# Part I

# PHASE EQUILIBRIA
# MOLECULAR TRANSPORT
# THERMODYNAMICS

## Phase Equilibrium at Elevated Pressures in Ternary Systems of Ethylene and Water with Organic Liquids. Salting Out with a Supercritical Gas

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Underlying most of the physical phase change separation operations carried out by the chemical industry on homogeneous mixtures are the basic phase equilibrium conditions. These equilibria determine the natural (single-stage) limits of such separation processes as distillation, extraction, and crystallization, and they usually must be determined experimentally before reliable design calculations can be made. Numerous chemical systems are used in industry, but there are relatively few systems for which the possible phase equilibria have been defined or systematically studied experimentally over the operable range of conditions. In particular, data for relatively few three-component (or ternary) systems have been reported over any appreciable range of temperature and pressure.

This article presents liquid-liquid and liquid-vapor phase equilibrium data at 15°C. for pressures in the range from 0 to 1000 p.s.i.g. for a number of typical three-component systems comprised of ethylene, water, and various organic liquids. It describes the conditions and compositions existing in several water-organic liquid mixtures which are normally either partially or completely miscible when they are subjected to ethylene under pressure. It further presents a generalization of the phase equilibrium behavior in three-phase patterns (typical isotherms) which cover all of the 26 systems studied. These qualitative and quantitative results show that ethylene, when dissolved in many water-organic liquid mixtures at elevated pressures, reduces the mutual solubilities of these liquid components. The result of this effect is to introduce a region of immiscibility or to increase the composition range covered by an existing miscibility gap. This phase behavior provides a basis for new separation methods for the dehydration of many types of organic compounds.

### EXPERIMENTAL METHOD

**Apparatus.** The investigation of the phase equilibria of a three-component system in which one, two, or three phases may coexist requires an equilibrium apparatus in which the phases present may be agitated at any desired temperature and pressure, and in which the material under examination may be closely observed at all times. The apparatus must allow for the removal of samples of any phase present in the system without disturbing equilibrium conditions. These requirements were met by using the apparatus shown in Figure 1.

The equilibrium chamber, or solubility "bomb," was a standard transparent type Jerguson gage with a stainless steel liquid chamber holding about 100 ml. The gage had two thick borosilicate glass windows. Adequate agitation was provided by a magnetically driven twisted strip of stainless steel. Four taps were provided in the bomb for the admission of gas or liquid and for the removal of samples by displacement with mercury. The two sample cartridges shown in Figure 1 were arranged so that equilibrium samples of two phases could be removed from the bomb nearly simultaneously.

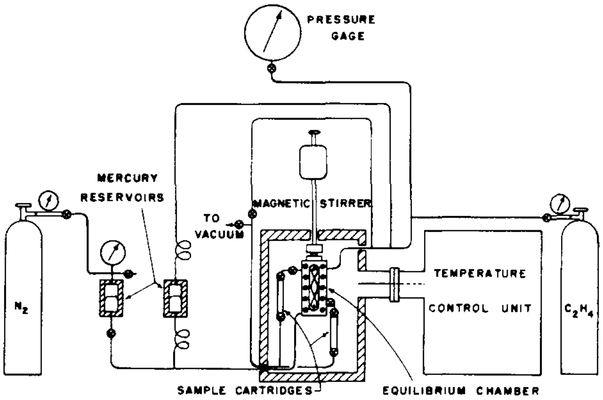

**Figure 1. Pressure apparatus for studying phase equilibria**

The desired temperatures in the thermostat enclosing the equilibrium chamber were controlled by a Tenny thermostatic circulated-air system to within about 0.1° and were measured with a calibrated thermometer. Desired pressures were applied from a compressed ethylene gas cylinder or by means of compressed nitrogen gas cylinder pressure through a mercury seal. Pressure measurements were made with calibrated Bourdon pressure gages. All lines

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carrying solvent, gases, samples, or mercury were 1/8-inch seamless steel tubing.

A second analytical apparatus was used for determining the volume of ethylene dissolved in each liquid sample. These measurements were made using glass capillary tubing to connect three calibrated gas-measuring bulbs and two burets to the sample cartridge by way of a glass-to-metal seal. The gas volumes contained in the burets and the pressure of the gas-measuring system were varied by means of adjustable mercury reservoir bulbs connected to the bottoms of the burets by thick-walled Tygon tubing.

