Phase Equilibria of Binary Mixtures of C_4 Hydrocarbons with Furfural and Furfural-Water

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The separation of close-boiling hydrocarbons by simple fractionation requires high reflux ratios and a large number of plates, and columns designed for such service are properly called "superfractionation" units. However, in many instances, the principle of solvent or extractive distillation may be used for ready separation of key components whose relative volatility is close to unity. A proper solvent for extractive distillation must have a considerably higher boiling point than either of the keys and selective affinity for one of these components. In plant operation, the solvent is introduced at the top of the tower and, by its selective nature, changes the relative volatility of the feed components to effect an equivalent separation with only a fraction of the trays required by straight distillation. For the hydrocarbon mixtures composed of C_4 hydrocarbons, furfural has proved very effective, as evidenced in Table I.

Table I. Relative Volatilities over Furfural-Water at 100° F.
Solvent mole fraction = 0.90

Hydrocarbon	Normal	Furfural	Furf. + 2% H_2O	Furf. + 4% H_2O
n-Butane	0.871	2.654	2.800	2.934
1-Butene	1.046	1.900	1.910	1.920
1,3-Butadiene	1.000	1.000	1.000	1.000
cis-2-Butene	0.776	1.250	1.265	1.275
Isobutane	1.209	3.960	4.160	4.420

Although the principles of extractive distillation are similar to those of liquid-phase solvent extraction, the application of theory is different. For efficient tower operation, only one liquid phase, the solvent, should be present on the fractionation trays. As the solvent phase becomes richer in hydrocarbon on the lower trays of the tower, the components of lower solubility or selectivity tend to separate as a liquid hydrocarbon phase of lower density than the solvent. This phase separation may lead to tower flooding as the liquid hydrocarbon phase preferentially overflows through the weirs and accumulates on the lowest plates of the tower. To minimize the required tower capacity, however, the enriching section of the tower must be operated near the point of incipient hydrocarbon phase separation, and the solvent circulation rate thus maintained as low as possible.

In commercial application of this process, steam is used to strip the hydrocarbon from the rich furfural bottoms. The presence of higher concentrations of water in the furfural solvent permits lower temperatures to be maintained in the solvent-stripper reboiler, and polymerization of the furfural is decreased. The resulting furfural-water solvent has two effects on extractive distillation operations. First, water lowers the solubility limit of a particular hydrocarbon in furfural; thus a higher solvent-hydrocarbon ratio is required to prevent hydrocarbon phase formation on the lower plates. Second, as may be seen from Table I, water in the furfural solvent increases the hydrocarbon relative volatilities at the same solvent concentration. It becomes apparent that both vapor-liquid and liquid-liquid equilibrium data for the C_4 hydrocarbons with furfural and with furfural-water solvents are essential to the optimum design and operation of the extractive distillation towers.

The use of furfural as a solvent for separating close-boiling C_4 fractions has been studied extensively during the past several years. Liquid-liquid and vapor-liquid equilibria for the systems of single C_4 and C_3 hydrocarbons with furfural and furfural-water have been reported by Griswold and associates (*6, 8*) and by Gerster, Mertes, and Colburn (*9, 10*), who have also reported vapor-liquid equilibrium data for binary mixtures of some C_4 hydrocarbons in furfural and furfural-water solutions (*4, 11*). This work presents liquid-liquid phase equilibria and solvent phase solubilities for binary mixtures of C_4 hydrocarbons with furfural and furfural-water and relates these data to those of the parent single hydrocarbon systems.

THE EXPERIMENTAL PROGRAM

In any study of physical equilibria, phase rule theory is of foremost importance in the consideration of the systems involved, especially systems that contain three or more liquid and vapor phases. The constituents of these reported systems consist of C_4 hydrocarbons, furfural, and water, and each liquid component normally has limited solubility in the remaining two. The principal variables which concern these systems are the number of constituents, the number of phases, the phase compositions, the equilibrium pressures, and the temperature. These variables are not all independent, and determination of the degrees of freedom was prerequisite to each series of experimental runs. The general statement of the phase rule for a system involving N constituents in physical equilibrium in P phases, with E arbitrary restrictions, may be expressed as a mathematical equation as follows:

$$F = (N - E) + 2 - P \tag{1}$$

where F represents the number of independent variables or degrees of freedom required to be fixed in order to establish a physical system at equilibrium. With the definition of the number of components, C, within a physical system:

$$C = N - E$$

Equation 1 reduces to the more familiar form of the phase rule.

$$F = C + 2 - P \tag{2}$$

As the number of constituents in physical equilibria in these reported systems varied from two to four and the number of phases varied from two to four, each case is indicated separately in Table II.

The restrictions which concern a fixed ratio of two constituents are fixed in only one phase, liquid furfural,

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TABLE II. Phase Rule Applications to Systems

Subscript No.	Component[a]
1	Hydrocarbon 1
2	Hydrocarbon 2
3	Furfural
5	Water

Phases	Restrictions	E	F	Variables
	Two-Constituent Systems			
2	None	0	2	P and T
3	None	0	1	P or T
3	Crit. soln. temperature	1	0	Invariant
	Three-Constituent Systems			
2	$x_1/x_2 = k$ (constant) or $x_3/x_5 = k'$	1	2	P and T
3	None	0	2	P and T
3	$x_1/x_2 = k$ or $x_3/x_5 = k'$	1	1	P or T
4	None	0	1	P or T
4	Crit. soln. temperature	1	0	Invariant
	Four-Constituent Systems			
2	$x_1/x_2 = k$ and $x_3/x_5 = k'$	2	2	P and T
3	$x_1/x_2 = k$	1	2	P and T
3	$x_1/x_2 = k$ and $x_3/x_5 = k'$	2	1	P or T
4	$x_1/x_2 = k$	1	1	P or T
4	$x_1/x_2 = k$, at critical point	2	0	Invariant

[a]All mole fractions refer to furfural phase.

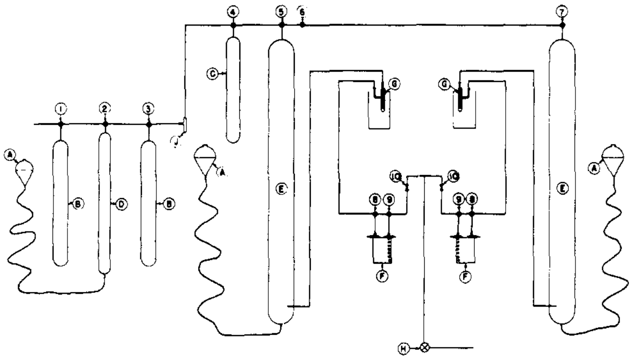


Figure 1. Gas analysis apparatus

as the distribution effect establishes the composition in the remaining conjugate phases. These arbitrary restrictions are imposed on the systems to maintain a maximum of two independent variables and to keep the number of degrees of freedom fixed for any given number of phases. The latter condition is necessary to relate ternary and quaternary phase equilibrium data at the same temperature. The maximum number of two degrees of freedom is established to simplify plotting of the data and to afford the maximum information from the minimum number of experimental runs. For all systems covered in this work there were no solid phases and a vapor phase was always present. The number of phases hereafter stated refer to the liquid phase only, and the presence of the vapor phase is understood.

EQUIPMENT AND PROCEDURE

The experimental procedure and equipment used for the parent ternary liquid-liquid equilibria and single hydrocarbon-solvent solubility have been described in part by Griswold, Klecka, and West (*6*).

The basic procedure consists of charging predetermined quantities of furfural and water into an evacuated, heavy-walled, cylindrical glass equilibrium cell. Liquid C_4 hydrocarbon is then forced into the cell by mercury displacement under nitrogen pressure. Stirring within the cell is accomplished by an internal rotor driven by three external electromagnets mounted on a circular laminated core. The cell and contents are brought to temperature by a preheated air stream, which is channeled through a glass jacket surrounding the equilibrium cell. Temperature control is facilitated by reset type instrumentation actuated by a thermocouple within the air jacket and connected, by means of a solenoid switch, to one of four 600-watt Finstrip heaters in air preheat service.

Pressure measurements are taken by means of a gage line leading from the top of the cell to the front instrument panel. Pressure-recording devices ranged from a mercury manometer for very low values to calibrated 0 to 300 pounds per square inch gage pressure gages. For experimental work involving hydrocarbon mixture, a prechanging system consisting of three Jerguson gages and two stainless steel hydrocarbon reservoirs is used to prepare and mix a measured quantity of liquid C_4 hydrocarbons in the desired ratio. Liquid hydrocarbons are transferred from the intermediate reservoirs by metered mercury displacement into a centrally located Jerguson gage. The hydrocarbons are mixed by localized heating of the mercury surface in the bottom of the gage by an infrared lamp, thus creating bubbling and turbulence of the liquid mixture.

The contents of the equilibrium cell are stirred at about 200 r.p.m. for approximately 2 hours at the desired temperature. The time required to reach equilibrium varies substantially with the liquid phases present and their relative densities. After sufficient agitation to assure equilibrium, the phases are allowed to separate and settle at constant temperature for about an hour before sampling. Only two liquid phases may be sampled concurrently; thus repeat determinations are always required for three-liquid-phase runs. Liquid samples are obtained at constant cell pressure and vapor space by means of mercury displacement and are caught in evacuated stainless steel bombs.

The methods used for the separation of samples for analysis were developed by Mertes and others (*4*, *9*, *11*).

The hydrocarbon and furfural phase sample bombs are placed in the train of the gas analysis apparatus (Figure 1), and the hydrocarbons are allowed to bubble slowly out of solution into the gas holders, displacing saturated potassium hydroxide solution. Water and furfural vapor entrained with hydrocarbons are removed in the traps, *G*, which are immersed in ice-salt baths. The last traces of hydrocarbons are stripped from the remaining liquid furfural-water mixture with research grade carbon dioxide from source *H*, and the carbon dioxide is absorbed by the potassium hydroxide solution in the gas holders, *E*. After a period of mixing of the hydrocarbon vapors within the holder, the gas mixture is passed through the contact pipet, *C*, filled with saturated potassium hydroxide solution to remove final traces of carbon dioxide. The gas mixture is then passed through a caustic knockout trap, *J*, and subsequently measured and separately analyzed by means of the Orsat train. The Orsat apparatus consists of two 200-ml. Francis autobubblers, *B*, containing a solution containing acidic silver and mercuric nitrates, similar to that described by Cuneo and Switzer (*3*). This Orsal solution quantitatively absorbs butadiene and 1-butene from *n*-butane gas mixtures. The stagnant gas flow is controlled and measured by the Burrell measuring buret, *D*, which is equipped with a leveling bulb and filled with a saturated potassium nitrate solution. After removal of the hydrocarbon, the furfural-water mixture left in the sample bombs is diluted with sufficient dry furfural to assure a single liquid phase at room temperature, and water in the resulting solution is determined by the cloud point method described by Klecka, Griswold, and West (*7*).

The limited solubility of the hydrocarbons in water normally leaves a vacuum in the water-phase sample bomb at room temperature. The hydrocarbon solubility in the water phase is taken therefore from the values reported by Griswold and Kasch (*5*) and no hydrocarbon analysis was made for this phase. The furfural content of both the ice-trap sample from the gas analysis apparatus and the water phase as sampled from the equilibrium cell is determined by the ultraviolet spectrophotometer method described by Klecka (*7*). The spectrophotometer is calibrated with known solutions of furfural in water, at a wave length of 345 mμ and a slit width of 0.2 mm.

