# PHASE EQUILIBRIA in Systems with Ethylene Above Its Critical Temperature

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**A study was made of the mutual solubility of ethylene with various polar and nonpolar relatively high-molecular-weight organic compounds at temperatures 1° and 10° C. respectively above the critical temperature of ethylene and at pressures up to 1,500 lb./sq.in.abs. For many compounds Henry's law was found to be applicable for the liquid phase up to approximately two thirds of the critical pressure of ethylene. In the critical region the solubility of ethylene was extremely sensitive to small changes in both temperature and pressure. The various types of phase behavior encountered were classified according to the nonideality involved. The results of this investigation indicate that a gas near its critical conditions is often capable of dissolving relatively nonvolatile materials in sufficient concentrations to warrant consideration of a separation process using such a gas as the extracting medium, namely fluid-liquid extraction.**

Phase behavior and equilibrium between phases are the fundamental bases of any phase-change separation process. They are profoundly influenced by the temperature, pressure, and concentration region considered as well as by the relative chemical structures and physical properties of the substances involved. Although various investigators have explored certain regions of phase equilibria rather extensively, comparatively few studies have however been made where the equilibrium compositions of the phases were measured in the critical region for components differing widely in chemical structure, molecular weight, and critical temperature. From the results of previous studies a general classification of binary vapor-liquid-phase behavior in terms of the nonideality involved can be made as follows:

*Ideal Solutions.* This class has been generalized and dealt with by means of Raoult's, Henry's, Dalton's, and the ideal gas laws. Thus the compositions of the phases can be related to each other and to pressure and temperature algebraically or graphically. This situation is rarely met exactly but is approximated closely by a few systems such as similar hydrocarbons and is an important standard of comparison for other systems.

*Nonideal Solutions at Low Pressures.* This classification contains the large majority of liquid systems at normal and low pressures where the perfect-gas laws are approximately valid. Differing degrees of nonideality in the liquid phase lead to azeotropy and partial or complete immiscibility. Liquid-phase nonideality is usually measured in terms of an activity coefficient.

*Nonideal Solutions at High Pressures.* This class is the most difficult to treat thermodynamically, since both phases require correction factors, and comparatively more data are required for generalization. It is also probably the least investigated of the cases, especially at conditions favoring nonideality. For liquids this case involves components of differing molecular weight; differing size, shape, and structure; differing polarity; and differing hydrogen-bonding tendencies. For vapors this means operating in the critical region of the mixture of chemically dissimilar components. Such systems offer interesting possibilities for extending and generalizing the present knowledge of phase behavior and theoretical possibilities for developing new separation processes by deliberately making use of nonideal behavior.

Because processes often operate at constant temperature or pressure, the most common binary-phase diagrams are those of composition vs. temperature at constant pressure or composition vs. pressure at constant temperature. The general interrelations of these and other representations have recently been outlined by Ricci (*4*).

Further consideration of these phase diagrams permits subdivisions of the classes outlined above. For the less-well-known classification of nonideal solutions at high pressures, at least three types of behavior can be differentiated for binary systems. Basically a $P$-$x$ diagram for a binary system of complete miscibility below the critical temperature of both components takes the familiar form shown in Figure 1. The intercepts on the $P$ axis are the vapor pressures of the two components of the system at the specified temperature.

As the temperature is increased

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above the critical for the more volatile component, a continuous loop (upper branch representing the liquid, lower branch the vapor phase) would be obtained originating from and ending with the vapor pressure of the less volatile component as in Figure 2. It is now possible to pass from a liquid to a vapor phase without crossing any phase boundaries. Above the critical temperature the material in equilibrium with a liquid phase is often referred to as a "fluid" phase.

As the dissimilarity in volatility and structure between the two components is increased, the two-phase area increases in spread and is distorted at low pressures, as depicted in Figures 3 and 4. These still represent a system of complete miscibility in the liquid phase and for purposes of reference are called here type 1.

With poorer liquid miscibility, the presence of the second component in the vapor, even in small amounts, materially increases the critical-pressure requirements for the system, leading to an "open" loop as in Figure 5. Here the slope of the $P$-$x$ liquid line no longer steadily decreases, as was noticed in Figure 4. This system, with no maximum pressure of the two-phase region, has been called type 2.

It is possible that one component is sufficiently dissimilar to the other for partial immiscibility to develop in the critical region. This interference may arise owing to differences in molecular weight, hydrogen bonding, polarity, or other properties. The resultant $P$-$x$ diagram, with partial immiscibility in the liquid phase, is shown in Figure 6 and is designated type 3.

The present investigation was undertaken as the initial study in a program of research designed to explore the nonideal-solution class in the region of high pressures, with the broad objective of systematizing behavior in this region and the ultimate goal of treating this information thermodynamically. A further objective was to explore the possibilities of applying unusual separation techniques such as fluid-liquid extraction or crystallization from a supercritical fluid. Particular systems and operating conditions were chosen that favored nonideality in both phases.

Ethylene was chosen for the gas because of its ready availability and its easily attained critical conditions (9.5° C. and 50.7 atm.). Other components, chosen for varying degrees of volatility, polarity, chain length, molecular weight, and chemical structure, were propionic, caproic, capric, stearic, and oleic acids; propyl, hexyl, decyl, and cetyl alcohols; decane, cetane, toluene, hexaldehyde, capronitrile, propyl propionate, and ortho and para dichlorobenzene. Generally compositions of the vapor and liquid phases were determined as a function of pressure at 1 and 10° respectively above the critical temperature of pure ethylene.

## EXPERIMENTAL METHOD

A modified Jerguson gauge equipped with a magnetic stirrer (*see* Figure 7) was used for the equilibrium determinations. Samples of vapor and

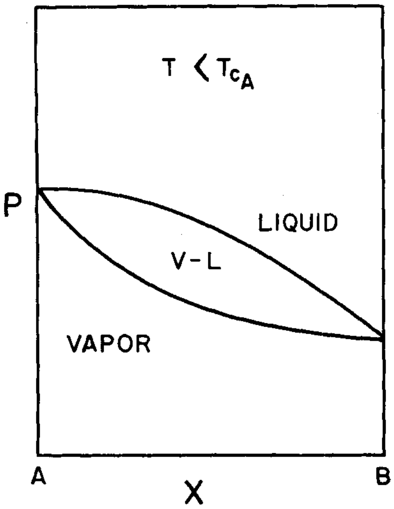

Fig. 1. Hypothetical $P$-$x$ Diagram for Binary System, $T<Tc_A$.