For obtaining a qualitative general understanding of the phase behavior existing in the systems under investigation, the 26 organic liquids listed in Table I were studied by visual observation to determine qualitatively the phases occurring in ternary compositions with water and ethylene. Each water-organic mixture was charged to the bomb and observed at a number of different equilibrium ethylene pressures over the range 0 to 1000 p.s.i. The type, number, and relative volumes of the phases present were noted, and from this information, generalized phase equilibrium diagrams were developed.

To verify the generalized phase behaviors indicated by the qualitative study, quantitative phase equilibrium diagrams for selected systems were then determined using the following procedure.

For each system, several binary liquid compositions were separately charged to the carefully cleaned bomb. While the desired equilibrium temperature was being established, agitation was begun and ethylene was admitted to the bomb. As ethylene dissolved in the liquid, more was added, or the system pressure was maintained with nitrogen pressure through a mercury seal. The liquids to be sampled were positioned for the appropriate sampling outlets. The cleaned, dried, and carefully weighed sample cartridges were put into position, and when the measured system temperature and pressure had remained, without adjustments, constant for 1 hour, the samples were taken by slowly flashing the sample into the previously evacuated cartridge while simultaneously displacing the liquid being removed from the bomb with mercury so as not to change the equilibrium system pressure. Using this technique, two phases could be sampled at the same time.

After both samples had been removed, the temperature-controlling unit was turned off, the bomb enclosure was opened, and the sample cartridges were removed. The excess liquid from the bomb-side tip of each cartridge was removed, the sample-containing cartridges were weighed, and the volume of ethylene contained in the sample was then determined by allowing it to escape

## Table I. Qualitative Results for Ethylene-Water-Solvent Phase Equilibria

| Ethylene-Water with | Vol. % $H_2O$ in Liquid Binary | Temp., °C. | Pressure, P.S.I.G. | 3-Phase Region Observed | Comments |
|---|---|---|---|---|---|
| Acetone | 30 | 10 | 0-700 | Yes | Light liquid phase forms at approx. 500 p.s.i.g. |
| | 30 | 20 | 0-800 | Yes | Light liquid phase forms at approx. 450 p.s.i.g. |
| Acetaldehyde | 20 | 10 | 0-1000 | No | Very low solubility of ethylene in liquid |
| Acetonitrile | 0 | 25 | 200, 400 700, 1000 | No | As temp. was lowered to 6° C. at 1000 p.s.i. gas phase became liquid phase |
| | 28 | 10 | 0 | No | |
| | | | 650 | Yes | |
| | 28 | 20 | 0-1000 | Yes | Three phases exist at all pressures above 200 p.s.i. |
| Acetic acid | 20 | 20 | 0-1000 | No | |
| | 20 | 10.5 | 0-1000 | Yes | Light liquid phase forms at approx. 700 p.s.i.g. |