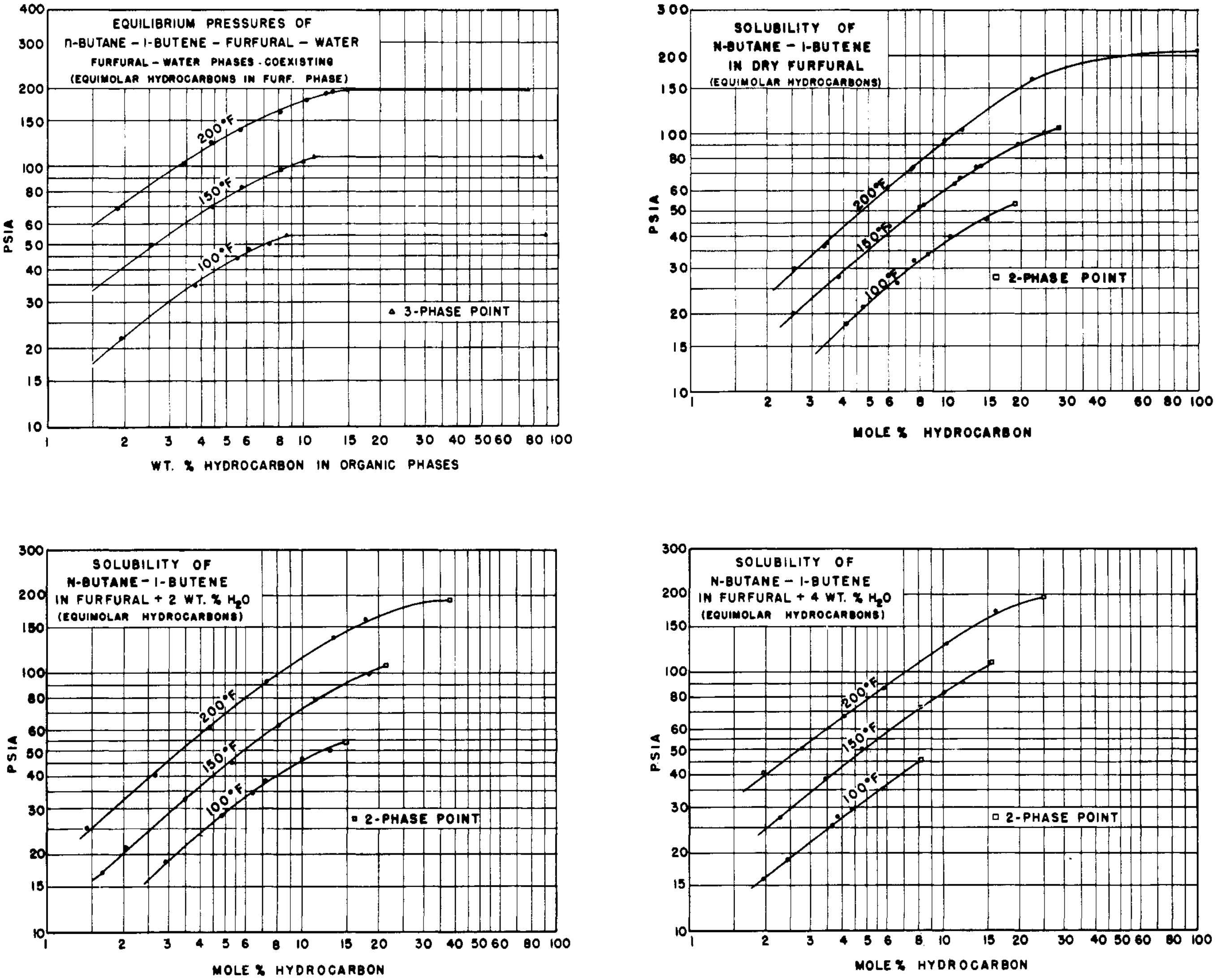


Figure 2. Equilibrium pressure on *n*-butane-1-butene-furfural-water, and solubility of *n*-butane-1-butene in dry furfural and in furfural plus water

SUMMARY OF EXPERIMENTAL RESULTS

In these present ternary and quaternary systems of binary mixtures of the C_4 hydrocarbons with furfural and furfural-water, equimolar ratios of hydrocarbons are maintained in the solvent phase. This arbitrary restriction is fixed on these systems to facilitate comparison of the quaternary data with the data for the parent ternary systems reported by Griswold, West, and McMillin (*8*). Maintaining an equimolar ratio of hydrocarbons in the liquid furfural phase requires a trial-and-error experimental procedure to determine the hydrocarbon distribution coefficients and the necessary composition and volume of the liquid hydrocarbon mixture charged to the equilibrium cell.

***n*-Butane-1-Butene-Furfural-Water.** The solubility data for equimolar *n*-butane-1-butene in the single liquid furfural phase are shown in Figure 2. The solubility of the equimolar hydrocarbon mixture in the dry furfural phase is limited at 100° and 150°F., and in these isotherms a hydrocarbon phase separates at the solubility limit. At 200°F. the hydrocarbon mixture is completely miscible with dry furfural. With the furfural plus 2 weight % water solution, the hydrocarbon mixture forms an immiscible system at all three temperatures. At each solubility limit, a hydrocarbon phase separates. The effect of water in the furfural phase is most pronounced for the 200°F. isotherm, as hydrocarbon solubility is reduced from 100 to less than 45 mole %. For the solvent of still higher water content (4 weight %) addition of hydrocarbon mixture again forms an immiscible system at all three temperatures. The solubility limit terminates with the formation of a water phase at 100°F. and a hydrocarbon phase at the higher temperatures. As expected, the incremental effect of water upon hydrocarbon solubility is greatest at 100°F. for the higher water concentrations.

The significance of these phase boundary data may be more easily seen in Figures 3 to 5, where the liquid-liquid phase equilibria are presented as a pseudoternary system and the data are shown as isothermal pressure projections. A three-liquid-phase region was found at all three temperatures, but the two-liquid-phase region with the hydrocarbon mixture and dry furfural does not exist at 200°F. At this temperature, the left face of the three-phase triangle is enclosed by a closed loop. It is interesting to note the effect of water and temperature upon the hydrocarbon distribution coefficient, *d*, identified as the mole ratio of hydrocarbons in the liquid hydrocarbon phase to that ratio in the conjugate liquid furfural phase.

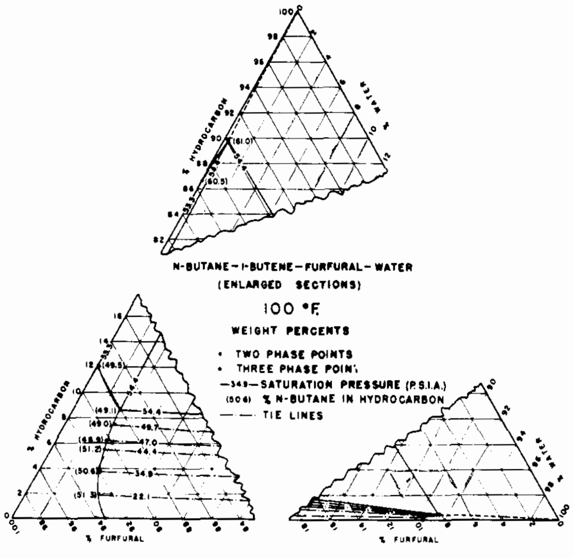


Figure 3. *n*-Butane–1-butene–furfural-water at 100 °F.

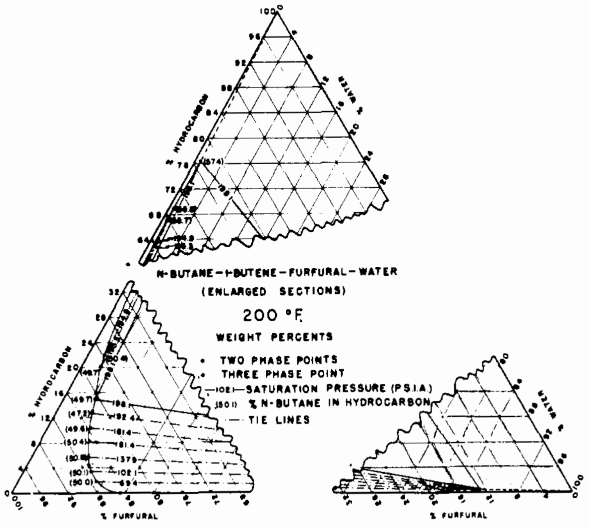


Figure 5. *n*-Butane–1-butene–furfural-water at 200 °F.

$$d = x_1 x'_2 / x_2 x'_1$$

The primed values refer to the furfural phase; subscript 1 refers to *n*-butane and 2 refers to 1-butene. Distribution coefficient values at corresponding temperatures are presented for furfural and furfural-water systems in the following table.

Hydrocarbon Distribution Coefficients

Temp., °F.	Dry Furfural	Furfural + 2% H_2O	Furfural + 4% H_2O
100	1.54	1.57	...
150	1.35	1.40	1.49
200	1.00	1.25	1.30

No conjugate hydrocarbon phase exists for furfural plus 4 weight % water at 100 °F. In general, *d* is inversely related to the temperature and directly related to the water content of the furfural phase. Figures 3 to 5 show the effect of hydrocarbon content of the furfural phase upon pressures for conjugate furfural and water phases. The three-liquid-phase point for both furfural and hydrocarbon phases is shown as an isobar at constant temperature.

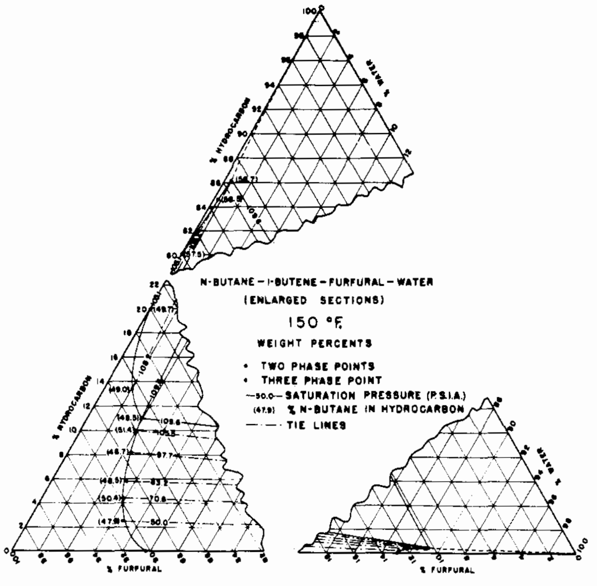


Figure 4. *n*-Butane–1-butene–furfural-water at 150 °F.

This system is not defined for the hydrocarbon phase beyond the conjugate furfural phase boundary, as the arbitrary restriction of equimolar hydrocarbons in the furfural phase is immediately lost.

The composition and pressure of conjugate liquid phases at the three-phase point are important, and the accuracy of this determination is reflected in later calculations. For this system at 150 °F., the three-liquid-phase point occurs in the region where the conjugate furfural and water phases have equal densities. Sampling coexisting, large volume furfural and water phases is impossible, because no phase separation occurs regardless of the settling time. It is necessary to determine the three-liquid-phase composition by the limiting approach method. By approaching the three-liquid-phase point with conjugate furfural and hydrocarbon phases and with conjugate furfural and water phases, an approximate composition of the furfural and water phases at the three-phase point may be established. By charging a furfural solution of slightly higher water content, it is possible to obtain three-liquid-phase equilibrium in which the volume of the water phase is less than 0.5 ml. In this manner, the conjugate liquid furfural and hydrocarbon phases can be sampled with reproducible results. A similar method is used with conjugate hydrocarbon and water phases to establish the three-phase water-phase composition in which the volume of the furfural phase is less than 2 ml.

n-Butane–1,3-Butadiene–Furfural-Water. The solubility data for equimolar *n*-butane–1,3-butadiene in the single liquid furfural phase are shown in Figure 6. The equimolar hydrocarbon mixture has limited solubility in dry furfural only in the 100 °F. isotherm. At the higher temperatures, the hydrocarbon mixture is completely miscible with dry furfural. With the furfural plus 2 weight % water solution, the hydrocarbon forms an immiscible system at 100° and 150 °F. At these temperatures, hydrocarbon solubility terminates with the formation of a hydrocarbon phase. Complete miscibility is evidenced by the hydrocarbon with furfural plus 2% water at 200 °F. As water in the solvent is increased to 4 weight %, the solubility of the hydrocarbons is lowered appreciably at all three temperatures.

