - \frac{A}{BC} \right]}{\left[x_C + x_{A'} \frac{A}{CA} \right]^2} \quad (21)$$

If the second term in the numerator of equation 21, is omitted, an approximation which can be justified in many cases, there results the equation:

$$\log \gamma_A = \frac{x_C^2 \frac{A}{AC}}{\left[x_C + x_{A'} \frac{A}{CA} \right]^2} \quad (21a)$$

From this equation, we may deduce the assumption used by Pennington and Marvil (11), that the activity coefficient of a hydrocarbon in a ternary with another hydrocarbon and a solvent may be taken as the value which the activity coefficient

of the hydrocarbon would have in the binary hydrocarbon-solvent system at the same solvent concentration as in the ternary.

When solving for the activity coefficient of the solvent in the ternary, the author used equation 18, which gave the log molal average of the activity coefficients of the solvent in the two binary hydrocarbon-solvent systems at the same solvent concentration, whereas in the method of Pennington and Marwil (11), the molal average of the activity coefficients of the solvent in the two binary hydrocarbon-solvent systems at the same solvent concentration was calculated. When solving for the activity coefficients of the hydrocarbons in the ternary, the author used equation 21, whereas Pennington and Marwil (11) used a procedure which was shown above to be equivalent to employing equation 21a.

The calculated results of systems I through VII, using the author's method, are shown in Table VIII. The calculated results of System I, using the method of Pennington and Marwil (11), was reproduced from their paper and is shown in Table VIII. The calculated results of Systems II through VII, as calculated by the author, using the method of Pennington and Marwil (11), are also shown in Table VIII.

DISCUSSION AND CONCLUSION

The method of predicting ternary equilibrium data of Pennington and Marwil (11) and that used by the author gave very consistent results - the author's method usually showing slightly better results. Table VII, which indicates the average deviation of predicted results from experimental results shows this.

Table VII. Average Deviation of Predicted Values of Mole Fractions from Experimental Values

	Hydrocarbon in Hydro- carbon Phase <u>a.d.</u>	Hydrocarbon in Solvent Phase <u>a.d.</u>	Solvent in Hydrocarbon Phase <u>a.d.</u>	Solvent in Solvent Phase <u>a.d.</u>
Method of Pennington & Marwil (11)	0.014	0.011	0.028	0.021
Author's Method	0.012	0.009	0.021	0.020

For systems where these two methods of prediction are applicable, the method of Pennington and Marwil (11) gave sufficiently accurate results.

As mentioned, either of these procedures should only be used where the assumptions used in deriving the equations are known to be valid. As can be seen from the results given in Table VIII, systems I through V show good agreement between predicted and experimental equilibrium data. In system VI, fair agreement is shown between the predicted data, as found using the author's method, with experimental equilibrium data,

but poor agreement using the method of Pennington and Marwil (11). In system VII, poor agreement is shown with both of the methods of prediction and experimental equilibrium data. In systems VI and VII, the prediction of the distribution, as pointed out by Pennington and Marwil (11), on a solvent free basis is fairly good, but the solvent concentration in the hydrocarbon phase is not correct.

In the derivation of the equations, one of the assumptions made was that hydrocarbons A and B form a system that is ideal and symmetrical. Based on this assumption, equation 15 resulted. Upon substituting the van Laar constants from Table IX for systems VI and VII in equation 15, it is found that equation 15 does not hold. This helps to explain why poor agreement was found for these systems, particularly system VII. In the case of systems I through V equation 15 was found to be approximately valid.

The weakness of both methods appears to be in the fact that if the solvent concentration is assumed too small in the hydrocarbon phase in step 1, then the activity coefficients of the solvent in that phase will come out too high in the last step and the calculated solvent concentration in the last step will come out too low, tending to agree with the assumed value, which was also too low.

In conclusion it may be stated that where the two methods of prediction are applicable, Pennington and Marwils(11) method is preferable to the author's, being the simpler of the two,

although slightly less accurate.