| *sec*-Butyl alcohol | 0 | 10 | 0-890 | No | 890 p.s.i.g. is approx. critical pressure at 10° C. |
| | Two phases | 10 | 0-900 | Yes[a] | Heterogeneous binary liquid at 1 atm.; additional separation of water occurs up to 600 p.s.i.g. |
| *tert*-Butyl alcohol | 25 | 30 | 900 | Yes[a] | Separation almost quantitative; volume of water phase does not increase as temp. is lowered to 10° C. |
| Ethyl alcohol | 5 | 20 | 0-1000 | No | 3 phases exist only at or below critical temp. of ethylene |
| | 5 | 5 | 0-1000 | Yes | |
| | 50 | 18 | 0-1000 | No | As temp. was lowered to 6° C. gas phase became liquid |
| Ethyl acetate | Two phases | 20 | 0-1000 | Yes | Liquid binary components are practically completely immiscible |
| Ethylenediamine | 20 | 20 | 0-1000 | No | Very low solubility of ethylene in liquid |
| Ethylene glycol | 40 | 10 | 0-1000 | No | |
| Formaldehyde | 63 | 10.7 | 0-900 | Yes | Light liquid phase exists between 700 and 730 p.s.i.g. |
| Formic acid | 25 | 10.5 | 0-1000 | Yes | Light liquid exists between 700 and 715 p.s.i.g. |
| Glyoxal | 70 | 22<br>11 | 0-950 | No | |
| Methanol | 0 | 10 | 0-1000 | No | Gottschlich and Jaglom (*5*) found small 3-phase regions in binary and ternary systems, respectively |
| Methyl ethyl ketone | 34 (two phases) | 10 | 0-1000 | No | |
| | | 11 | 0-800 | Yes[a] | Water is precipitated nearly quantitatively from satd. MEK at ethylene pressure of 350 p.s.i.g. |
| Methyl Cellosolve | 20 | 20 | 0-1000 | No | Very low solubility of ethylene in liquid |
| | 20 | 10 | 0-1000 | No | Very low solubility of ethylene in liquid |
| Methylal | 20 (two phases) | 21 | 0-1000 | Yes | Ethylene decreases the solubility of methylal in water |
| Morpholine | 25 | 20 | 0-1000 | No | Extremely low solubility of ethylene in liquid |
| | 25 | 10 | 0-1000 | No | Extremely low solubility of ethylene in liquid |
| Isopropyl alcohol | 1 | 20 | 0-930 | No | 930 p.s.i.g. is critical pressure at 20° C. |
| | 1 | 10 | 0-800 | No | 800 p.s.i.g. is critical pressure at 10° C. |
| | 50 | 10 | 0-1000 | No | |
| *n*-Propyl alcohol | 15 | 10 | 0-1000 | No[a] | At 780 p.s.i.g. and 10° C., five phases coexist: solid $C_2H_4$-hydrate, water-rich liquid, propanol-rich liquid, ethylene-rich liquid, ethylene vapor |
| | 25 | 10 | 1000 | Yes[a] | |
| Propionaldehyde | Two phases | 11 | 0-800 | Yes | Ethylene causes no additional separation above that occurring in liquid binary |
| Propionic acid | 27 | 10.5 | 0-1000 | Yes | Light liquid phase forms at 680 p.s.i.g. |
| Pyridine | 25 | 10.4 | 0-1000 | Yes | Light liquid exists between 700 and 790 p.s.i.g. |
| Triethylamine | 25 | 10.5 | 0-1000 | Yes | Heavy liquid phase forms at about 400 p.s.i.g.; separation appears to be quantitative |
| Triethanolamine | 40 | 10.5 | 0-1000 | No | Extremely low solubility of ethylene in liquid |
| Triethyl phosphate | 40 | 10.5 | 0-1000 | Yes[a] | Light liquid phase forms at approx. 740 p.s.i.g. |