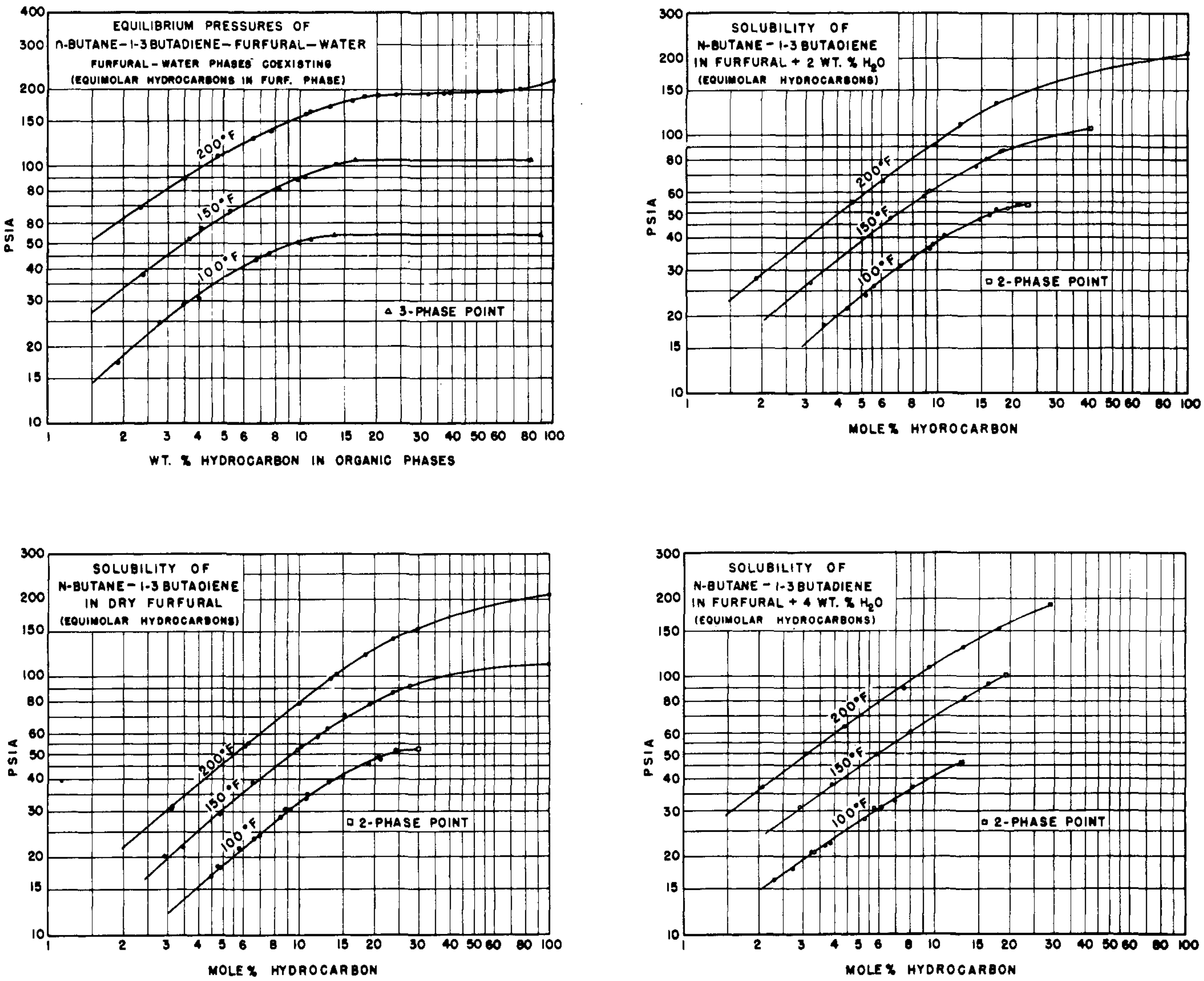


Figure 6. Equilibrium pressures of *n*-butane-1,3-butadiene-furfural-water, and solubility of *n*-butane-1,3-butadiene in dry furfural

For each isotherm, an immiscible system is encountered and in each case the hydrocarbon solubility terminates with the formation of a water phase. For these systems, the incremental effect of water upon hydrocarbon solubility is the greatest in the 200°F. isotherm.

The liquid-liquid phase equilibria are shown as isothermal pressure projections in Figures 7, 8, and 9. An investigation of the pseudo-ternary data discloses all the types of liquid-liquid equilibria encountered in the study of individual C_3 and C_4 hydrocarbons with furfural and water. At 100°F., the three-conjugate-liquid phase region occurs, as do two conjugate-liquid phases in the hydrocarbon-furfural pseudo-binary. At 150°F., immiscibility between the equimolar hydrocarbon mixture and dry furfural disappears, but the three-phase region is still present. At 200°F., the three-liquid-phase region disappears and a band-type solubility predominates, with conjugate organic and water phases. The critical temperatures for both two-liquid-phase and three-liquid-phase regions were encountered between 100° and 200°F.

In Figure 6, the plot of equilibrium pressures of *n*-butane-1,3-butadiene-furfural-water clearly shows the remembrance of the three-liquid-phase point at 200°F. This plot denotes an extremely flat three-liquid-phase envelope near the critical temperature. The three-liquid-phase point at 100°F. occurs very near the region of equal density of the furfural and water phases, and it was necessary to determine phase analysis by the limiting approach method previously described. Complete tables of the hydrocarbon distribution coefficient, *d*, are not presented, because the 200°F. isotherm of this system contains no conjugate liquid hydrocarbon phase. The values of the distribution coefficient at the three-liquid-phase point for the 100° and 150° isotherms were 2.53 and 2.26, respectively, and the value for the hydrocarbon mixture-dry furfural system at 100°F. was 2.10.

Some conjugate furfural-phase data from the parent binary and ternary systems (*8*), as well as comparable data from the present four-constituent systems, are summarized in Table III. A comparison of the quaternary data for the butane-butadiene mixture with equivalent parent ternary data indicates that the *n*-butane within the hydrocarbon mixture controls the liquid-liquid equilibria at the lower temperatures, and that the butadiene controls this equilibrium at the higher temperatures. This is borne out by the comparatively low hydrocarbon content of the 100°F.

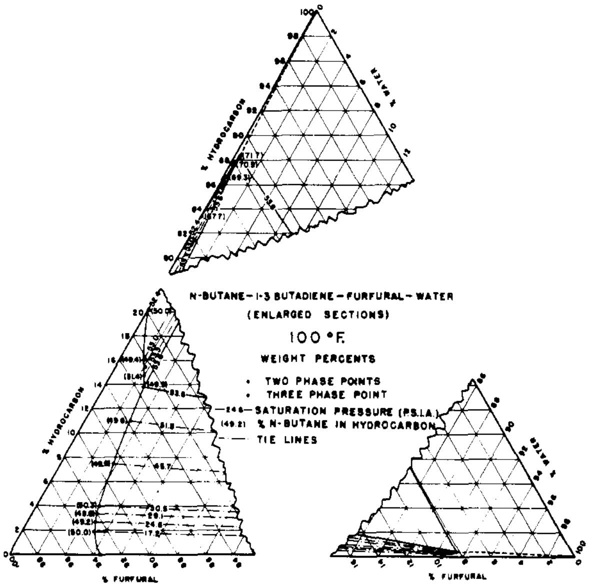


Figure 7. *n*-Butane–1,3-butadiene–furfural-water at 100° F

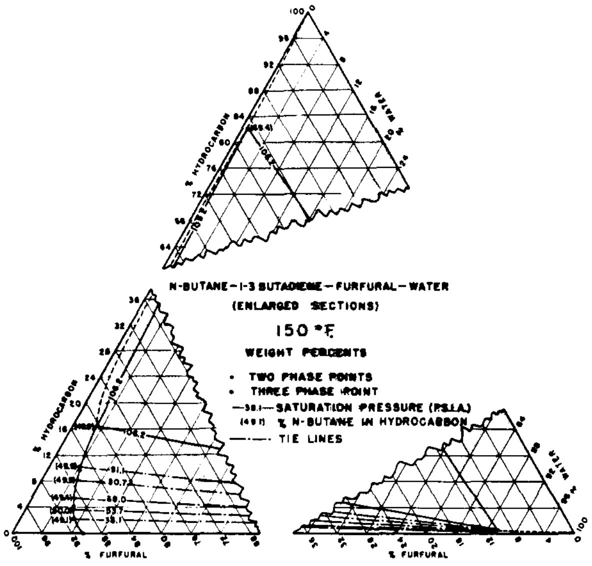


Figure 8. n-Butane–1,3-butadiene–furfural-water at 150 °F.

furfural phase at the three-liquid phase point (13.7 weight %), and by the disappearance of the three-liquid-phase region at 200°F. This latter occurrence is similar to the behavior of the butadiene-furfural-water systems.

ACTIVITY COEFFICIENTS AND RELATIVE VOLATILITY CORRELATIONS

Theory of Activity Coefficients. The thermodynamic relations of individual constituents within a homogeneous liquid phase are of primary importance for subsequent distillation applications. The property of activity is defined as the ratio of the fugacity of a constituent in a given state to its fugacity in an arbitrarily defined standard state at the same temperature.

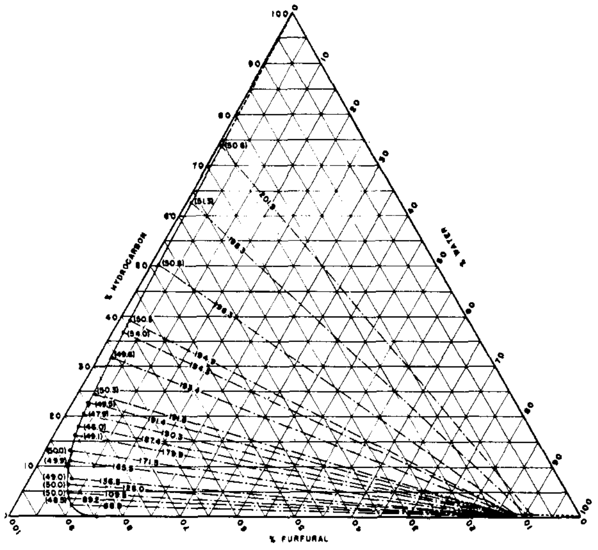


Figure 9. *n*-Butane–1,3-butadiene–furfural-water at 200 °F.