SAMPLE CALCULATIONS

Method of Pennington and Marwil (11) n-heptane, cyclohexane, furfural System

Let us assume that it is desired to estimate the furfural content of the hydrocarbon phase and the composition of the solvent phase when the hydrocarbon phase has a composition of 0.7940 mole fraction n-heptane and 0.2060 mole fraction cyclohexane on a solvent-free basis. Trial-and-error solution follows:

Step 1. The concentration of furfural in each of the two ternary phases is estimated by assuming that it will be the weighted average of the furfural concentration in the binary systems. For the first trial calculation, the solvent-free composition of the hydrocarbon phase is used to estimate the furfural concentration in both phases. The estimated furfural concentrations are confirmed or rejected by subsequent calculations. The initial estimation of the furfural concentration in both phases is shown in Table I.

Table I. Estimated Furfural Concentrations

Component	<u>Hydrocarbon Phase</u>			<u>Solvent Phase</u>	
	Mole Fract.	Soly. at 86°F., mole fract. furfural	Partial Soly.	Soly. at 86°F., mole fract. furfural	Partial Soly.
n-Heptane	0.7940	0.059	0.0468	0.936	0.7432
Cyclohexane	0.2060	0.065	0.0134	0.846	0.1743
	<u>1.0000</u>		<u>0.0602</u>		<u>0.9175</u>

Step 2. Determine the activity coefficients for normal heptane and cyclohexane at the furfural concentrations estimated in step 1. The binary van Laar equations 6 and 7 are used. From the activity coefficients obtained in this manner, the ratio of the activity coefficient in the solvent phase to the activity coefficient in the hydrocarbon phase for n-heptane and cyclohexane was calculated. These ratios were used to estimate the composition of n-heptane and cyclohexane in the solvent phase. The calculations are shown in Table II.

<u>Solvent Phase</u>		<u>Hydrocarbon Phase</u>	
n-Heptane	Cyclohexane	n-Heptane	Cyclohexane
$A_{BA} = 1.365$	1.358	1.365	1.358
$A_{AB} = 1.334$	1.023	1.334	1.023
$x_A = 0.0825$	0.0825	0.9398	0.9398
$x_B = 0.9175$	0.9175	0.0602	0.0602

Table II. Estimation of Distribution in Solvent Phase

Component	Mole Fract.	γ_h	γ_v	$\frac{\gamma_h}{\gamma_v}$	Estd. Hydrocarbon Concn. in Solvent Phase
n-heptane	0.7940	13.48	1.013	13.31	$(0.7940)(0.9400)/13.31 = 0.0561$
Cyclohexane	0.2060	7.80	1.016	7.68	$(0.2060)(0.9400)/7.68 = 0.0252$
					<u>0.0813</u>

Step 3. Check the furfural concentration in the solvent phase calculated in step 2, against the value used in step 1, to obtain the activity coefficients for the solvent phase.

By difference, the furfural mole fraction is 0.9187, which compares favorably with 0.9175 estimated in step 1. Therefore, a second approximation of the furfural concentration in the solvent phase is not necessary.

Step 4. Check the furfural concentration in the hydrocarbon phase estimated in step 1, using the activity coefficients of furfural in n-heptane and furfural in cyclohexane. The activity coefficients are evaluated at the estimated furfural concentration in the hydrocarbon phase from step 1, and the calculated furfural concentration in the solvent phase from step 3. The activity coefficient of furfural in each of the ternary phases is estimated by assuming that it will be the weighted average of the furfural activity coefficients in the binary system. The calculations are shown in Table III.

	<u>Solvent Phase</u>		<u>Hydrocarbon Phase</u>	
	n-Heptane	Cyclohexane	n-Heptane	Cyclohexane
$A_{DA} =$	1.334	1.023	1.334	1.023
$A_{AB} =$	1.365	1.358	1.365	1.358
$x_A =$	0.9187	0.9187	0.0602	0.0602
$x_B =$	0.0813	0.0813	0.9398	0.9398

Table III. Estimated Furfural Activity Coefficients
in Equilibrium Phases

Component	Hydrocarbon Phase			Solvent Phase		
	0.0602 Mole Frac. Furfural Solvent-free Compn.	γ_v	Partial activity coeff.	0.9187 Mole Fract. Furfural Solvent-free Compn.	γ_h	Partial activity coeff.
n-Heptane	0.7940	16.0	12.70	0.6900	1.030	0.711
Cyclohexane	0.2060	14.2	2.93	0.3100	1.020	0.316
	<u>1.0000</u>		<u>15.63</u>	<u>1.0000</u>		<u>1.027</u>

The ratio of the activity coefficient of furfural in the hydrocarbon phase to the activity coefficient of furfural in the solvent phase is $15.63/1.027 = 15.22$. Then the calculated furfural concentration in the hydrocarbon phase is equal to the furfural concentration in the solvent phase divided by the inverse ratio of the activity coefficients, or $0.9187/15.22 = 0.0604$. The calculated concentration of 0.0604 provides a satisfactory check with the concentration of 0.0602 estimated in step 1; therefore, a second trial calculation is not necessary. The results are shown in Table IV.