[a] Solid ethylene hydrate forms in heavy or water-rich liquid phase.

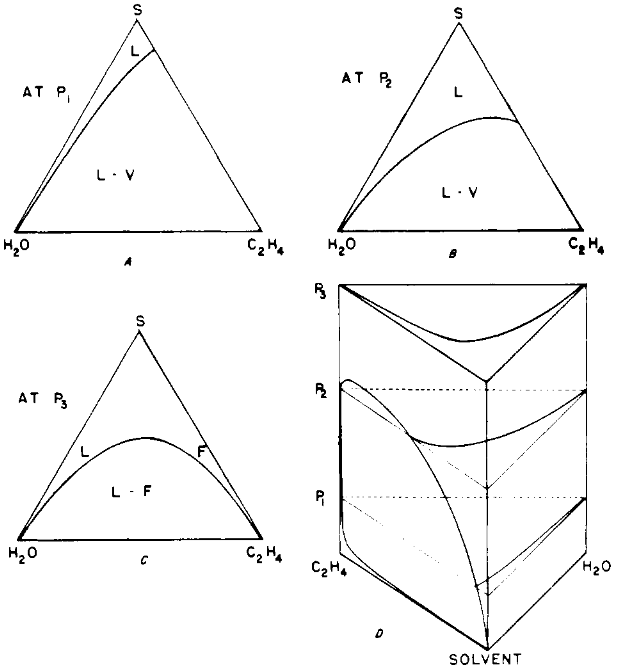

**Figure 2. Type 1 phase behavior in ethylene-water-solvent systems (Pattern 1)**

Schematic isobaric isotherms and pressure-composition isotherm

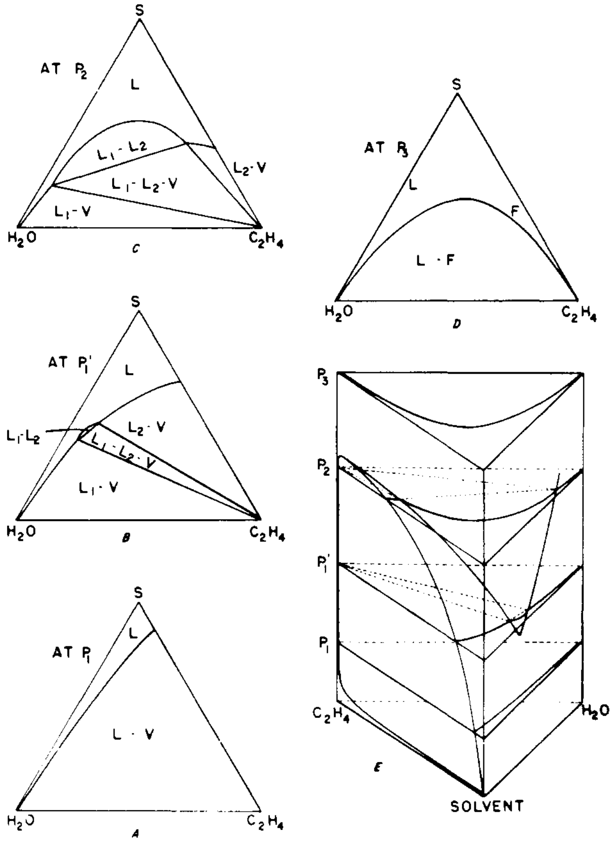

**Figure 3. Type 2 phase behavior in ethylene-water-solvent systems (Pattern 2)**

Schematic isobaric isotherms and pressure-composition isotherm

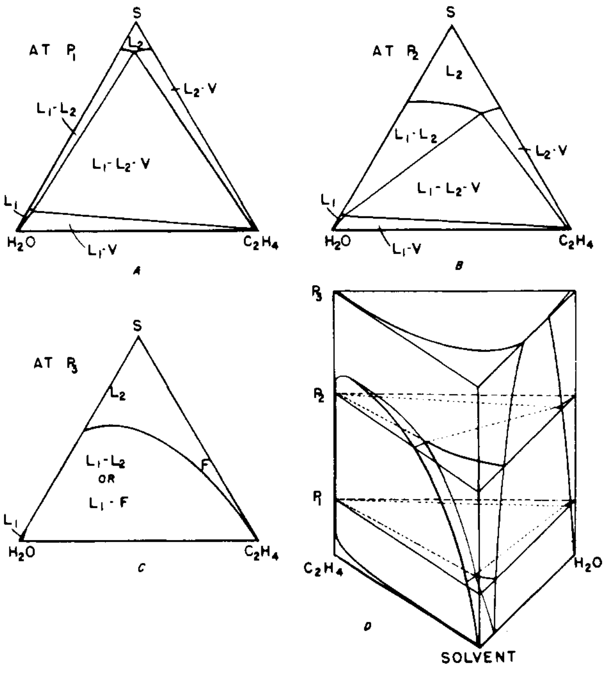

**Figure 4. Type 3 phase behavior in ethylene-water-solvent systems (Pattern 3)**

Schematic isobaric isotherms and pressure-composition isotherm

slowly (at dry ice temperature) into the gas-measuring apparatus. Analysis of the remaining binary liquid was obtained by means of density or refractive index determinations.

## RESULTS

**Qualitative Observations.** Qualitatively, the phase behavior observed for all systems studied can be classified into three generalized phase behavior patterns. These are shown diagramatically by the triangular diagrams of Figures 2, 3, and 4. In these diagrams, *S* represents a liquid organic compound, and pure ethylene is in the gas state (supercritical). *F* is a fluid phase. At the low temperatures under study, 10° to 30°, the vapor pressures of both water and the organic liquids are so small that the composition of the gaseous ethylene phase is almost pure ethylene and coincides with the vortex representing pure gas. The classification into which the individual systems studied fall in relation to these patterns may be seen from Table I together with the particular conditions of pressure, temperature, and composition under which they were observed. Two liquid phases apparently result from two different sources: (1) development of mutual immiscibility between water and the organic liquid in the presence of dissolved ethylene, and (2) liquefaction of gaseous ethylene above its critical temperature because of nonideality induced in the vapor phase by the presence of relatively small amounts of the vapor of the organic liquid. A liquid ethylene phase containing relatively small amounts of the liquid results.