○ Two-phase points
–136.5–Saturation pressure, lb./sq. inch gage
(49.0) % *n*-butane in hydrocarbon
— — Tie lines

$$a = \frac{(f)}{(f^0)}$$

For the systems covered in this work, the standard state of reference will be the fugacity of the pure substance at the temperature and pressure of the system. The term "activity coefficient" then refers to the ratio of the activity of a system constituent to a numerical expression of its concentration.

$$\gamma_1 = a_1/n_1 = f_1/n_1f_1^{\circ}$$

At moderate pressures, the effect of pressure upon the fugacity of a liquid is negligible; hence f°_1 may be approximated as the fugacity of the liquid constituent under its own vapor pressure. With the further assumption of the validity of Dalton's law, which applies to the vapor phase, an approximate value, $\bar{\gamma}$, for the activity coefficient may be defined as follows:

$$\bar{\gamma}_1 = \bar{P}_1/x_1P^{\circ}_1 = y_1\pi/x_1P^{\circ}_1 \qquad (3)$$

This approximate activity coefficient may be further corrected. If the deviations of the vapor from the state of an ideal gas, as well as the effect of pressure on liquid fugacities, are taken into consideration, the following relation is obtained for the thermodynamically corrected activity coefficient (*14*).

$$\gamma_1 = \bar{\gamma}_1 \times e^{(V_1 - \beta)(P^{\circ}_1 - \pi)/RT} \qquad (4)$$

The use of Equation 4 required data on specific volume and a knowledge of the second virial coefficient, β, for the simplified equation of state.

$$P(V - \beta) = RT$$

Wohl (*14*) has developed a relationship by which the second virial coefficients may be calculated from the critical constants over a wide range of temperature.

$$\beta = \frac{RT^{\left(0.74 - 0.045T_r - \frac{1.50}{T_r} - \frac{0.55}{T_r3.27}\right)}}{3.75P_c} \qquad (5)$$

Table III. Solubility Limits of C_4 Hydrocarbons in Furfural-Water Systems

Hydrocarbon	Dry Furfural		Furfural + 2 Wt. % Water			Furfural + 4 Wt. % Water		
	Lb./sq. inch abs.	Mole % hydrocarbon	Lb./sq. inch abs.	Mole % hydrocarbon	Conjugate phase[a]	Lb./sq. inch abs.	Mole % hydrocarbon	Conjugate phase
100 °F.								
1-Butene	57.6	44.05	58.8	28.0	HC	44.5	11.0	W
1-Butene–n-butane[b]	53.3	18.84	53.8	14.30	HC	46.1	8.30	W
n-Butane	48.3	13.15	48.9	9.95	HC	49.2	8.25	HC
n-Butane–1,3-butadiene[b]	52.4	30.15	53.5	23.50	HC	50.0	11.50	W
1,3-Butadiene	Miscible		48.0	40.30	W	31.1	14.5	W
150 °F.								
1-Butene	Miscible		117.0	67.5	W	109.5	26.0	W
1-Butene–n-butane[b]	105.1	29.63	108.0	20.50	HC	109.0	15.50	HC
n-Butane	99.6	16.73	102.0	13.44	HC	102.9	10.63	HC
n-Butane–1,3-butadiene	Miscible		103.5	41.60	HC	100.5	19.50	W
1,3-Butadiene	Miscible		104.0	66.20	W	90.3	40.50	W
200 °F.								
1-Butene	Miscible			Miscible	W	204.0	52.5	W
1-Butene–n-butane[b]	Miscible		193.5	38.2	HC	196.5	24.50	HC
n-Butane	175.4	29.55	181.0	18.80	HC	183.5	13.71	HC
n-Butane–1,3-butadiene[b]	Miscible			Miscible	W	192.8	28.50	W
1,3-Butadiene	Miscible			Miscible	W	163.0	42.50	W

[a] HC, hydrocarbon.
W, water.

[b] Equimolar hydrocarbons in furfural phase.

The relationship between the activity coefficient and temperature, at constant phase composition and temperature, may be expressed by the following partial differential equation:

$$\frac{\partial \ln \gamma_1}{\partial T} = -\frac{H - H_1^{\circ}}{RT^2} \tag{6}$$

Equation 6, however, imposes the conditions of constant pressure and phase composition before integration may be approximated. If the thermodynamic activity coefficient from Equation 4 is used, corrected for pressure variation within the system, the following relationship may be developed over a limited temperature range in which the heat of solution may be assumed constant.

$$\log \frac{\gamma_1}{\gamma_2} x = \frac{(\bar{H} - H^{\circ})_{\text{av}}}{2.303\,R} \; \frac{1}{T_1} - \frac{1}{T_2} \tag{6a}$$

The quantity, $\bar{H}_1 - H_1^{\circ}$, is the partial molal enthalpy of solution relative to the pure components at the temperature of the solution. Where the enthalpy of solution is positive, the activity coefficient generally becomes numerically greater with decreasing temperature. As the temperature decreases in a potentially immiscible system, the activity of a component, $x_1\gamma_1$, approaches a critical value normally close to unity and a conjugate liquid phase may separate.

The properties of a single constituent distributed between several conjugate phases in physical equilibrium are not independent functions. Qualitatively, these properties are related by the phase rule and, quantitatively, by thermodynamic free energy considerations. The criterion for equilibrium under conditions of constant temperature and pressure is that the total free energy of the components in one phase be equal to that in each coexisting conjugate phase. This fact makes it possible to predict the thermodynamic functions for all phases, once the values for one phase are established. Similarly, it may be shown that the individual thermodynamic properties of the constituents within a single homogeneous phase are not all independent. Phase rule considerations have shown that there is a maximum of $(N - 1)$ degrees of freedom. The thermodynamic relationship for mixtures of constituents within a given liquid phase is found in the Duhem equation. For a binary mixture of components a and b within a homogeneous phase at constant temperature and pressure, the Duhem relationship may be written as follows:

$$x_a \partial \ln \gamma_a + x_b \partial \ln \gamma_b = 0 \tag{7}$$

This relationship is of importance, as it is the basis upon which many correlations for the prediction of activity coefficients are based.

Determination of Experimental Activity Coefficients. In general, this work is concerned principally with the hydrocarbon activity coefficients, and the values of furfural and water activities are important only in that their approximate values are needed to determine the partial pressure of hydrocarbon within the accuracy of the experimental data. In all calculations, the experimental activity coefficient was corrected for the effect of pressure by the use of Equation 4, which may be expressed more simply as follows:

$$\gamma_1 = \bar{\gamma}_1 \times z = \frac{P_1}{P^{\circ}_1 x_1} \times z \tag{4a}$$

where

$$z = e^{(V_1 - \beta)(P^{\circ} - \pi)/RT}$$

Values for the second virial calculated coefficient, β, critical properties, vapor pressure, P°, and liquid molar volumes, V, for the constituents comprising these systems are shown in Table IV.

The binary and ternary data for the parent hydrocarbon-furfural and hydrocarbon-furfural-water systems (*8*) consist of liquid-liquid equilibrium data and of hydrocarbon solubilities in the solvent phase in which the total system pressure, temperature, and liquid phase composition are known. The total pressure of the systems is comprised of the sum of the partial pressure of each constituent.

$$\pi = P_{hc} + P_f + P_w$$

Thus, to determine the activity coefficient of the hydrocarbon, the partial pressure of the furfural and water must first be determined.

$$\gamma_{hc} = \frac{P_{hc}}{x_{hc} P^{\circ}_{hc}} \times z = \frac{(\pi - P_w - P_f)}{x_{hc} P^{\circ}_{hc}} \times z \tag{8}$$

Table IV shows that at all temperatures the vapor pressure of the hydrocarbons is at least 20 times that of water and 170 times that of furfural. In mixtures of these components, however, where the concentration of hydrocarbon is small and the temperature high, the partial pressure of hydrocarbon is reduced to 20 times that of furfural and only three times the maximum partial pressure of water. It is necessary, therefore, to determine the activity of the water as accurately as possible. However, the partial pressure of furfural may be approximated by the use of all available data and maximum use of thermodynamic relations.

In the determination of the activities of furfural and water in the ternary solution, it is first necessary to establish the limiting case for the furfural-water binary. Liquid-liquid and vapor-liquid equilibria on the furfural-water system (*12*) were utilized to predict activity coefficients for the furfural and water phases by applying Equations 3 and 4 to the reported experimental data. These values are shown in Figure 10. Also shown are furfural activity coefficients in the water phase for the ternary systems of *n*-butane, 1-butene, and 1,3-butadiene, separately, with furfural-water data reported by the Phillips Petroleum Co. The agreement of these water-phase data from independent sources serves to show that the furfural activity coefficient, γ_f, in the water phase varies only with its concentration and the temperature, and is substantially independent of the pressure in the system or the presence of C_4 hydrocarbons. Because of the very limited solubilities of furfural and hydrocarbon, the activity coefficient of water in the water phase is substantially unity. Furfural activities in the furfural phase for both furfural-water and furfural-hydrocarbon binaries were determined by a trial and error procedure involving the method of Beatty and Calingaert (*1*).

Table V. Application of Margules Three-Suffix Binary Equation

Experimental Binary Constants for Margules 3-Suffix Equation

Temp., °F.	*n*-Butane A_{13}	*n*-Butane A_{31}	1-Butene A_{23}	1-Butene A_{32}	1,3-Butadiene A_{43}	1,3-Butadiene A_{34}
100	1.094	0.275	0.852	1.035	0.555	0.785
150	0.992	1.164	0.772	0.956	0.527	0.721
200	0.908	1.068	0.710	0.885	0.505	0.680

Comparison of Experimental and Calculated Pseudo-Binary Constants for Margules 3-Suffix Equation

Temp., °F.	A_{n3}'	$A_{n3}^{a}{}'$	$A_{3'n}$	$A_{3'n}^{a}$
	n-Butane in Furfural + 2 Wt. % Water			
100	1.210	1.157	1.319	1.342
150	1.086	1.077	1.188	1.174
200	1.009	1.000	1.075	1.030
	n-Butane in Furfural + 4 Wt. % Water			
100	1.294	1.226	1.411	1.431
150	1.161	1.156	1.253	1.240
200	1.069	1.082	1.115	1.083
	1-Butene in Furfural + 2 Wt. % Water			
100	0.939	0.910	1.068	1.071
150	0.860	0.837	0.965	0.972
200	0.816	0.778	0.880	0.899
	1-Butene in Furfural + 4 Wt. % Water			
100	1.015	0.978	1.115	1.110
150	0.936	0.912	0.985	0.992
200	0.890	0.853	0.905	0.902

[a] Colburn's calculated values.

For coexisting furfural and water phases in the ternary systems, C_4 hydrocarbon-furfural-water, the limiting furfural and water activity coefficients were determined from the conjugate phase relationships.

$$(\gamma_w x_w)_w = (\gamma_w x_w)_f \quad \text{and} \quad (\gamma_f x_f)_w = (\gamma_f x_f)_f \qquad (9)$$

where the subscripts on the parentheses refer to the liquid phase. Equation 9 results from free energy considerations which denote that a component distributed among several conjugate liquid phases must have the same activity in each phase. Where only conjugate furfural and hydrocarbon liquid phases are present in the ternary system, there is no direct means of determining water or furfural partial pressures. However, the partial pressures of the hydrocarbon at the three-liquid-phase and the binary two-liquid-phase points are almost identical. This close agreement discloses that for all of the ternary systems studies, the presence of water had little effect on the limiting hydrocarbon activity at the furfural-hydrocarbon phase boundary. By assuming a linear relation between the corresponding furfural activities at the two- and three-liquid-phase points, water activity coefficients may be calculated along the furfural-hydrocarbon phase boundary.