Table IV. Comparison of Calculated and Experimental
Equilibrium Data

Component	<u>Composition, Mole Fraction</u>			
	<u>Experimental</u>		<u>Estimated</u>	
	Hydrocarbon Phase	Solvent Phase	Hydrocarbon Phase	Solvent Phase
n-Heptane	0.745	0.050	0.746	0.056
Cyclohexane	0.194	0.020	0.194	0.025
Furfural	0.061	0.930	0.060	0.919
	<u>1.000</u>	<u>1.000</u>	<u>1.000</u>	<u>1.000</u>

Author's Method

Step 1. Same as step 1, in method of Pennington and Marwil (11).

Step 2. Determine the activity coefficients for normal heptane and cyclohexane at the furfural concentrations estimated in step 1. This was done using equation 21. Since equation 21 requires values of the mole fractions of the hydrocarbon in the solvent phase, the values from Table II were used as trial values. From the activity coefficients obtained in this manner, the ratio of the activity coefficient in the solvent phase to the activity coefficient in the hydrocarbon phase for n-heptane and cyclohexane was calculated. These ratios were used to estimate the composition of n-heptane and cyclohexane in the solvent phase. The calculations are shown in Table II.

<u>Solvent Phase</u>		<u>Hydrocarbon Phase</u>	
n-Heptane	Cyclohexane	n-Heptane	Cyclohexane
$\gamma_A = ?$?	?	?
$x_C = 0.9175$	0.9175	0.0602	0.0602
$x_B = 0.0252$ (from Table II)	0.0561 (from Table II)	0.1936	0.7462
$x_A = 0.0561$ (from Table II)	0.0252 (from Table II)	0.7462	0.1936
$A_{AC} = 1.334$	1.023	1.334	1.023
$A_{CA} = 1.365$	1.358	1.365	1.358
$A_{BC} = 1.023$	1.334	1.023	1.334
$x_{A'} = 0.0825$	0.0825	0.9398	0.9398

Table V. Estimation of Distribution in Solvent Phase

Component	Mole Fract.	<u>Activity Coefficient</u>			Estd Hydrocarbon Conc. in Solvent Phase
		γ_h	γ_v	$\frac{\gamma_h}{\gamma_v}$	
n-Heptane	0.7940	13.55	1.014	13.36	$(0.7940)(0.9400)/13.36 = 0.0558$
Cyclohexane	0.2060	7.36	0.980	7.51	$(0.2060)(0.9400)/7.51 = 0.0258$
					<u>0.0816</u>

Since the calculated hydrocarbon mole fractions check approximately the assumed values, recalculation is not necessary.

Step 3. Check the furfural concentration in the solvent phase calculated in step 2, against the value used in step 1, to obtain the activity coefficients for the solvent phase. By difference, the furfural mole fraction is 0.9184, which compares favorably with 0.9175, estimated in step 1. Therefore, a second approximation of the furfural concentration in the solvent phase is not necessary.

Step 4. Check the furfural concentration in the hydrocarbon phase estimated in step 1, using the activity coefficients of furfural in n-heptane and furfural in cyclohexane. The activity coefficients are evaluated at the estimated furfural concentration in the hydrocarbon phase from step 1, and the calculated furfural concentration in the solvent phase from step 3. This was done using equation 18.

	<u>Hydrocarbon Phase</u>	<u>Solvent Phase</u>
γ_C =	?	?
x_A =	0.7462	0.0558
x_B =	0.1936	0.0258
x_C =	0.0602	0.9184
$x_{A'}$ =	0.9398	0.0816
A_{AC} =	1.334	1.334
A_{CA} =	1.365	1.365
A_{CB} =	1.358	1.358

The estimated furfural activity coefficient in the hydrocarbon phase is 15.88 and in the solvent phase 1.020. Then the calculated furfural concentration in the hydrocarbon phase is equal to the furfural concentration in the solvent phase divided by the inverse ratio of the activity coefficients, or $(0.9184)(1.020)/15.88 = 0.0590$. The calculated concentration of 0.0590 provides a satisfactory check with the concentration of 0.0602 estimated in step 1; therefore, a second trial calculation is not necessary. The results are shown in Table VI.