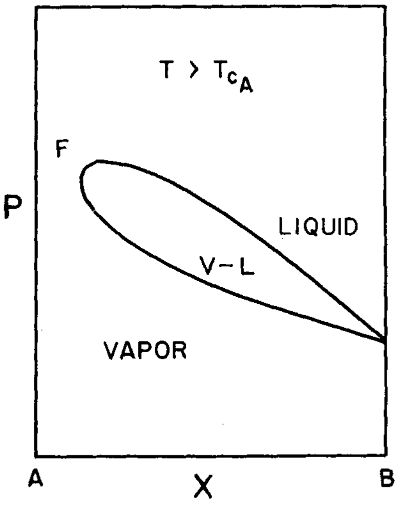

Fig. 2. Hypothetical $P$-$x$ Diagram for Binary System, $T>Tc_A$.

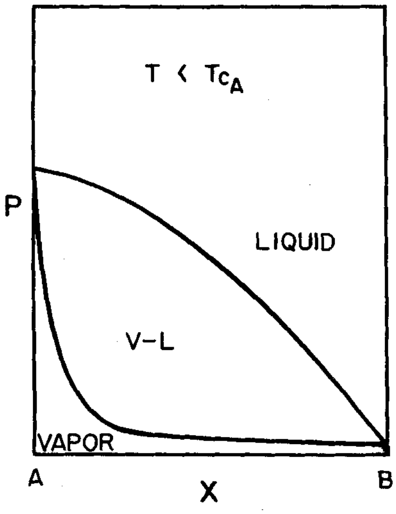

Fig. 3. $P$-$x$ Diagram for Type-1 System, $T<Tc_A$.

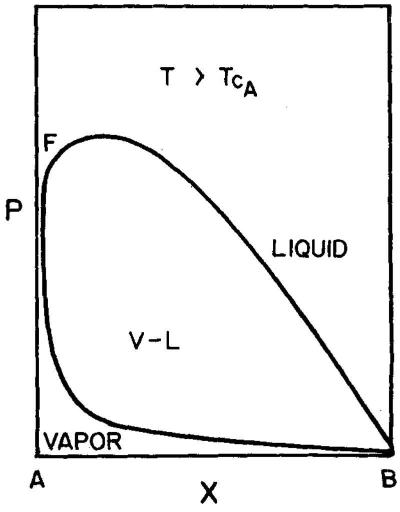

Fig. 4. $P$-$x$ Diagram for Type-1 System, $T>Tc_A$.

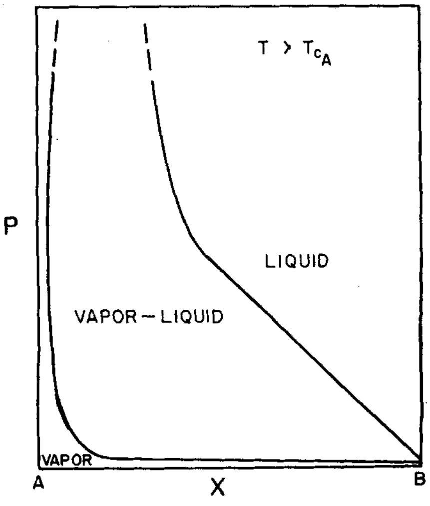

Fig. 5. $P$-$x$ Diagram for Type-2 System.

liquid phases were flashed into evacuated cartridges, *B*. Subsequent cooling in a dry-ice and acetone bath precipitated the component other than ethylene, permitting the ethylene to be withdrawn and measured volumetrically. The remaining part of the sample was flushed from the cartridge with a known amount of suitable solvent, the resulting concentration being determined by refractive index. Thus the composition of the original sample was readily calculated.

The procedure involved in bringing the system to equilibrium was as follows. The equilibrium chamber was completely dismantled and equipped with new gaskets before each series of runs. Solids to be studied were introduced during reassembly; liquids were introduced through line *A*. The mercury reservoir *F* was set to seal the bottom of the Jerguson gauge. Adjusting the height of the reservoir also permitted changing the level of either phase to the correct height for sampling through valve *D*. Ethylene was introduced directly from the cylinder. After long and vigorous stirring with the magnetic stirrer *E*, equilibrium was presumed attained when no further pressure change could be detected. The equilibrium chamber was kept at constant temperature (± 0.1° C.) by the cooling system *C*. Generally a judicious choice of the amount of solid or liquid originally introduced permitted operation in the visible range of the equilibrium chamber, with the amount of ethylene

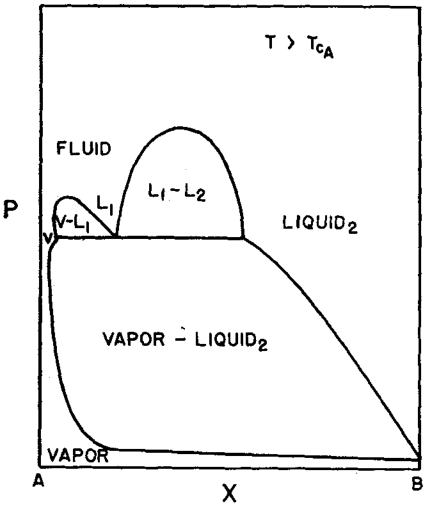

FIG. 6. *P-x* DIAGRAM FOR TYPE-3 SYSTEM.

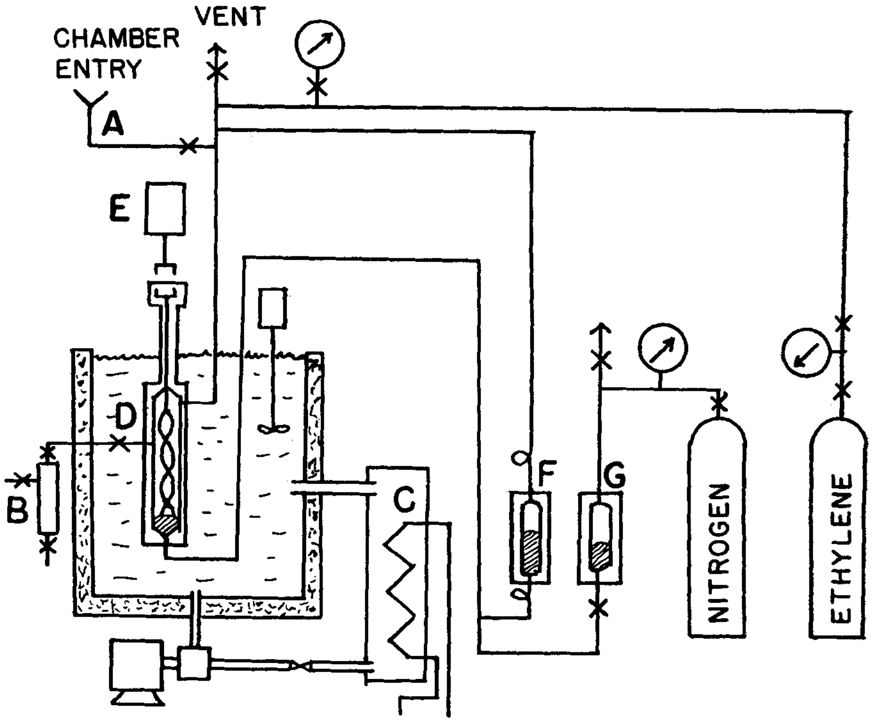

FIG. 7. EXPERIMENTAL APPARATUS.