$$\gamma_w = \frac{\pi - P_{hc} - p_f}{P^0_w x_w}(Z_w)$$

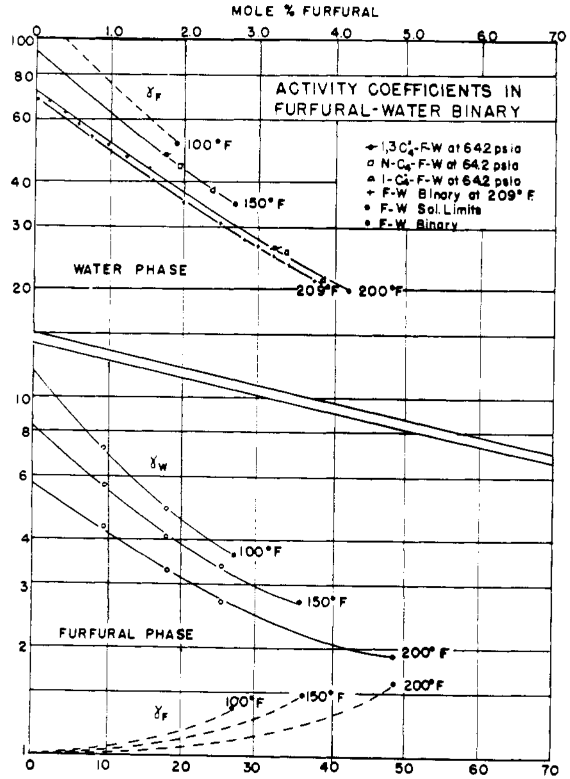
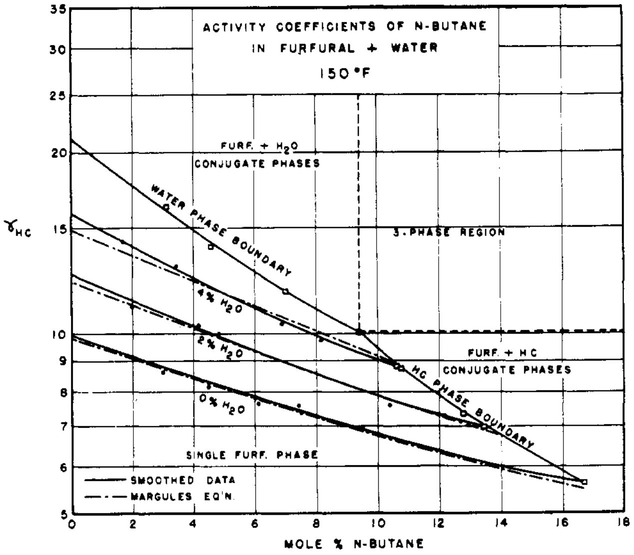
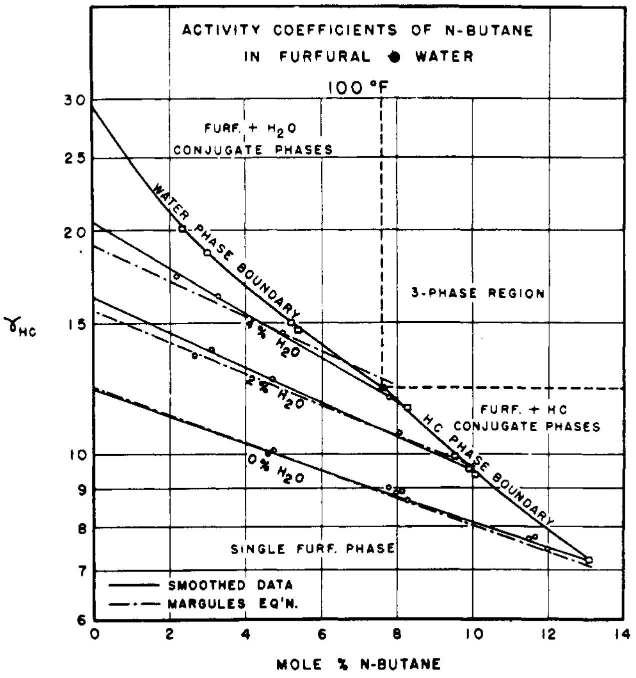


Figure 10. Activity coefficients in furfural-water binary

Table IV. Physical Properties of System Components

Substance	Critical Constants T_c, °R.	Critical Constants P_c, lb./sq. inch abs.	Critical Constants T_c, °F.	Liquid Molar Volumes, Cc./G. Mole 100°F.	Liquid Molar Volumes, Cc./G. Mole 150°F.	Liquid Molar Volumes, Cc./G. Mole 200°F.	Second Virial Coefficient, Cc./G. Mole 100°F.	Second Virial Coefficient, Cc./G. Mole 150°F.	Second Virial Coefficient, Cc./G. Mole 200°F.	Vapor Pressure, Lb./Square Inch Abs. 100°F.	Vapor Pressure, Lb./Square Inch Abs. 150°F.	Vapor Pressure, Lb./Square Inch Abs. 200°F.
n-Butane	765.2	551.3	490.8	103.9	111.1	121.2	−712	−578	−478	50.99	105.5	195.3
1-Butene	756.6	588.0	480.4	98.8	106.2	116.6	−642	−522	−432	61.5	125.2	228.9
1,3-Butadiene	765.2	627.7	483.8	90.4	96.7	105.4	−625	−507	−420	57.8	121.0	223.5
Water	1153.0	3335.0	671.7	18.15	18.38	18.71	−547	−436	−354	0.95	3.73	11.52
Furfural	–	–	–	84.13	86.6	89.0	–	–	–	0.09	0.43	1.49





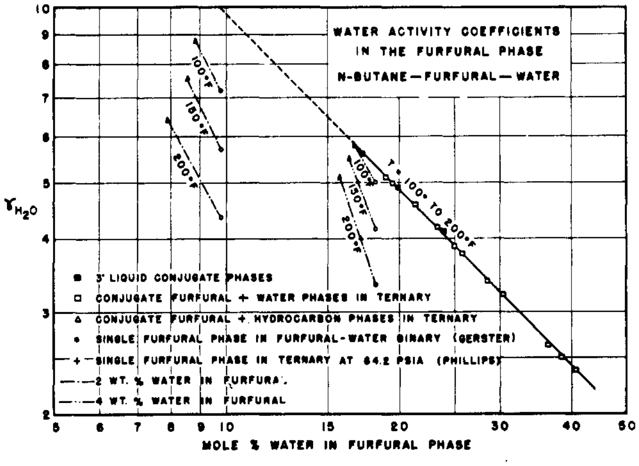
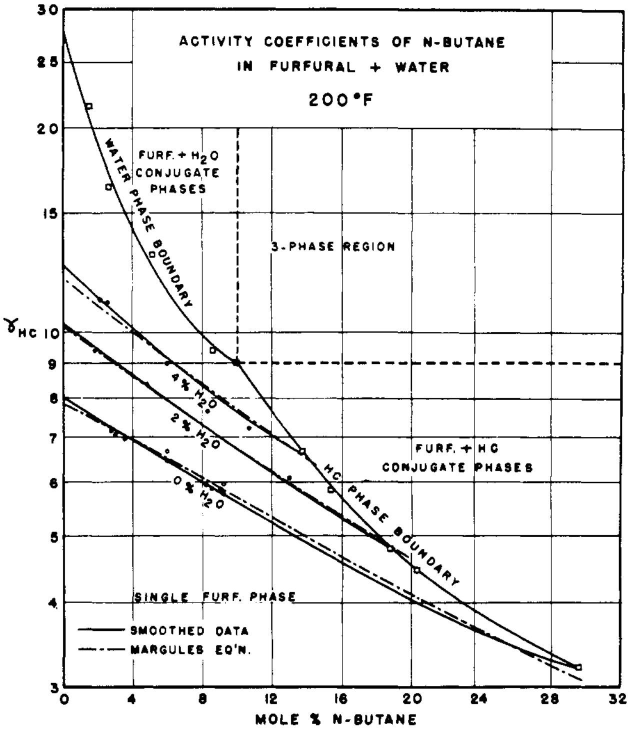


Figure 11. Activity coefficients of water and on *n*-butane in furfural, plus water at 100°, 150°, and 200° F.



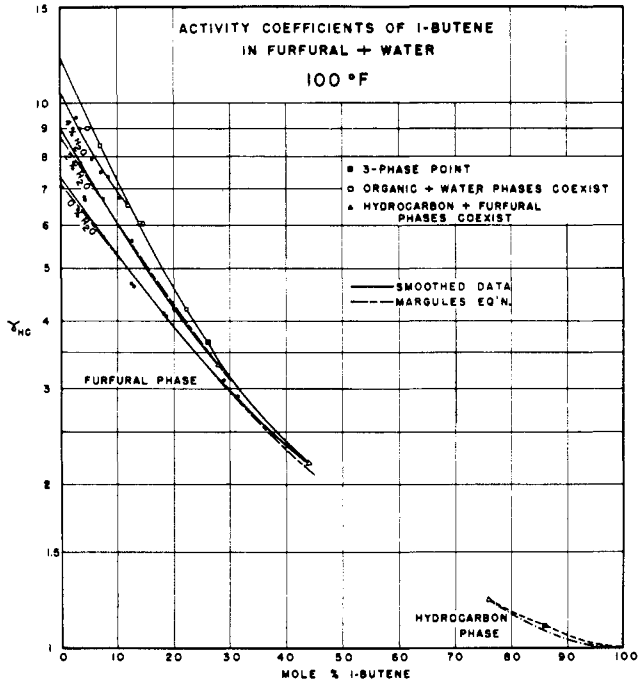
The water activity coefficients within a single liquid furfural phase of the ternary system are calculated by interpolation between the limiting binary data of Gerster and the calculated values at the appropriate liquid phase boundaries. Figure 11 denotes the activity coefficients of water for the *n*-butane–furfural-water system. The data of the Phillips Petroleum Co. obtained at 64.2 pounds per square inch absolute are also contained in Figure 11. With the complete system of furfural and water activities determined for each ternary system, hydrocarbon activity coefficients may be obtained from the total pressure-phase composition data by use of Equation 8. Hydrocarbon activity coefficients thus determined of *n*-butane, 1-butene, and 1,3-butadiene are graphically presented for the furfural phase and phase boundaries in Figures 11 to 13.

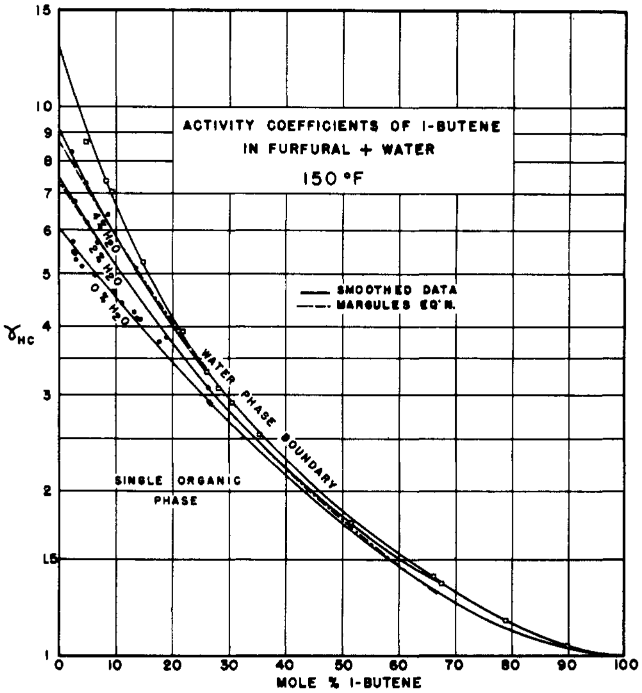
In general, the method for determining the partial pressure of the combined hydrocarbons in the four constituent systems was identical to that for ternaries. For the ternary systems of two C_4 hydrocarbons with dry furfural, however, it was necessary to determine the partial pressure of furfural by assuming a linear relationship between the limiting binary hydrocarbon–furfural systems.

Correlation of Hydrocarbon Activity Coefficients. Margules Binary Equation. The general solution of the Gibbs-Duhem equation has been recently modified by Jordan, Gerster, Colburn, and Wohl (*9*) to increase its utility, and its thermodynamic basis has been covered in detail by Scatchard and Hamer (*13*) and by Wohl (*14*). The simplest form of this solution is known as the three-suffix Margules equation for a binary system, and may be expressed as follows:

$$\log \gamma_a = (1 - x_a)^2 [A + 2(B - A)x_a] \quad (10)$$

$$\log \gamma_b = (x_a)^2 [B + 2(A - B)(1 - x_a)] \quad (10a)$$





From the nature of the equation, it is apparent that A is the limiting value of log γ_a as x_a approaches zero, and conversely, B is that value limiting log γ_b as x_b approaches zero. In the equations following, consistent usage is employed for the suffixes designating the system constituents.