Table VI. Comparison of Calculated and Experimental
Equilibrium Data

Component	<u>Composition, Mole Fraction</u>			
	<u>Experimental</u>		<u>Estimated</u>	
	Hydrocarbon Phase	Solvent Phase	Hydrocarbon Phase	Solvent Phase
n-Heptane	0.745	0.050	0.747	0.056
Cyclohexane	0.194	0.020	0.194	0.026
Furfural	0.061	0.930	0.059	0.918
	<u>1.000</u>	<u>1.000</u>	<u>1.000</u>	<u>1.000</u>

TABLE VIII

Experimental and Estimated Equilibrium Concentrations in the following systems.

System I - n-Heptane - Cyclohexane - Furfural at 86°F

	Case No.		
	1	2	3
Experimental Equilibrium Concentrations, Mole Fraction (11).			
Hydrocarbon Phase			
n-Heptane	0.745	0.490	0.180
Cyclohexane	0.194	0.450	0.761
Furfural	$\frac{0.061}{1.000}$	$\frac{0.060}{1.000}$	$\frac{0.059}{1.000}$
Solvent Phase			
n-Heptane	0.050	0.038	0.016
Cyclohexane	0.020	0.060	0.114
Furfural	$\frac{0.930}{1.000}$	$\frac{0.902}{1.000}$	$\frac{0.870}{1.000}$
Estimated Equilibrium Concentrations, Mole Fraction ^a			
Hydrocarbon Phase			
n-Heptane	0.746	0.490	0.179
Cyclohexane	0.194	0.449	0.757
Furfural	$\frac{0.060}{1.000}$	$\frac{0.061}{1.000}$	$\frac{0.064}{1.000}$
Solvent Phase			
n-Heptane	0.056	0.042	0.018
Cyclohexane	0.025	0.064	0.120
Furfural	$\frac{0.919}{1.000}$	$\frac{0.894}{1.000}$	$\frac{0.862}{1.000}$

TABLE VIII (cont.)

System I - n-Heptane-Cyclohexane-Furfural at 86°F (cont.)

	Case No.		
	1	2	3
Estimated Equilibrium Concentrations, Mole Fraction ^b			
Hydrocarbon Phase			
n-Heptane	0.747	0.491	0.180
Cyclohexane	0.194	0.450	0.761
Furfural	$\frac{0.059}{1.000}$	$\frac{0.059}{1.000}$	$\frac{0.059}{1.000}$
Solvent Phase			
n-Heptane	0.056	0.041	0.016
Cyclohexane	0.026	0.063	0.109
Furfural	$\frac{0.918}{1.000}$	$\frac{0.896}{1.000}$	$\frac{0.875}{1.000}$

System II - Iso-octane-n-Hexane-Furfural at 86°F

Experimental Equilibrium Concentration, Mole Fraction (11)

Hydrocarbon Phase			
Iso-Octane	0.790	0.495	0.194
n-Hexane	0.149	0.444	0.749
Furfural	$\frac{0.061}{1.000}$	$\frac{0.061}{1.000}$	$\frac{0.057}{1.000}$
Solvent Phase			
Iso-Octane	0.040	0.027	0.011
n-Hexane	0.012	0.036	0.060
Furfural	$\frac{0.948}{1.000}$	$\frac{0.937}{1.000}$	$\frac{0.929}{1.000}$

TABLE VIII (cont.)

System II - Iso-octane - n-Hexane - Furfural at 86°F (cont.)