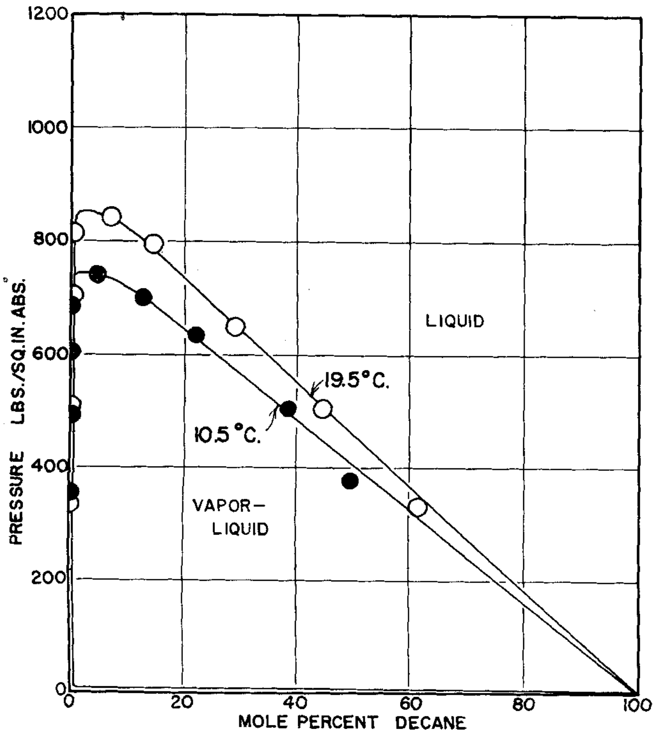

FIG. 8. DECANE-ETHYLENE ISOTHERMS.

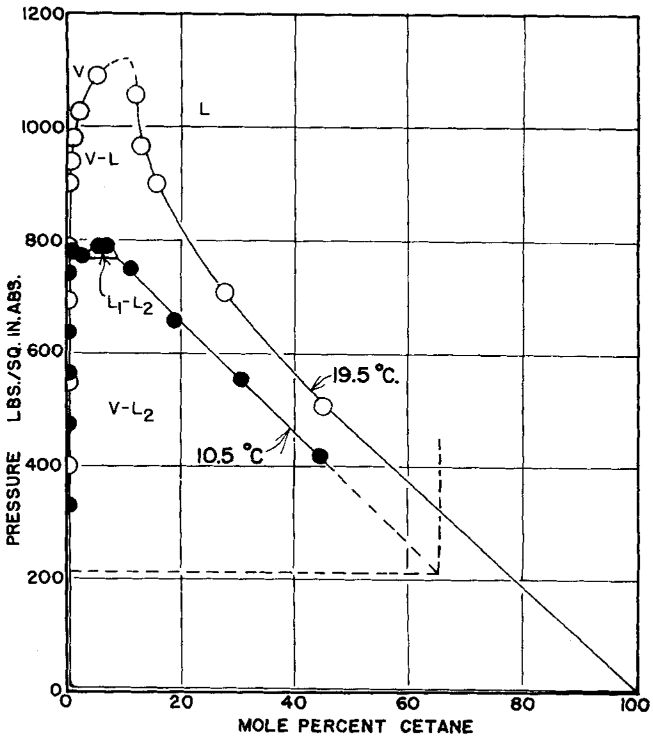

FIG. 9. CETANE-ETHYLENE ISOTHERMS.

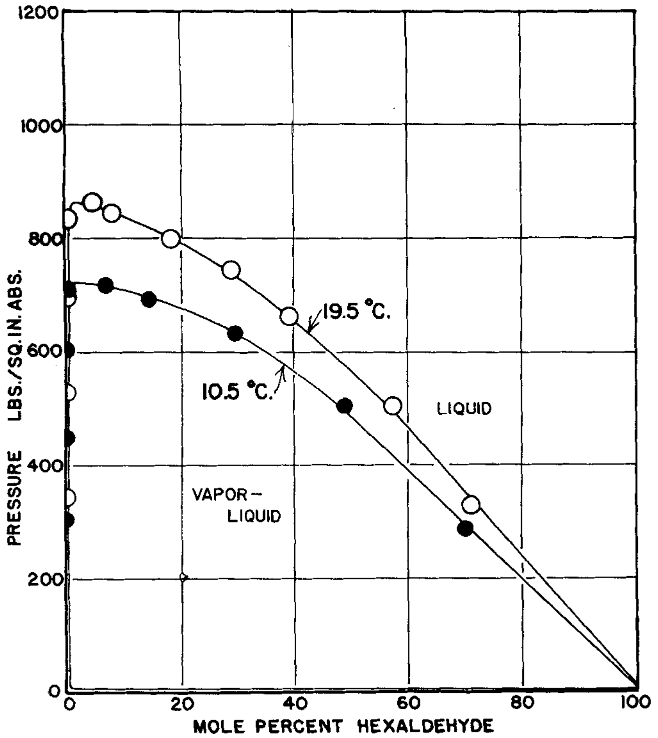

FIG. 10. HEXALDEHYDE-ETHYLENE ISOTHERMS.