Component	Subscript
n-Butane	1
1-Butene	2
1,3-Butadiene	4
Furfural	3
Water	5

Subscript n is used to designate any single hydrocarbon constituent.

Equation 10 may be rearranged (*9*) to give the following expression for the hydrocarbon-furfural binaries:

$$\log \gamma_n/(1 - x_n)^2 = A_{n3} + 2\,(A_{3n} - A_{n3})x_n \qquad (11)$$

In this relationship, A_{n3} is analogous to constant A in Equation 10, and represents the limiting value of log γ_n in the hydrocarbon-furfural or suffix $n-3$ system. A_{3n} conversely corresponds to B for the furfural component. The method described by Jordan, Gerster, Colburn, and Wohl (*9*) was used to determine the numerical value of the Margules constants from the hydrocarbon activity coefficients data in the binary system with dry furfural. A plot was made of the data points with the function $(\log \gamma_n)/(1 - x_n)^2$ *vs.* x_n. If the data for the hydrocarbon activity coefficients follow the Margules three-suffix relationship, a straight-line plot should result, with an intercept of A_{n3} and a slope of $2(A_{3n} - A_{n3})$. Values of the Margules constants for the binary systems of hydrocarbon–dry furfural thus obtained are presented in Figure 14 as a function of $1/T\,°R$.

Margules Ternary Equation. The prediction of multicomponent data from binary data is one of the major purposes of all activity coefficient correlations. Wohl (*14*) has shown that many of the empirical equations commonly used represent special cases of the following general equation, relating the excess free energy G^E of any mixture in physical equilibrium.

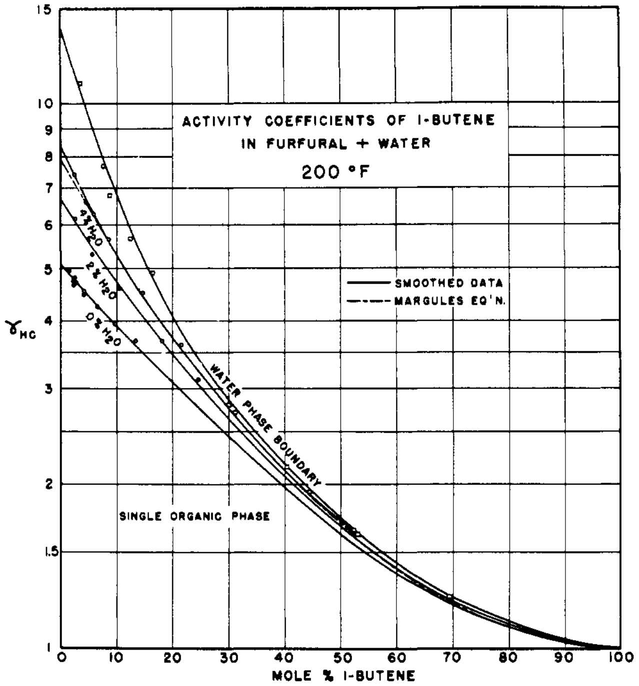
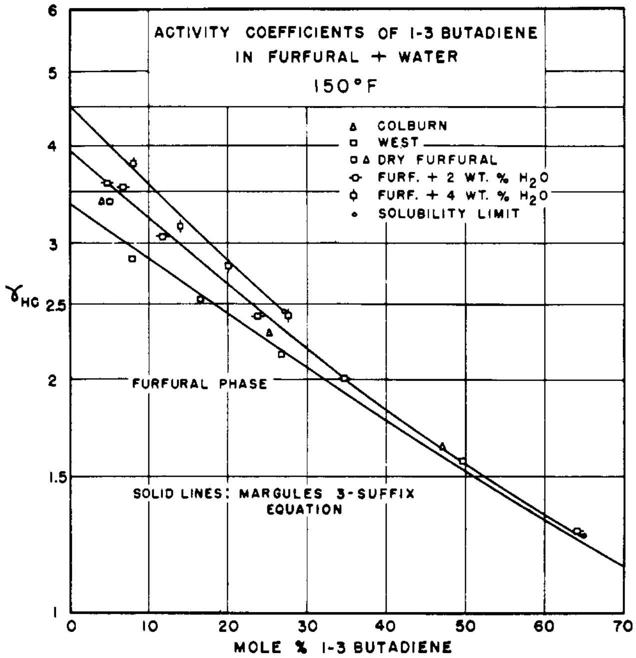
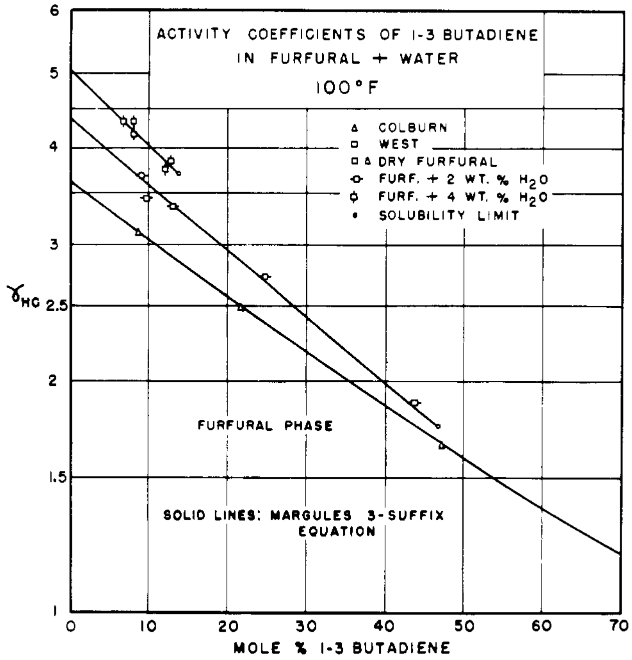


Figure 12. Activity coefficients of 1-butene in furfural plus water at 100°, 150°, and 200°F.

$$\frac{G^E}{RT(\Sigma q_i x_i)} = \Sigma_{ih}\, \bar{v}_i \bar{v}_h a_{ih} + \Sigma_{ihj}\, \bar{v}_i \bar{v}_h \bar{v}_j a_{ihj} \qquad (12)$$

Equation 12 is designated as a three-suffix equation, as characterized by the number of suffixes in the last term. Summation is made of all possible combinations of constituents in unlike groups of the indicated size. When the assumption of equal molar volumes, q_i, is made, the Duhem relationship for a ternary mixture may be applied to obtain the following expression.





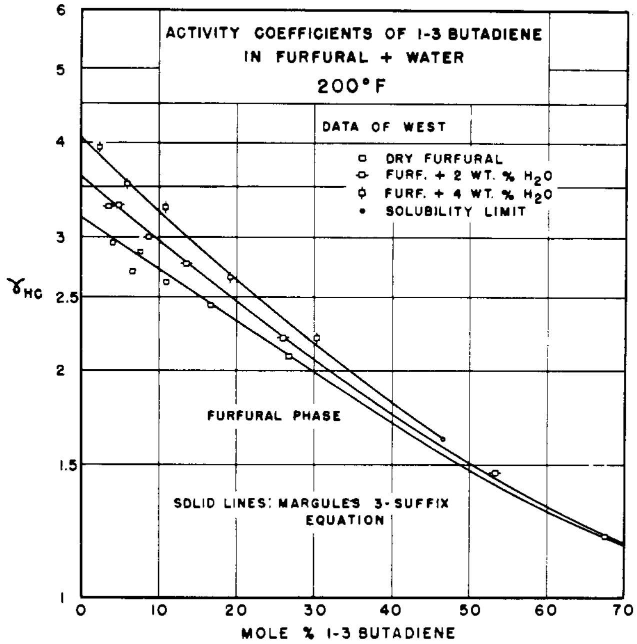


Figure 13. Activity coefficients of 1,3-butadiene in furfural plus water at 100°, 150°, and 200° F.

$$\log \gamma_n = x_3^2[A_{n3} + 2x_n(A_{3n} - A_{n3})] + x_5^2[A_{n5} + 2x_n(A_{5n} - A_{n5})] + x_3x_5[A_{3n} + A_{n3} - A_{53} + 2x_n(A_{5n} - A_{n5}) + 2x_5(A_{53} - A_{35}) - C_{n35}(1 - 2x_n)] \qquad (13)$$

Equation 13 is known as the Margules three-suffix ternary equation for components n. The A values represent the limiting constants for each constituent in the three parent binaries n-3, n-5, and 3-5, while constant C is characterized solely by the nature of the ternary mixture. The specific system shown is that of hydrocarbon-furfural-water, and the activity coefficient is that of the hydrocarbon. The activity coefficients of other components may be expressed in similar equations by transposing the suffixes in the order $n \rightarrow 3 \rightarrow 5 \rightarrow n$.

Where the ratio of furfural to water is maintained constant in the furfural phase, the above-mentioned ternary system may be treated as a pseudo-binary. The mole fraction of the pseudo-component is denoted by $x_{3'}$ and it is defined as

$$x'_3 = x_3 + x_5 \quad \text{and} \quad x_3/x_5 = k'$$

Substitution of these relations in the ternary three-suffix Equation 13 results in the following pseudo-binary equation:

$$\log \gamma_n = x'^2_3\,[A_{n3'} + 2x_n(A_{3'n} - A_{n3'})] \qquad (11a)$$

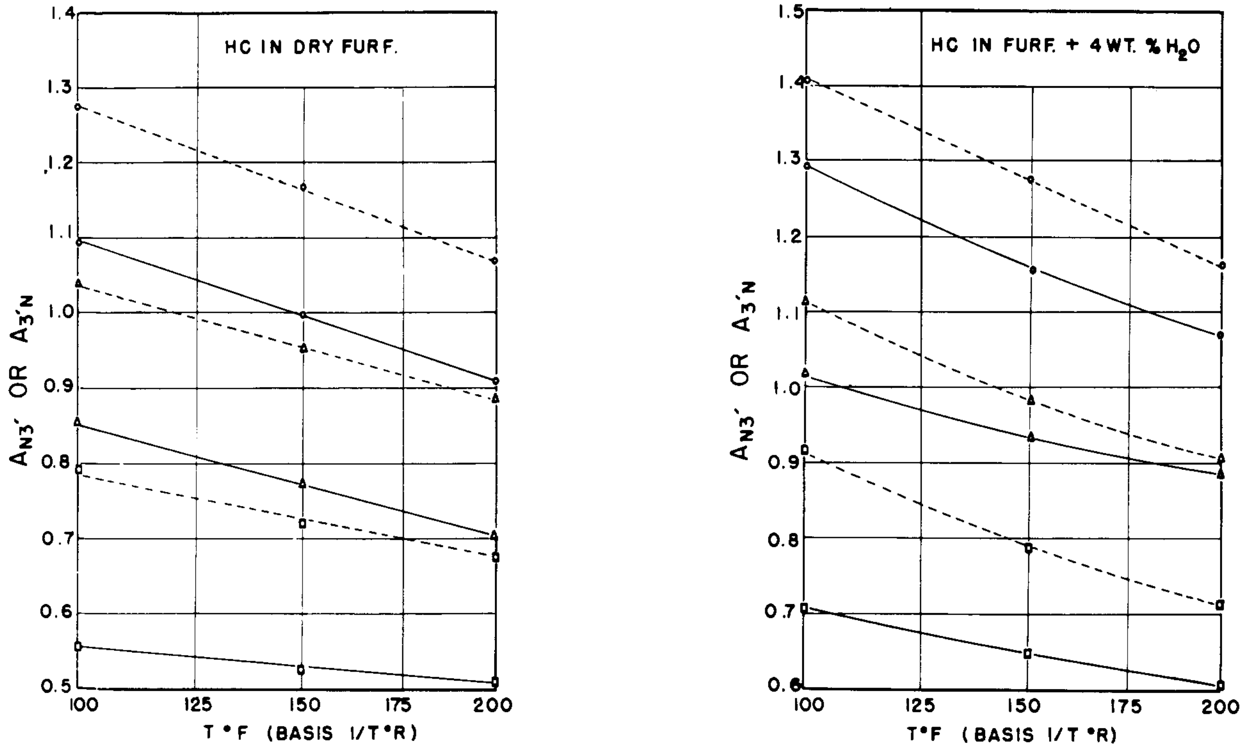
The Margules three-suffix constants for the pseudo-binaries of hydrocarbon in furfural plus 2% and 4% water solutions were determined by the method previously described for true binaries. These values are also shown in Figure 14 as a function of $1/T\,^{\circ}R$ and tabulated in Table V. The plots of the limiting values, A, vs. reciprocal temperature are essentially linear for the true binary systems, but deviations from the linear temperature relationship occur at the higher water contents of the solvent.