The three types of behavior differ in the degree of solubility exhibited in the water-solvent binaries and in the ternary systems. Two or even all three forms of the pressure-composition isotherms described may possibly occur in a single system at different temperatures. At a given temperature (all quantitative data reported later are at 15.0°C.), the phase behavior appears to depend primarily upon the hydrogen bond-forming tendency of the solvent.

Pattern 1. Systems of ethylene and water with organic solvents having a strong tendency to form hydrogen bonds, exhibit in the region of 10° to 15°C. the behavior illustrated in Figure 2. This is designated as Type 1. Representative compounds of this class are ethylene glycol, triethanolamine, glyoxal, methyl Cellosolve, morpholine, ethylenediamine, and possibly acetaldehyde*, isopropyl alcohol*, and methanol*. (The experimentally indicated phase behavior classification for the starred compounds here and below is subject to some uncertainty because of the limited number of observations made.) Other classes of compounds may exhibit this type of behavior at higher temperatures—i. e., temperatures above the upper critical solution temperature for any liquid phase miscibility gaps which exist in the three-component system.

Figure 2, *A*, illustrates the equilibrium which exists at $P_1$, a moderately low pressure at which the solubility of ethylene in both water and the solvent is low. The mutual solubilities of ethylene and water are very small, and they do not vary materially over the entire range of pressures used in this work (1 to 70 atm.) at ordinary temperatures. At a given temperature, however, the solubility of ethylene in the organic solvent increases markedly with pressure, in contrast to its solubility in water, so that at $P_2$ (an intermediate pressure level) the solvent-rich liquid phase in equilibrium with essentially pure ethylene contains about 50% of ethylene (Figure 2, *B*). As the pressure is raised above the critical pressure of the solvent-ethylene binary (Figure 2, *C*), this binary becomes completely miscible as a single fluid phase, *F*, and an isobaric cross section of the pressure-composition isotherm assumes the form of the familiar ternary diagram with a single nonconsolute pair (Figure 2, *D*). In this phase behavior pattern, there exists a maximum of two phases (liquid in equilibrium with vapor or fluid) over the entire range of pressures.

Pattern 2. Compounds which display this behavior pattern (Type 2, illustrated in Figure 3) with ethylene and water at temperatures of about 10° to 15°C. are liquids which have a lesser tendency to form hydrogen bonds, but have structures indicating both active hydrogen atoms and donor atoms. These include acetonitrile; *n*-propyl alcohol; *tert*-butyl alcohol; acetone; formic, acetic, and propionic acids; and triethyl phosphate*, triethylamine*, pyridine*, and formaldehyde*. The last four contain no active hydrogen atoms. Characteristic of this behavior type is the existence of a liquid phase miscibility gap within the pressure-composition prism which does not extend to the ethylene-solvent face of the prism.

At a low pressure $P_1$ the equilibrium is identical with that of Pattern 1. As the pressure is increased to a point between $P_1$ and $P_2$—e.g., $P_1'$—however, the equilibrium shifts to the form represented by the Figure 3, *B*. At this intermediate pressure, a second liquid phase forms at some intermediate water-solvent composition. This creates both a liquid-liquid area and a three-phase liquid-liquid-vapor region on an isobaric cross section of the pressure-composition isotherm. As the pressure is further increased to $P_2$, the solubility of ethylene in the lighter liquid phase (the solvent-rich phase) increases, and the miscibility gap becomes larger as is shown in Figure 3, *C*. This three-phase region vanishes again at an upper pressure point as the light liquid phase merges with the ethylene vapor phase (above the critical pressure of the ethylene-solvent binary). The result then, is a fluid phase in equilibrium with the water-rich liquid phase (Figure 3, *D*). Under these conditions, the isobaric composition triangle again becomes identical with that for similar pressures in Pattern 1.