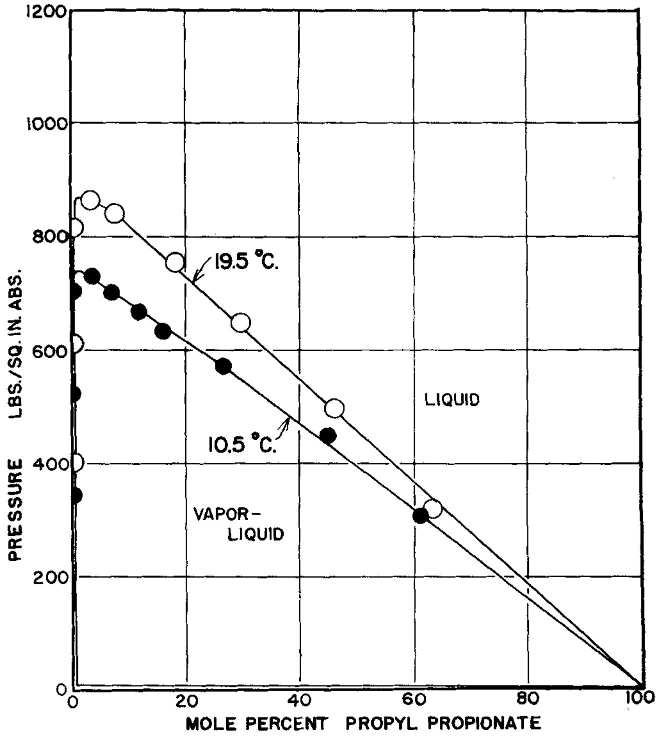

FIG. 11. PROPYL PROPIONATE–ETHYLENE ISOTHERMS.

determining the pressure. Changes in pressure could also be brought about by the back pressure of nitrogen against the second mercury reservoir *G*. During flashing, the volume occupied by the sample was simultaneously replaced by admission of mercury from reservoir *G*.

The source and purity of the compounds used in this investigation are listed in Table 3. The materials were used as obtained, without any attempt at further purification, and the effect of possible impurities on the absolute values reported was not determined.

## RESULTS

The *P-x* diagrams for the various systems studied are represented in Figures 8 to 22.* At low pressures the composition of the vapor phase was not determined; however the vapor line has been illustrated as returning to the vapor pressure of the pure organic constituent. Subscript 1 refers to a liquid richer in ethylene than in

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*Complete tabular data for experimentally measured values of phase compositions and pressures at each of the temperatures studied, Tables 4 through 19 of this paper, are on file with A.D.I., Auxiliary Publications Photoduplications Service, Library of Congress, Washington 25, D.C., as document 4476 and may be obtained for $1.75 for microfilm and $2.50 for photoprints.

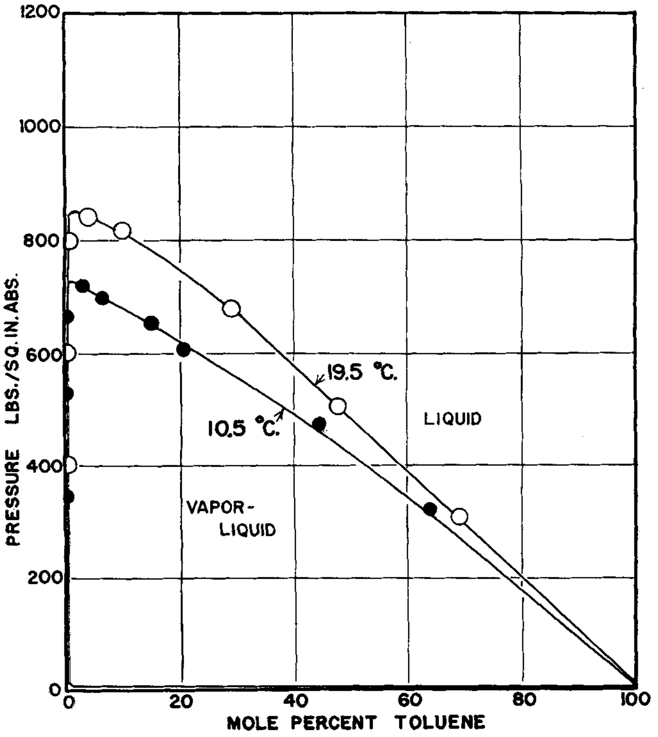

FIG. 12. TOLUENE-ETHYLENE ISOTHERMS.

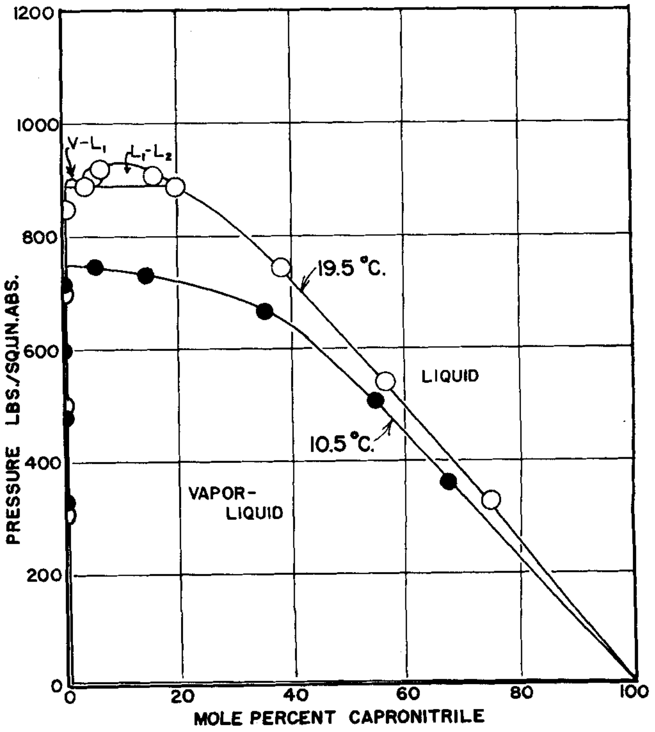

FIG. 13. CAPRONITRILE-ETHYLENE ISOTHERMS.

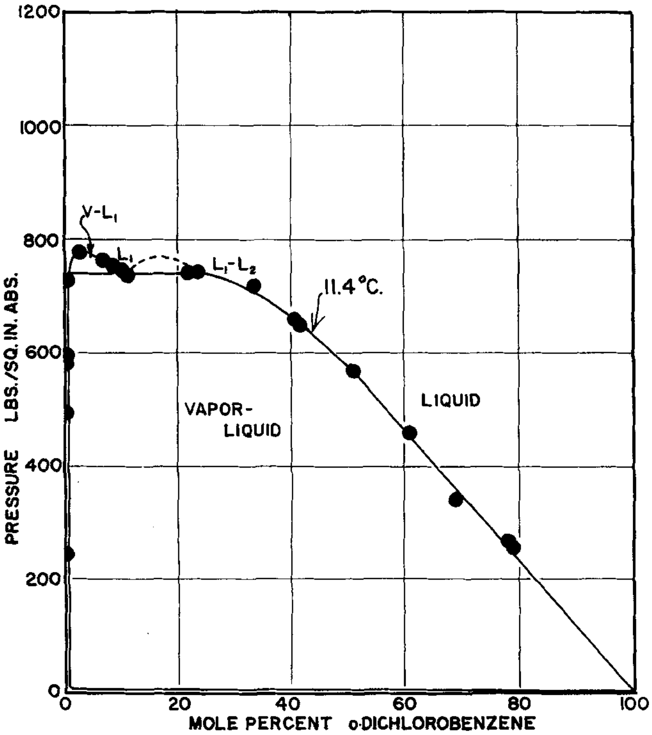

FIG. 14. *o*-DICHLOROBENZENE-ETHYLENE ISOTHERM.