By comparison of the pseudo-binary Equation 11a with the ternary Equation 13, the relationships may be established by which pseudo-constants $A_{n3'}$ and $A_{3'n}$ can be calculated from the experimental binary constants.

$$A_{n3'}(1 + k')^2 = A_{n3} + k'A_{3n} + k'(1 + k')A_{n5} - \left(\frac{k'}{1 + k'}\right)[(1 - k')A_{53} + 2k'A_{35}] - k'C_{n35} \qquad (14)$$

$$A_{3'n}(1 + k')^2 = (1 + k')A_{3n} + k'(1 + k')A_{5n} - \frac{k}{1 + k'}(A_{53} + k'A_{55}) \qquad (14a)$$

Gerster, Mertes, and Colburn have used relations 14 and 14a to determine the values for the pseudo-constants from the experimental data of the respective binary systems. In Table VI, Colburn's calculated values are compared to those determined from the experimental ternary systems by Equation 11a.



Binary Mixtures of Hydrocarbons with Furfural. The single liquid furfural-phase data for the three-constituent system of two hydrocarbons in furfural is treated as a ternary, even though the ratio of the hydrocarbons remains constant. This is necessary to evaluate the activity coefficients of the individual hydrocarbon components. These present data on the hydrocarbon mixtures give only the total pressure of the combined hydrocarbon and phase composition when subjected to the same analysis as for the parent systems. There are no present correlations for the prediction of vapor-liquid equilibria from ternary pressure measurements, even when the individual partial pressure of one component is known. An indirect solution can be reached, however, by the use of the Margules three-suffix ternary equation.

An investigation of the component binaries discloses the fact that the binary mixture comprised of the two hydrocarbons closely approximates Raoult's law. This means that the values of the corresponding Margules constants are equal to zero and the three-suffix ternary equation may be expressed as:

$$\log \gamma_1 = x_3^2\,[A_{13} + 2x_1(A_{31} - A_{13})] + x_2x_3[A_{13} - A_{32} + 2x_1(A_{31} - A_{13}) + 2x_3(A_{32} - A_{23}) - C(1 - 2x_1)] \quad (15)$$

The constant ratio of hydrocarbon in the furfural phase permits further simplification in that $x_1 = x_2$ and $x_3 = 1 - 2x$. Equation 15 may be expressed as:

$$\log \gamma_1 = [A_{23} - A_{32} + \tfrac{1}{2}(A_{13} - A_{31} + C)]x_3^3 + [\tfrac{1}{2}(3A_{32} + A_{31} - C) - A_{23}]x_3^2 + \tfrac{1}{2}(A_{31} - A_{32})x_3 \quad (15a)$$

$$\log \gamma_2 = [A_{23} - A_{32} + \tfrac{1}{2}(A_{13} - A_{31} - C)]x_3^3 + [A_{31} + \tfrac{1}{2}(A_{32} - A_{13} - C)]x_3^2 + \tfrac{1}{2}(A_{32} - A_{31})x_3 \quad (15b)$$

The resulting expression for the prediction of ternary activity coefficients from binary data requires the evaluation of the ternary constant, C. The ternary constants were evaluated by a trial and error procedure from the present experimental data, and are tabulated in Table VI.

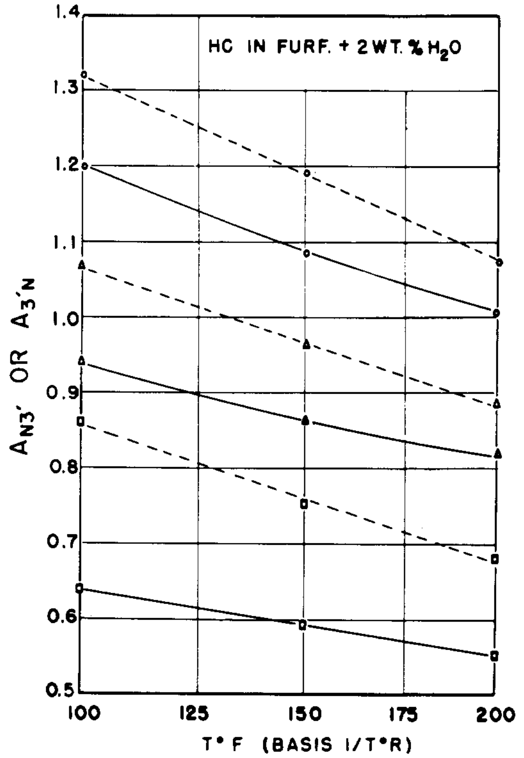


Figure 14. Binary and pseudo-binary constants for Margules 3-suffix equations

○ n-Butane
△ 1-Butene
□ 1,3-Butadiene
Solid lines for A_{n3}'
Dashed lines for $A_{3}'_{n}$

where

$$\text{Log } \gamma_n = X_3'^2\,[A_{n3}' + 2X_n\,(A_3'_n - A_{n3}')]$$
$$\text{Log } \gamma_3' = X_n^2\,[a_3'_n + 2X_3'\,(A_{n3}' - A_3'_n)]$$

Table VI. Application of Margules Three-Suffix Ternary Equation

Ternary and Pseudo-Ternary Margules Constants[a]

Temp., °F.	C	C′	C″
n-Butane–1-Butene–Furfural-Water			
100	0.30	0.40	0.40
150	0.25	0.30	0.30
200	0.20	0.20	0.15
n-Butane–1,3-Butadiene–Furfural-Water			
100	0.30	0.40	0.40
150	0.25	0.30	0.25
200	0.20	0.20	0.10

Comparison of Calculated and Semiexperimental Activity Coefficients[b]

Run No.	Mole % Total HC	Total HC Press.	α	γ'' *n*-C_4	γ' *n*-C_4	γ'' 1,3-C_4	γ' 1,3-C_4
n-Butane–1,3-Butadiene–Furfural at 100 °F.							
391	4.48	16.7	2.84	11.35	10.85	3.61	3.29
394	19.02	46.0	2.37	6.85	6.59	2.50	2.42
395	4.90	18.3	2.82	11.30	10.62	3.42	3.25
396	8.57	28.4	2.70	9.75	9.45	3.25	3.04
397	10.79	34.9	2.63	9.28	8.71	3.18	2.90
401	24.41	51.4	2.21	5.54	5.50	2.28	2.18
421	7.00	24.2	2.75	10.25	9.87	3.37	3.16
434	21.24	48.2	3.32	6.09	6.17	2.37	2.35
478	21.37	47.5	2.31	6.00	6.10	2.36	2.34
480	9.27	30.5	2.68	9.60	9.21	3.25	3.01
481	15.97	40.7	2.46	7.08	7.23	2.62	2.60

[a] ′, furfural plus 2 wt. % water. ″, furfural plus 4 wt. % water.

[b] γ', calculated from Margules ternary equation.
γ'', obtained from calculated relative volatilities and experimental hydrocarbon pressures.

Table VII. Comparison of Calculated Relative Volatilities of *n*-Butane to 1-Butene

x (Total HC)	α_{12} Margules	α_{12} Graphical
In Furfural + 2% Water at 100 °F.		
0.00	1.56	1.51
0.03	1.53	1.50
0.05	1.52	1.49
0.10	1.48	1.45
0.15	1.43	1.40
In Furfural + 4% Water at 100 °F.		
0.00	1.59	1.64
0.03	1.58	1.61
0.05	1.57	1.59
0.08	1.53	1.54

The three-suffix Margules equation for quaternary systems may be derived in a manner analogous to the development of the ternary relationships. The quaternary relationship contains 12 binary and four ternary constants necessary to describe the six binary and four ternaries parent to a four-constituent system. However, the control of a constant water-furfural ratio in the furfural phase makes it possible to reduce this quaternary to a pseudo-ternary system, where the hydrocarbons constitute two of the components and the furfural-water solution comprises the third. With these restrictions, the Margules quaternary equation reduces to the form of Equation 15, the suffix 3 being replaced by 3′. The pseudo-binary constants were available from the treatment of the parent ternary systems. After determination of the pseudo-ternary constant, C, it was possible to predict the hydrocarbon total partial pressure from the predicted activity coefficients.

$$P_{hc} = P_1 + P_2 = \gamma_1 x_1 P_1^{\circ} + \gamma_2 x_2 P^{\circ}_2$$

The predicted and observed hydrocarbon partial pressures are compared in Table VII for typical runs.

Relative Volatilities. Relative volatility may be expressed as a function of the thermodynamic acitivity coefficients at the component vapor pressure.

$$\alpha_{12} = \frac{y_1 x_1}{y_2 x_2} = \gamma_1 P_1^{\circ} z_2/\gamma_2 P_2^{\circ} z_1 \qquad (16)$$

The ratio of the activity coefficients for components 1 and 2 in a ternary or pseudo-ternary system can be predicted by the modified ternary Equation 15.

$$\log (\gamma_1/\gamma_2) = x_3[A_{13} + A_{32} + 2x_1(A_{31} - A_{13}) - x_3(A_{23} - A_{32}) - C(x_2 - x_1)] \qquad (17)$$

In the furfural phase, the equimolar ratio of hydrocarbon cancels the effect of the ternary constant.

$$\log (\gamma_1/\gamma_2) = x_3 \{A_{13} - A_{23} + 2x[(A_{31} - A_{13}) - (A_{32} - A_{23})]\} \qquad (17a)$$

Values of hydrocarbon relative volatilities for the experimental systems were calculated from Equations 17 and 17a, as modified with the subscript 3′ for the pseudo-ternary systems, and the predicted relative volatility values are shown in Figure 15. These calculated relative volatilities were used to predict the partial pressure of the individual hydrocarbons from the experimental total hydrocarbon pressures.

$$\alpha_{12} = \bar{P}_1 x_2/\bar{P}_2 x_1 \quad \text{and} \quad \bar{P}_{hc} = \bar{P}_1 + \bar{P}_2 \qquad (18)$$

By using these values for the hydrocarbon pressure, semiexperimental activity coefficients are calculated from Equation 8a.

$$\gamma_1 = \bar{P}_1 z_1/P_1^{\circ} x_1$$

These activity coefficients are compared to those predicted directly from the three-suffix Margules Equation 14 in Table VI. This method is not a direct check; however, the predicted value of relative volatility, although based upon the Margules equation, is developed from a much simpler expression which is independent of the ternary constant, and the hydrocarbon total pressure data are completely independent of the Margules relationships.