	Case No.		
	1	2	3
Estimated Equilibrium Concentrations, Mole Fraction ^a			
Hydrocarbon Phase			
Iso-Octane	0.790	0.490	0.189
n-Hexane	0.149	0.440	0.728
Furfural	$\frac{0.061}{1.000}$	$\frac{0.070}{1.000}$	$\frac{0.083}{1.000}$
Solvent Phase			
Iso-Octane	0.046	0.031	0.013
n-Hexane	0.012	0.036	0.064
Furfural	$\frac{0.942}{1.000}$	$\frac{0.933}{1.000}$	$\frac{0.923}{1.000}$
Estimated Equilibrium Concentrations, Mole Fraction ^b			
Hydrocarbon Phase			
Iso-Octane	0.788	0.438	0.188
n-Hexane	0.149	0.439	0.727
Furfural	$\frac{0.063}{1.000}$	$\frac{0.073}{1.000}$	$\frac{0.085}{1.000}$
Solvent Phase			
Iso-Octane	0.041	0.028	0.011
n-Hexane	0.012	0.038	0.068
Furfural	$\frac{0.947}{1.000}$	$\frac{0.934}{1.000}$	$\frac{0.921}{1.000}$

TABLE VIII (cont.)

System III - n-Hexane-Methylcyclopentane-Aniline at 77°F

	Case No.		
	1	2	3
Experimental Equilibrium Concentrations, Mole Fraction ^h			
Hydrocarbon Phase			
n-Hexane	0.736	0.480	0.136
Methylcyclopentane	0.187	0.430	0.744
Aniline	$\frac{0.077}{1.000}$	$\frac{0.090}{1.000}$	$\frac{0.120}{1.000}$
Solvent Phase			
n-Hexane	0.073	0.050	0.028
Methylcyclopentane	0.022	0.080	0.141
Aniline	$\frac{0.905}{1.000}$	$\frac{0.870}{1.000}$	$\frac{0.831}{1.000}$
Estimated Equilibrium Concentrations, Mole Fraction ^a			
Hydrocarbon Phase			
n-Hexane	0.736	0.479	0.136
Methylcyclopentane	0.187	0.429	0.744
Aniline	$\frac{0.077}{1.000}$	$\frac{0.092}{1.000}$	$\frac{0.120}{1.000}$
Solvent Phase			
n-Hexane	0.078	0.063	0.024
Methylcyclopentane	0.035	0.092	0.196
Aniline	$\frac{0.887}{1.000}$	$\frac{0.845}{1.000}$	$\frac{0.780}{1.000}$

TABLE VIII (cont.)

System III - n-Hexane-Methylcyclopentane-Aniline at 77°F (cont.)

	Case No.		
	1	2	3
Estimated Equilibrium Concentrations, Mole Fraction ^b			
Hydrocarbon Phase			
n-Hexane	0.736	0.479	0.136
Methylcyclopentane	0.187	0.429	0.746
Aniline	$\frac{0.077}{1.000}$	$\frac{0.092}{1.000}$	$\frac{0.118}{1.000}$
Solvent Phase			
n-Hexane	0.077	0.062	0.023
Methylcyclopentane	0.034	0.095	0.196
Aniline	$\frac{0.889}{1.000}$	$\frac{0.843}{1.000}$	$\frac{0.781}{1.000}$

System IV - Heptane-Cyclohexane-Aniline at 77°F

Experimental Equilibrium Concentrations, Mole Fraction (8)

Hydrocarbon Phase			
n-Heptane	0.227	0.440	0.706
Cyclohexane	0.649	0.457	0.210
Aniline	$\frac{0.124}{1.000}$	$\frac{0.103}{1.000}$	$\frac{0.084}{1.000}$
Solvent Phase			
n-Heptane	0.031	0.046	0.056
Cyclohexane	0.139	0.068	0.017
Aniline	$\frac{0.830}{1.000}$	$\frac{0.886}{1.000}$	$\frac{0.927}{1.000}$

TABLE VIII (cont.)

System IV - Heptane-Cyclohexane-Aniline at 77°F (cont.)

	Case No.		
	1	2	3
Estimated Equilibrium Concentrations, Mole Fraction ^a			
Hydrocarbon Phase			
n-Heptane	0.227	0.440	0.705
Cyclohexane	0.650	0.457	0.210
Aniline	$\frac{0.123}{1.000}$	$\frac{0.103}{1.000}$	$\frac{0.085}{1.000}$
Solvent Phase			
n-Heptane	0.038	0.055	0.062
Cyclohexane	0.180	0.108	0.041
Aniline	$\frac{0.782}{1.000}$	$\frac{0.837}{1.000}$	$\frac{0.897}{1.000}$
Estimated Equilibrium Concentrations, Mole Fraction ^b			
Hydrocarbon Phase			
n-Heptane	0.230	0.441	0.706
Cyclohexane	0.655	0.459	0.210
Aniline	$\frac{0.115}{1.000}$	$\frac{0.100}{1.000}$	$\frac{0.084}{1.000}$
Solvent Phase			
n-Heptane	0.035	0.052	0.060
Cyclohexane	0.179	0.106	0.026
Aniline	$\frac{0.736}{1.000}$	$\frac{0.842}{1.000}$	$\frac{0.914}{1.000}$

TABLE VIII (cont.)