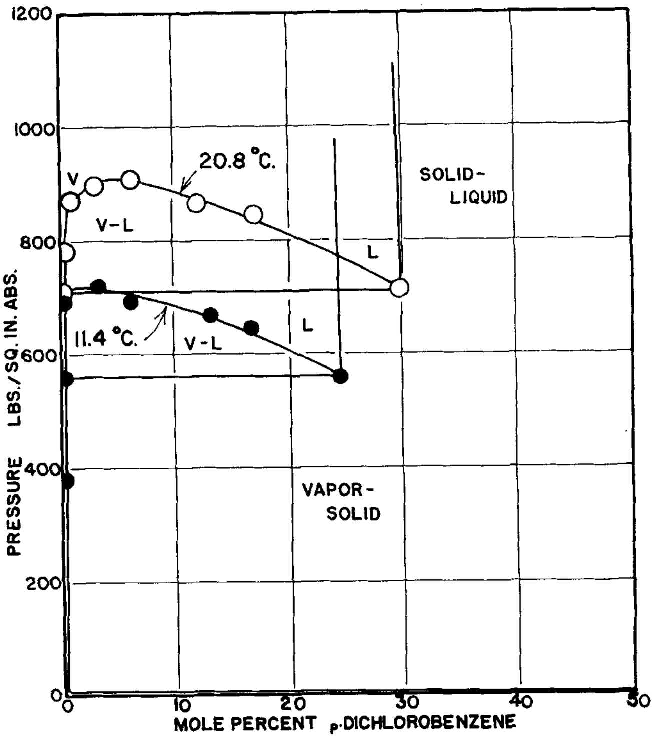

FIG. 15. *p*-DICHLOROBENZENE-ETHYLENE ISOTHERMS.

the liquid (subscript 2) which coexists with it.

The compounds forming the type-1 systems with ethylene are decane (Figure 8), hexaldehyde (Figure 10), propylpropionate (Figure 11), and toluene (Figure 12). At the temperatures studied, the variation of liquid composition with pressure was approximately linear over almost the entire pressure range. As the temperature is increased, the liquidus line is raised, and the critical point is reached at a high pressure and at a composition richer in the less volatile component. The phase diagram obtained for the ethylene-cetane system (Figure 9) indicates that this aliphatic system no longer strictly follows type-1 behavior. Since cetane is a solid at 10.5° C., no liquid was formed until the pressure of ethylene had been increased to 216 lb./sq.in.abs. Near the critical pressure of the mixture, a region of immiscibility occurred, indicating type-3 behavior. The formation of this ethylene-rich liquid is probably attributable to the nonideality arising from the great difference in molecular weight and volatility.

Regions of coexisting liquid phases near the critical pressure (type-3 behavior) were found also for the ethylene-capronitrile system at 19.5° C. (Figure 13), the ethylene-acetonitrile system at 10.5° C. (*2*), the ethylene-orthodichlorobenzene system at 11.4° C. (Figure 14), and the systems of ethylene with lower molecular-weight alcohols at 10.5° C. Figure 16 represents the composition in the three-phase region for the ethylene – *n*-propyl alcohol system (*3*). The secondary liquid exists over a narrower composition and pressure region in the ethylene – *n*-hexyl alcohol system (Figure 17). With decyl alcohol (Figure 18) formation of an ethylene-rich liquid could not be detected. Also, the critical pressures at these temperatures could not be attained with the present equipment indicating type-2 behavior. It is interesting that an ethylene-rich liquid phase can exist in these systems at temperatures above the critical temperature of ethylene.

Type-2 behavior was found also for the higher molecular weight acids. *P*-*x* isotherms are given for the ethylene–oleic acid system in Figure 22. Apparently at a pressure above 900 lb/sq.in.abs. the composition of the phases is relatively insensitive to further pressure change.

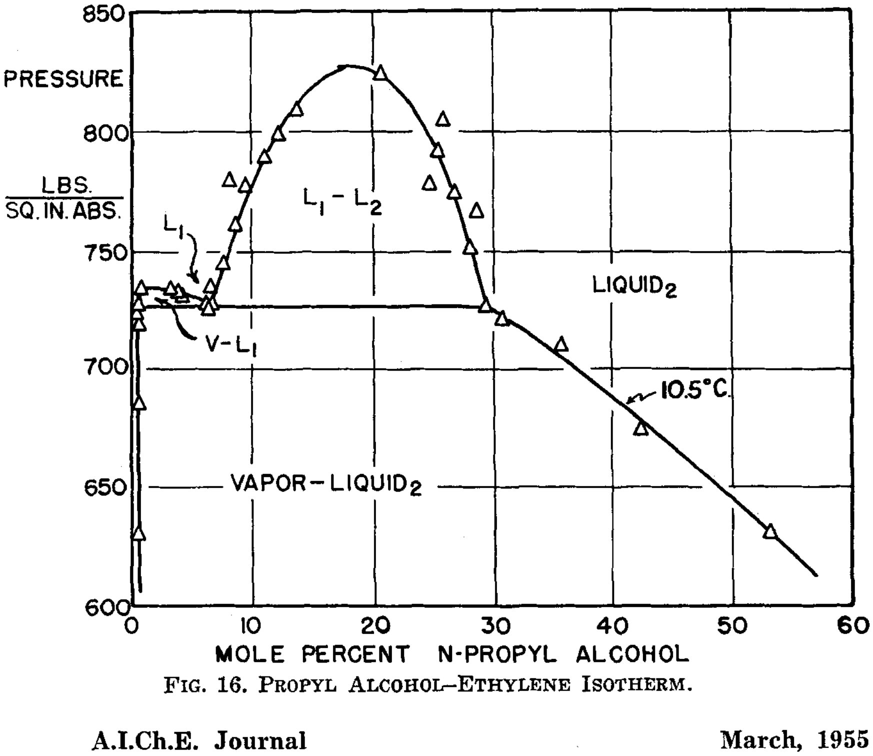

FIG. 16. PROPYL ALCOHOL–ETHYLENE ISOTHERM.