Graphical Determination. The symmetry of the Margules binary and ternary equations lends itself to a simple graphical representation. For a ternary mixture of solvent containing two hydrocarbons, whose binary obeys Raoult's law, in a specified ratio, $x_2/x_1 = k$, the Margules equation for the ratio of activity coefficients may be expressed very simply where the effect of the ternary constant, C, may be neglected.

$$\frac{\log (\gamma_1/\gamma_2)}{x^3} = A_{13} - A_{23} + 2x_1 \left[(A_{31} - A_{13}) - \frac{(1 + k)}{2} (A_{32} - A_{23})\right] \qquad (19)$$

For the corresponding binaries, let the pseudo mole fraction of components 1 and 2 equal x'_1 and x'_2, respectively. Indicating the binary activity coefficients as the primed values, the following relationship may be calculated from binary Margules Equations 10 and 10a.

$$\frac{\log \gamma_1'}{(1 - x_1')^2} - \frac{\log \gamma_2'}{(1 - x_2')^2} = A_{13} - A_{23} + 2(A_{31} - A_{13})x_1' - 2(A_{32} - A_{23})x_2' \qquad (20)$$

The right-hand sides of Equations 19 and 20 become equal when $x_1' = x_1$ and $x_2 = (k + 1)x_1/2$. As $x_3 = 1 - x_1 - x_2 = 1 - (k + 1)x_1$, a general expression may be written:

$$\log \frac{(\gamma_1)}{(\gamma_2)} = \left[\frac{1 - (1 + k)x_1}{(1 - x_1)^2}\right] \log \gamma_1' - \left\{\frac{1 - (1 + k)x_1}{\left[1 - \frac{(1 + k)}{2}x_1\right]^2}\right\} \log \gamma_2' \qquad (21)$$

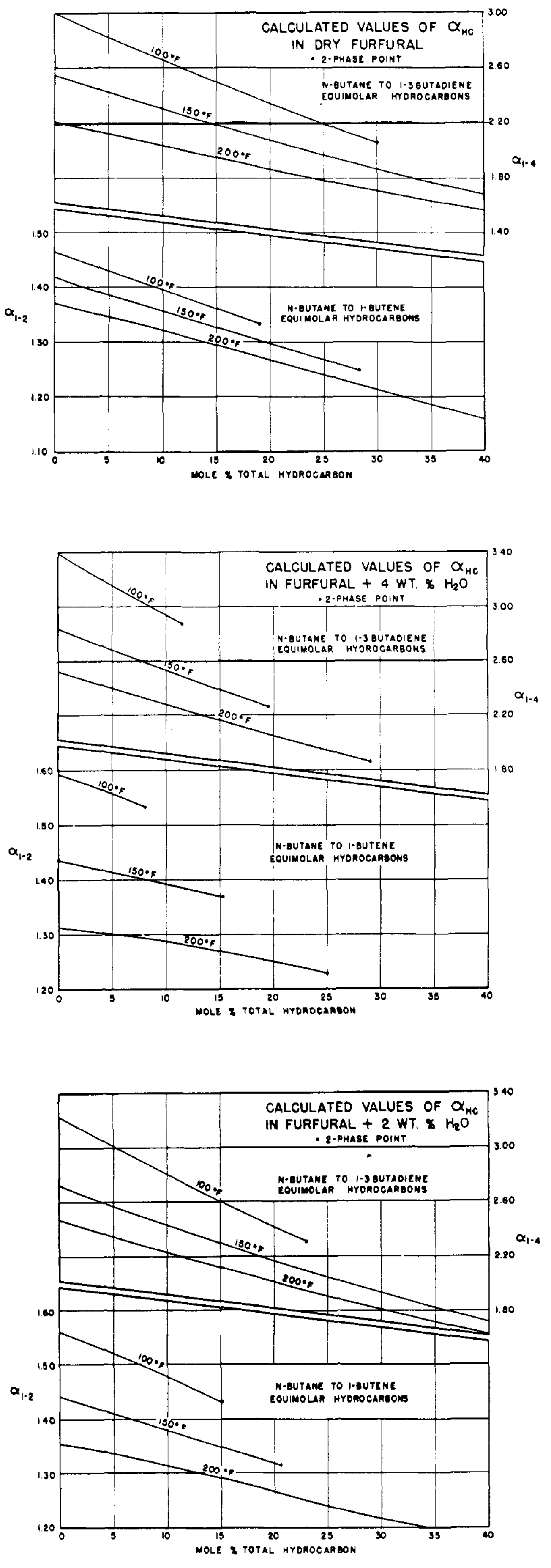


Figure 15. Calculated relative volatilities of hydrocarbons in furfural and in furfural plus water

It is seen from Equation 21 that it is not necessary to determine the particular Margules constants. The value of $\log \gamma_1'$ is read from binary activity coefficient data plot at the ternary composition, x_1. However, the value of $\log \gamma_2'$ must be obtained at the concentration $\frac{(k+1)}{2}x_1$, rather than kx_1, from the corresponding binary activity coefficient data for component 2. In the case of the present data, where $k = 1.0$, the equation becomes simplified.

$$\log(\gamma_1/\gamma_2) = \frac{1-2x_1}{(1-x_1)^2}\log(\gamma_1'/\gamma_2') \tag{21a}$$

Relative volatilities of hydrocarbons in ternary solvent mixtures then directly may be calculated from the binary solvent data by using Equation 21 and further applying Equation 16.

$$\alpha_{12} = (\gamma_1/\gamma_2)(P_1^0 z_2/P_2^0 z_1) \tag{22}$$

Table VII compares the value of the relative volatilities of n-butane to 1-butene, calculated by the three-suffix Margules ternary equation and by the graphical method. The 2% and 4% water in furfural at 100°F. are shown, as these systems disclosed the largest deviations of the calculated Margules activity coefficient values from experimental data. Consequently, comparisons for these systems should give the maximum discrepancy between the relative volatilities calculated by the two methods. A summary of these results showed a maximum deviation of 4%; other isotherms gave comparisons that checked within 2%.

Phase Boundary Relations. A most important factor is that the agreement of predicted pressures with the experimental values gives no assurance that the individual activity coefficients are correct. A high value for one component and a corresponding low value for the remaining hydrocarbon might compensate to give the correct total pressure. The relative volatility, a function of the ratio of the activity coefficients, consequently would be in serious error. For these systems, however, liquid-liquid data on the phase boundary may be used as a check.

In the region of low total hydrocarbon concentration, the individual hydrocarbon activity coefficients must be very near that value of the corresponding hydrocarbon-furfural binary. As the concentration of total hydrocarbon increases in the solvent phase, in many of these systems, a hydrocarbon phase will separate. The ratios of the activity coefficients of the hydrocarbon in the two resulting liquid phases are related to the distribution constant, d, as follows:

$$(\gamma_1/\gamma_2)_l = d(\gamma_1/\gamma_2)_{hc} \tag{22a}$$

Equation 22 is used to calculate the distribution constant by using the corresponding activity coefficient ratios at the phase boundaries. The Margules Equation 17a is applied to the equimolar hydrocarbons in the furfural phase

Table VIII. Calculated and Experimental Distribution Constants for n-Butane-1-Butene and Furfural

Temp., °F.	k_{HC}	$x_{n\text{-}C_4}$	$\gamma'_{n\text{-}C_4}$	$\gamma'_{1\text{-}C_4}$	$(\gamma_1/\gamma_2)_l$	$d_{calcd.}$	$d_{exptl.}$
			Conjugate Phases				
100	0.65	0.554	1.73	2.13	1.58	1.56	1.54
150	0.74	0.497	1.86	2.00	1.47	1.36	1.35
			Plus 2% Water Conjugate Phases				
100	0.64	0.560	1.72	2.13	1.68	1.61	1.57
150	0.715	0.515	1.81	2.00	1.51	1.44	1.40
200	0.80	0.402	2.28	2.18	1.37	1.27	1.25
			Plus 4% Water Conjugate Phases				
150	0.705	0.526	1.77	2.05	1.57	1.52	1.49
200	0.770	0.445	2.05	2.15	1.38	1.31	1.30

at the phase boundary to determine the activity coefficient ratio. The binary values of γ_1' and γ_2' for the hydrocarbon phase are read off the smoothed activity coefficient plots of the binary or pseudo-binary experimental data at the respective mole fractions required by the graphical method. Where the corresponding pseudo-mole fraction occurs in an immiscible region, the activity coefficient is determined by dividing the constant hydrocarbon activity by the pseudo-mole fraction. The ratio of the ternary or pseudo-ternary activity coefficients in the hydrocarbon phase is then calculated by the graphical method, using Equation 21. Calculated and experimental distribution constants, *d*, are compared in Table VIII for the system *n*-butane-1-butene-furfural-water.

Although Table VIII shows the calculated value of *d* is slightly higher than the experimental value in all cases, the agreement was better than expected. This check strongly implies the correct ratio of calculated activity coefficients at high hydrocarbon concentrations near the phase boundary. As the binary hydrocarbon activity coefficient data control the ternary ratio at low hydrocarbon concentrations, the agreement of experimental and predicted system pressures adds more rigorous support to the correctness of the calculated relative volatilities and individual hydrocarbon activity coefficients. Unfortunately, the nature of the *n*-butane-1,3-butadiene-furfural-water system is such that a hydrocarbon phase occurs only at 100°F. with the dry furfural and furfural plus 2 weight % water systems. The distribution constant, *d*, for these points disclosed similar agreement between calculated and experimental results. This is insufficient justification for a general statement on this system.

SUMMARY

Liquid-liquid equilibria and solubility data at 100°, 150°, and 200°F. have been presented for the systems *n*-butane-1-butene-furfural-water and *n*-butane-1,3-butadiene-furfural-water, the control of equimolar hydrocarbons being maintained in the liquid furfural phase. Activity coefficients of the parent single-hydrocarbon systems with furfural-water have been correlated by using the Margules three-suffix equation. Numerical and graphical methods have been used to determine activity coefficients and relative volatilities for the systems of two C_4 hydrocarbons with furfural-water. A comparison of these methods disclosed close agreement for the calculated relative volatilities of 1-butene and 1,3-butadiene to *n*-butane in furfural-water solution. The graphical method offers a rapid technique for the determination of hydrocarbon relative volatilities in a solvent-binary hydrocarbon system by the direct use of activity coefficient data from the parent solvent-single hydrocarbon systems. This procedure eliminates the need for curve fitting for the parent activity coefficient data as well as the subsequent tedious calculations of the Margules ternary equations. The graphical technique may be extended to give approximate hydrocarbon relative volatilities for solvent-multicomponent hydrocarbon systems. The limitations on the accuracy of the graphical method are summarized as follows:

1. The parent activity coefficient data must be approximated by the Margules equation.
2. The hydrocarbons should exhibit negligible interaction in the solvent solution.

NOMENCLATURE

A = limiting value constant for component a in semiempirical activity coefficient equations
A_{12} = Margules 3-suffix equation binary constant A for component 1 in binary 1 − 2
A_{21} = Margules 3-suffix equation binary constant B for component 2 in the binary 1 − 2
B = limiting value constant for component b in semiempirical activity coefficient equations
C = arbitrary ternary constant in Margules 3-suffix ternary equation
F = number of independent variables required to establish a physical system, or number of degrees of freedom
G^E = excess free energy of mixing of a physical system
H = enthalpy
P = pressure
$\overline{P}$ = partial pressure
P^r = vapor pressure
P_0 = pressure corresponding to unit activity
P_c = critical pressure
R = universal gas constant
T = temperature
T_c = critical temperature
T_r = reduced temperature
V = liquid molar volume of a pure component
V_g = molar gaseous volume of a pure component at temperature and pressure of a system
a = activity of a component at given conditions
a_0 = activity of a component in its standard state
d = distribution constant $(x_1/x_2)'/(x_1/x_2)''$, where primes indicate different liquid phases
f = fugacity of a component at given conditions
f_0 = fugacity of a component in its standard state
k = ratio of mole fractions of hydrocarbon 1 to hydrocarbon 2, where held constant
k' = ratio of mole fractions of furfural to water, where held constant
q = effective molar volume of a component within a liquid mixture
v = partial molar volume of a component in a liquid mixture
x = mole fraction in liquid
y = mole fraction in vapor
z = nonideality correction factor for observed activity coefficients
α = relative volatility
β = second virial coefficient in expansion for nonideal gas
$\overline{\gamma}$ = observed activity coefficient
γ = true activity coefficient

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