System V - n-Heptane-Methylcyclohexane-Aniline at 77°F

	Case No.		
	1	2	3
Experimental Equilibrium Concentrations, Mole Fraction (17)			
Hydrocarbon Phase			
n-Heptane	0.825	0.497	0.157
Methylcyclohexane	0.093	0.411	0.734
Aniline	$\frac{0.082}{1.000}$	$\frac{0.092}{1.000}$	$\frac{0.109}{1.000}$
Solvent Phase			
n-Heptane	0.056	0.038	0.013
Methylcyclohexane	0.008	0.057	0.125
Aniline	$\frac{0.936}{1.000}$	$\frac{0.905}{1.000}$	$\frac{0.862}{1.000}$
Estimated Equilibrium Concentrations, Mole Fraction ^a			
Hydrocarbon Phase			
n-Heptane	0.829	0.497	0.156
Methylcyclohexane	0.094	0.412	0.731
Aniline	$\frac{0.077}{1.000}$	$\frac{0.071}{1.000}$	$\frac{0.113}{1.000}$
Solvent Phase			
n-Heptane	0.056	0.042	0.017
Methylcyclohexane	0.012	0.059	0.125
Aniline	$\frac{0.932}{1.000}$	$\frac{0.899}{1.000}$	$\frac{0.858}{1.000}$

TABLE VIII (cont.)

System V - n-Heptane-Methylcyclohexane-Aniline at 77°F (cont.)

	Case No.		
	1	2	3
Estimated Equilibrium Concentrations, Mole Fraction ^b			
Hydrocarbon Phase			
n-Heptane	0.830	0.497	0.157
Methylcyclohexane	0.094	0.412	0.735
Aniline	<u>0.076</u> 1.000	<u>0.091</u> 1.000	<u>0.108</u> 1.000
Solvent Phase			
n-Heptane	0.068	0.041	0.016
Methylcyclohexane	0.011	0.059	0.124
Aniline	<u>0.921</u> 1.000	<u>0.900</u> 1.000	<u>0.860</u> 1.000

System VI - n-Heptane-Methylcyclohexane-Furfural at 140°F

Experimental Equilibrium Concentrations, Mole Fraction (6)

Hydrocarbon Phase			
n-Heptane	0.215	0.432	0.634
Methylcyclohexane	0.613	0.404	0.212
Furfural	<u>0.172</u> 1.000	<u>0.164</u> 1.000	<u>0.154</u> 1.000
Solvent Phase			
n-Heptane	0.036	0.064	0.084
Methylcyclohexane	0.139	0.080	0.038
Furfural	<u>0.825</u> 1.000	<u>0.856</u> 1.000	<u>0.878</u> 1.000

TABLE VIII (cont.)

System VI - n-Heptane-Methylcyclohexane-Furfural at 140°F (cont.)

	Case No.		
	1	2	3
Estimated Equilibrium Concentrations, Mole Fraction ^a			
Hydrocarbon Phase			
n-Heptane	0.239	0.450	0.701
Methylcyclohexane	0.679	0.449	0.235
Furfural	$\frac{0.082}{1.000}$	$\frac{0.071}{1.000}$	$\frac{0.064}{1.000}$
Solvent Phase			
n-Heptane	0.039	0.069	0.092
Methylcyclohexane	0.159	0.097	0.048
Furfural	$\frac{0.802}{1.000}$	$\frac{0.834}{1.000}$	$\frac{0.860}{1.000}$
Estimated Equilibrium Concentrations, Mole Fraction ^b			
Hydrocarbon Phase			
n-Heptane	0.207	0.443	0.679
Methylcyclohexane	0.590	0.411	0.227
Furfural	$\frac{0.203}{1.000}$	$\frac{0.143}{1.000}$	$\frac{0.094}{1.000}$
Solvent Phase			
n-Heptane	0.040	0.070	0.091
Methylcyclohexane	0.154	0.092	0.044
Furfural	$\frac{0.806}{1.000}$	$\frac{0.838}{1.000}$	$\frac{0.865}{1.000}$

TABLE VIII (cont.)