The lower molecular-weight acids fall into type-1 behavior (Figures 19 and 20); the transition to type 2 apparently depends upon the size of the acid molecule (Figure 21). As the chain length is increased, the melting point also is increased. Consequently not all the acids could be studied in this temperature region. The *P-x* diagram for the ethylene-caproic acid system (Figure 20) typifies the behavior for the lower molecular-weight acids. Here the increase of acid concentration at the critical pressure is much more noticeable. No liquid formation was detected in the ethylene–stearic acid system. A very narrow region of ethylene-rich liquid was obtained at 10.5°C. in the ethylene–cetyl alcohol system (*5*). Compression of ethylene on another solid, *p*-dichlorobenzene, caused formation of a liquid over a wide composition and pressure range (Figure 15). The effect of ethylene pressure on the melting point of this solid is noteworthy. The triple-point pressures determined here are some 25% lower than those reported by Diepen and Scheffer (*1*) possibly because of differences in the impurities present in the compounds used.

As the solubility of ethylene was found to increase linearly with pressure to about three fourths of the critical pressure for many of the systems, many of the data for the composition of the liquid phase can be represented in the form of Henry's law if it is assumed that the partial pressure of ethylene is equal to the total pressure of the system. Where applicable, Henry's law constants have been calculated and are listed in Table 1. At about the maximum valid pressure indicated, the slope of the composition vs. pressure curve decreases for type-1 and type-3 systems and increases for type-2 systems.

TABLE 1.—HENRY'S-LAW CONSTANTS FOR THE SOLUBILITY OF ETHYLENE

$p_g$ = partial pressure of ethylene, lb./sq. in. abs.
N = mole fraction of ethylene in liquid phase
$k$ = Henry's law constant. lb./sq. in. abs., $p_g = k$N

| Solvent | Temp., °C. | *k*, lb./sq. in. abs. | Maximum valid pressure, lb./sq. in. abs. |
|---|---|---|---|
| Hexyl alcohol | 10.5 | 149 | 590 |
| | 19.5 | 159 | 900 |
| Decyl alcohol | 10.5 | 100 | 300 |
| | 19.5 | 134 | 600 |
| Decane | 10.5 | 82 | 680 |
| | 19.5 | 92 | 800 |
| Cetane | 19.5 | 94 | 500 |
| Hexaldehyde | 10.5 | 98 | 500 |
| | 19.5 | 117 | 500 |
| Capronitrile | 10.5 | 113 | 500 |
| | 19.5 | 125 | 680 |
| Propyl propionate | 10.5 | 78 | 680 |
| | 19.5 | 92 | 800 |
| Toluene | 10.5 | 86 | 500 |
| | 19.5 | 97 | 680 |
| Oleic acid | 10.3 | 98 | 600 |
| | 20.0 | 114 | 680 |
| *o*-Dichlorobenzene | 11.4 | 118 | 580 |

## DISCUSSION

From the phase diagrams it can be seen that the phase relations encountered in this investigation

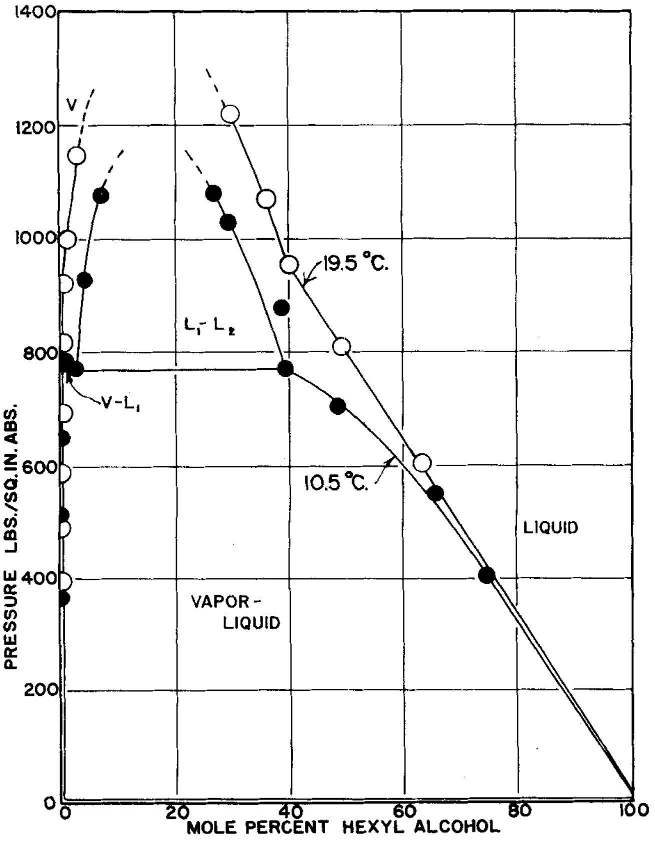

FIG. 17. HEXYL ALCOHOL–ETHYLENE ISOTHERMS.

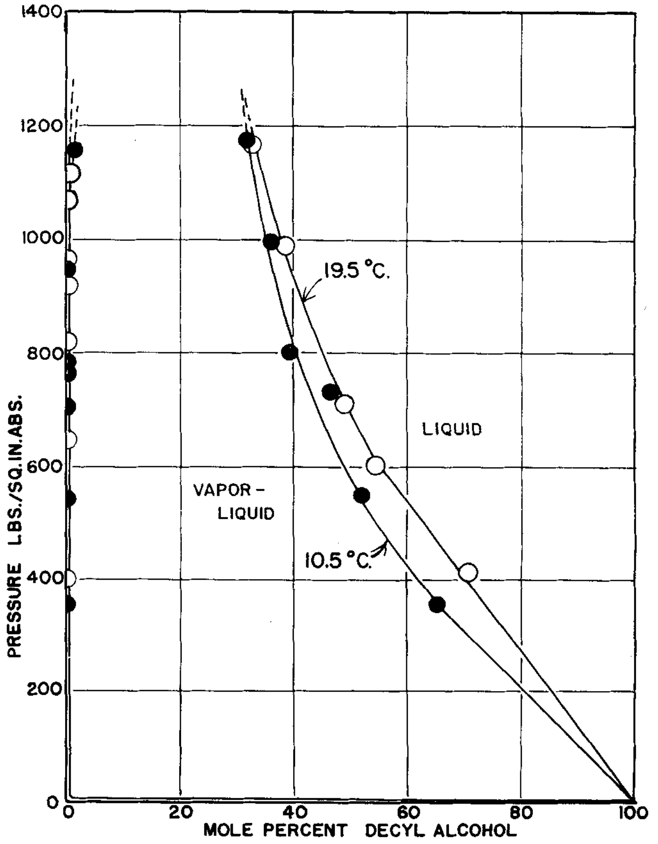

FIG. 18. DECYL ALCOHOL–ETHYLENE ISOTHERMS.

TABLE 2.—CONCENTRATION OF VAPOR PHASE IN SYSTEMS WITH ETHYLENE

| Compound | Temp., °C. | Vapor pressure, mm. Hg | Pressure, lb./sq. in. abs. | Mole % in "vapor" | Wt. % in "vapor" |
|---|---|---|---|---|---|
| Capric acid.......... | 19.5 | 0.000003 | 1,200 | 0.47 | 2.8 |
| Caproic acid......... | 19.5 | 0.0035 | 1,014 | 3.2 | 12.1 |
| Cetane.............. | 19.5 | 0.0017 | 1,090 | 4.9 | 29.3 |
| Hexyl alcohol........ | 19.5 | 0.69 | 1,150 | 2.6 | 9.0 |
| Propyl alcohol........ | 10.5 | 8.0 | 800 | 12.5 | 23.4 |

can be grouped into the three types of behavior enumerated under the classification of nonideal solutions at high pressures. Into which type any other system might fall may be estimated by a consideration of the factors involved in the systems already studied; for example, it is probable that combinations of a polar low-molecular-weight gas, e.g., ammonia or sulfur dioxide or carbon dioxide, with relatively high-molecular-weight nonpolar compounds such as hydrocarbons will exhibit behavior in the critical region analogous to that of these classes.

Type-1 behavior would be expected where differences in chemical structure and molecular size are not great. Systems of paraffins or olefins with other similar paraffins, aldehydes, or esters would probably be classed in this type.

For minor differences in chain length, type-3 behavior would be produced by differences in chemical structure, polarity, or hydrogen-bonding tendencies. The ethylene-alcohol and ethylene-nitrile systems are evidence of this. Although the acids are strongly polar and tend to form relatively strong hydrogen bonds, it is believed that these molecules act as dimers and thus somewhat nullify these strong effects. For members of a homologous series, sufficient dissimilarity in chain length could also cause type-3 behavior (for example ethylene and cetane).

With dissimilar components either Type 2 or 3 behavior would be expected. Difference in volatility and size of molecule would eventually lead to type 2. The two-liquid-phase phenomena (type 3) can occur only if the less volatile component is sufficiently volatile to enter the vapor phase in a high enough concentration to interfere with the densely packed molecules of the more volatile component and thus to lead to gas-phase nonideality similar to that of the liquid phase.

When one of the components is a solid, compression of a super critical gas upon it may cause a liquid to form or may yield a region of increased solids solubility manyfold greater than that predicted from vapor pressure alone (*1*).

Besides the theoretical interest in the unusual phase behavior encountered in these systems, the principles involved can be applied in operations wherein the nonideality is intentionally created. The magnitude of solubility of a compound of low volatility in a gas above its critical temperature (*see* Table 2) is sufficient to consider the gas as an extracting medium, that is fluid-liquid or fluid-solid extraction analogous to liquid-liquid extraction and leaching. In this case the solute is removed and the solvent recovered by partial decompression. For the cases cited in Table 2, decompression to 900 lb./sq.in. abs. at 19.5° C. or to 700 lb./sq.in.abs. at 10.5° C. reduces the nonvolatile-component concentration in the vapor phase to less than 1% by weight. Thus compression of a gas over a mixture of compounds could selectively dissolve one compound, permitting it to be removed from the mixture. Partial decompression of the fluid

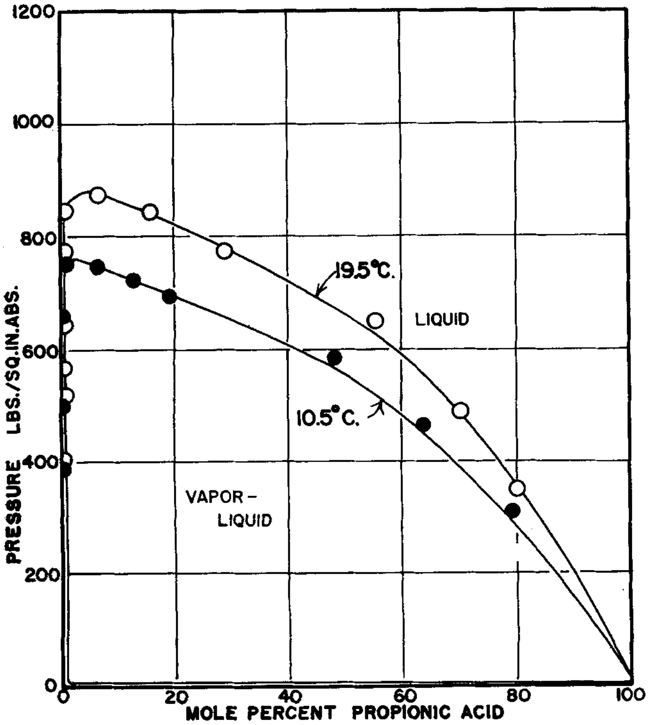

FIG. 19. PROPIONIC ACID–ETHYLENE ISOTHERMS.

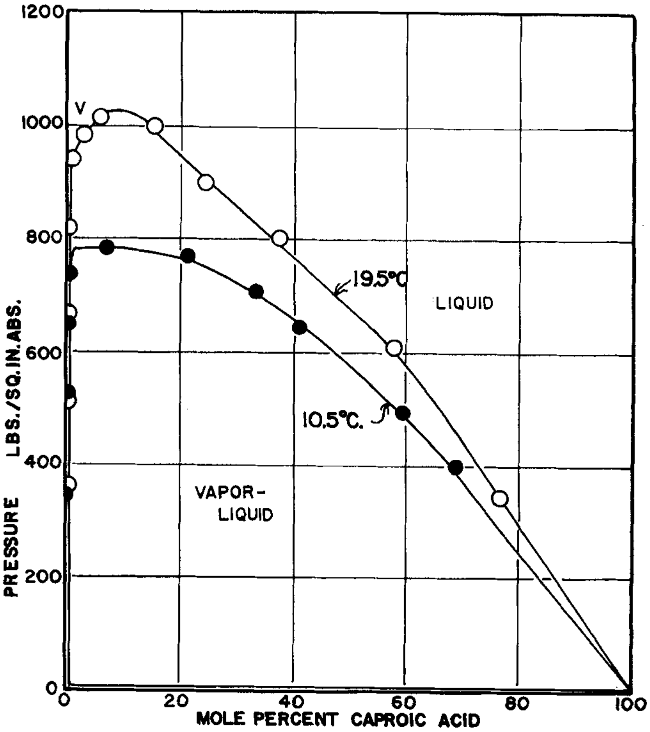

FIG. 20. CAPROIC ACID–ETHYLENE ISOTHERMS.