System VII - n-Heptane-Methylcyclohexane-Methylcarbitol at 140°F

	Case No.		
	1	2	3
Experimental Equilibrium Concentrations, Mole Fraction (6)			
Hydrocarbon Phase			
n-Heptane	0.228	0.465	0.684
Methylcyclohexane	0.668	0.439	0.232
Methylcarbitol	$\frac{0.104}{1.000}$	$\frac{0.096}{1.000}$	$\frac{0.084}{1.000}$
Solvent Phase			
n-Heptane	0.040	0.070	0.097
Methylcyclohexane	0.154	0.086	0.044
Methylcarbitol	$\frac{0.806}{1.000}$	$\frac{0.844}{1.000}$	$\frac{0.859}{1.000}$
Estimated Equilibrium Concentrations, Mole Fraction ^a			
Hydrocarbon Phase			
n-Heptane	0.253	0.509	0.736
Methylcyclohexane	0.742	0.482	0.250
Methylcarbitol	$\frac{0.005}{1.000}$	$\frac{0.009}{1.000}$	$\frac{0.014}{1.000}$
Solvent Phase			
n-Heptane	0.041	0.074	0.078
Methylcyclohexane	0.194	0.122	0.062
Methylcarbitol	$\frac{0.765}{1.000}$	$\frac{0.804}{1.000}$	$\frac{0.840}{1.000}$

TABLE VIII (cont.)

System VII - n-Heptane-Methylcyclohexane-Methylcarbitol at 140°F (cont.)

	Case No.		
	1	2	3
Estimated Equilibrium Concentrations, Mole Fraction ^b			
Hydrocarbon Phase			
n-Heptane	0.253	0.510	0.737
Methylcyclohexane	0.743	0.483	0.251
Methylcarbitol	$\frac{0.004}{1.000}$	$\frac{0.007}{1.000}$	$\frac{0.012}{1.000}$
Solvent Phase			
n-Heptane	0.039	0.076	0.097
Methylcyclohexane	0.192	0.117	0.058
Methylcarbitol	$\frac{0.769}{1.000}$	$\frac{0.807}{1.000}$	$\frac{0.845}{1.000}$

a Estimated results using method of Pennington & Marwil

b Estimated results using author's method

TABLE IX - van Laar Activity Coefficient Constants

<u>System</u>	<u>Λ_{BA}</u>	<u>Λ_{AB}</u>	<u>Temp. °F</u>
Furfural with			
n-Hexane (11) ^a	1.239	1.116	86
n-Heptane (11) ^a	1.334	1.365	86
Iso-octane (11) ^a	1.446	1.371	86
Cyclohexane (11) ^a	1.023	1.358	86
n-Heptane (6) ^b	1.082	1.775	140
Methylcyclohexane (6) ^b	0.829	2.657	140
Aniline with			
n-Hexane (11) ^a	1.248	1.309	77
n-Heptane (11) ^a	1.371	1.284	77
Methylcyclopentane (11) ^a	0.918	1.089	77
Cyclohexane (11) ^a	0.861	1.117	77
Methylcyclohexane (11) ^a	1.041	1.140	77
Methylcarbitol with			
n-Heptane (6) ^b	1.043	2.008	140
Methylcyclohexane (6) ^b	0.667	2.724	140

^a As given in reference indicated.

^b As calculated from data as indicated by reference.

NOMENCLATURE

- A = constant in van Laar equation.
 $\lim_{x \rightarrow 0} \log Y_A$ = limit of $\log Y_A$ as $x \rightarrow 0$.
 C_i = component of a solution.
 a_i = activity.
 B_i = component of a solution.
 C_i = component of a solution.
 \ln = natural logarithm.
 \log = common logarithm
 x_i = mole fraction in solvent phase or in solution,
if only one phase is present.
 y_i = mole fraction in hydrocarbon phase.
 β = selectivity.
 γ = activity coefficient.
 ∂ = partial differential operator.

Subscripts:

- A = component A.
 B = component B.
 C = component C.
 AB = component A in a B-rich solution, etc.
 h = pertains to solvent phase.
 v = pertains to hydrocarbon phase.

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