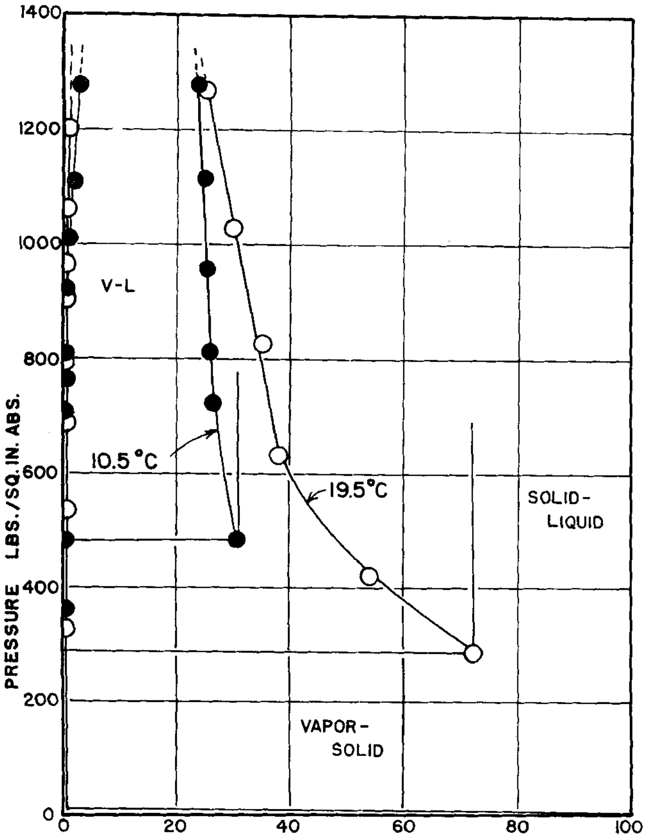

FIG. 21. CAPRIC ACID–ETHYLENE ISOTHERMS.

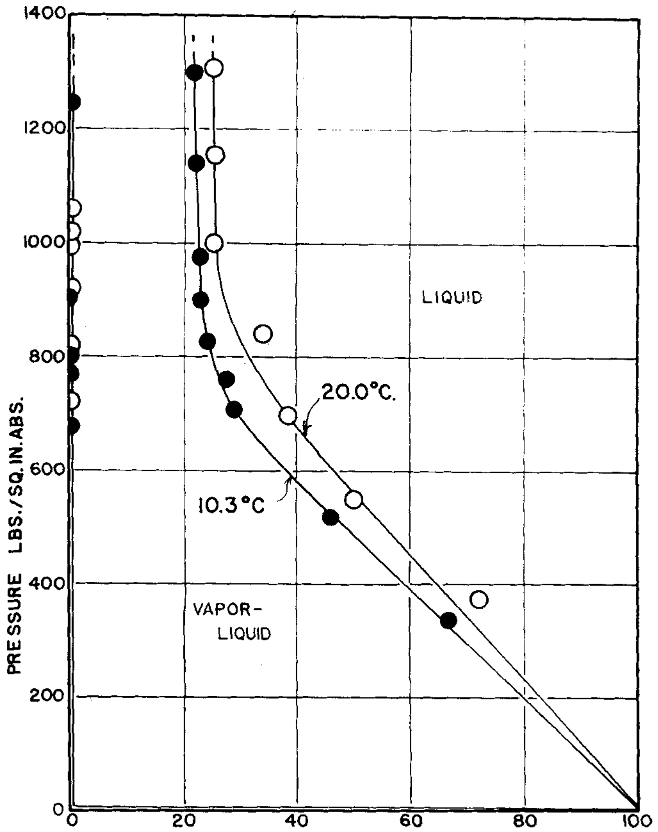

FIG. 22. OLEIC ACID–ETHYLENE ISOTHERMS.

elsewhere would drop out the dissolved compound, and the gas could be reused for further extraction.

Weinstock(*6*) has recently completed a study of ternary systems involving ethylene and water with various organic liquids wherein the ethylene under pressure is used to force a phase separation, splitting out the water from the organic solution. The behavior with supercritical ethylene is analogous to the use of a solid such as sodium chloride as a "salting-out" agent.

Supplying the energy for phase creation in the form of pressure rather than heat would also provide a means of separation and purification of those temperature-sensitive materials not suited for normal distillation. Because of the relatively high densities involved in such a process, the capacity would be greater than for the molecular distillation now frequently in use. A range of temperature regions is available because of the various extractant gases that might be chosen.

## ACKNOWLEDGMENT

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## NOTATION

$A$ = substance in binary system with high volatility
$B$ = substance in binary system with low volatility
$F$ = fluid phase
$L$ = liquid phase
$P$ = pressure
$T$ = temperature
$T_c$ = critical temperature
$V$ = vapor phase
$x$ = composition

TABLE 3.—MATERIALS USED

| Compound | Source | Purity |
|---|---|---|
| Propionic acid | Matheson Co. | C.P. grade |
| *n*-Caproic acid | Matheson Co. 2756 | 98%, B.P. 94-95°C./8 mm. |
| *n*-Capric acid | Matheson Co. 5168 | 98.5%, M.P. 29-30°C. |
| Stearic acid | Merck & Co. 0.04282 | U.S.P. triple pressed |
| Oleic acid | Merck & Co. 0.03221 | U.S.P. |
| *n*-Hexyl alcohol | Matheson Co. P5236 | 95.0%, B.P. 153-156°C. |
| *n*-Decyl alcohol | Matheson Co. P5189 | 94.0%, B.P. 90% 229-233°C. |
| Cetyl alcohol | Matheson Co. 2602 | 98.5%, M.P. 48-49°C. |
| *n*-Decane | Matheson Co. 5845 | 99.0%, B.P. 173-175°C. |
| Cetane | Matheson Co. P5829 | 95.0% M.P. 15-17°C. |
| *n*-Hexaldehyde | Matheson Co. P5169 | 95%, B.P. 90% 124-130°C. |
| *n*-Capronitrile | Matheson Co. 6612 | 98.0%, B.P. 161-163°C. |
| *n*-Propylpropionate | Matheson Co. 4296 | 98.5%, B.P. 122-125°C. |
| Toluene | Merck & Co. 74951 | A.C.S. Specs., B.P. range 1°C. |
| *p*-Dichlorobenzene | Matheson Co. 2779 | 99.0%, M.P. 52-5-53°C. |
| *o*-Dichlorobenzene | Matheson Co. 1289 | 99.5%, B.P. 53-55°C./10 mm. |
| Ethylene | U.S. Industrial Chem. | 99.5% |

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*(Presented at A.I.Ch.E. San Francisco meeting)*