Although phase equilibria for liquid-liquid-gas (supercritical) ternary systems of the type studied here do not appear to have been previously reported in the literature, liquid-liquid-solid systems exhibiting phase diagrams similar to that of Figure 3, *C*, are well known and several have been quantitatively measured. Typical among these is the sodium chloride-ethanol-water system. In (*10*) these liquid-liquid-solid systems, the *T–x* isobars are similar in appearance to the *P–x* isotherms described above for liquid-liquid-gas systems. The phase equilibrium phenomenon exhibited by such systems in which an aqueous organic solution is caused to split into two phases by the addition of a solid solute, normally an inorganic salt, is commonly called "salting out" and has long been employed in both laboratory and plant as a method of separating organic compounds from water. The solid used is commonly called a salting out agent. Here by analogy, is a salting out process in which a supercritical gas, $C_2H_4$, is the salting out agent. The advantages of a salting out process employing a gaseous separating agent over a solid are obvious when the simplicity of separating and recovering the gas from both phases, contrasted with removing a solid solute, is considered.

Pattern 3. When the miscibility gap in the three-component system is large enough to intersect the water-solvent face of the pressure-composition prism, the phase relationships become as shown in Figure 4. The larger miscibility gap may occur either because of the chemical nature of the third (solvent) component or through a lowering of the temperature. Compounds which exhibit behavior of this type at about 10° to 15°C. are those liquids whose structures possess donor but no active hydrogen atoms. Specifically, they include methyl ethyl ketone, ethyl acetate, propionaldehyde, methylal, and *sec*-butyl alcohol.

The constant-pressure cross sections for this case differ from those of Pattern 2 at the same pressures only in that at all pressures considered here the solvent-water binary consists of two liquids over a wide range of binary compositions. The immiscibility is enhanced by increasing the ethylene content as it is for Pattern 2. Hence, it is possible further to dehydrate such solvents—e.g., methyl-ethyl-ketone—by using supercritical ethylene as a separating agent even though the solvents themselves are still partially miscible with water in the absence of ethylene.

**Quantitative Results.** Phase equilibrium data for the systems quantitatively studied are presented graphically in the triangular phase diagrams of Figures 5 to 14, inclusive. Compositions in all cases are expressed in weight per cent. The dashed lines are experimentally determined tie lines.

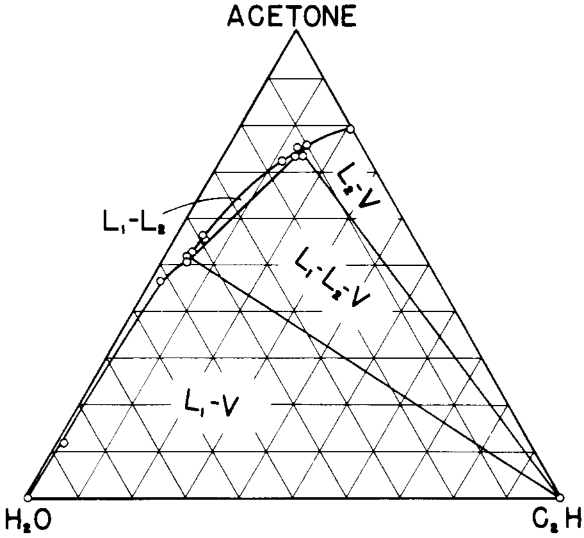

Figure 5. Phase equilibrium diagram for ethylene-water-acetone at 415 p.s.i.a. and 15°C.

The two samples determining each were taken nearly simultaneously, as described in the procedure.

Because the phase behavior type which appeared to hold most interest at the conclusion of the qualitative exploratory study was that in which a liquid phase split occurred, a series of compounds found qualitatively to exhibit Behavior Pattern 2 or 3 was selected for quantitative investigation. These compounds are acetone, *n*-propyl alcohol, *tert*-butyl alcohol, acetic acid, propionic acid, and acetonitrile, and methyl ethyl ketone (Pattern 3). The latter is an important industrial solvent—e.g., in lubricating oil, dewaxing—and one which is somewhat difficult to dehydrate to very low water contents. A single isobaric composition diagram was determined for each of these compounds (with ethylene and water) at 15°C. For the acetone system the diagrams were determined at three different pressures in order to construct and examine the pressure-composition isotherm.

Acetone. Figures 5, 6, and 7 show the isobaric cross sections of the pressure-composition isotherm constructed from the experimentally determined phase compositions for the acetone-water-ethylene system at 415, 515, and 715 p.s.i.a., respectively, each at 15.0°C. The complete isotherm is given in the three-dimensional diagram of Figure 8. At 415 p.s.i.a., the difference between the solubilities of ethylene in water and in acetone is just sufficient to split the liquid into two layers. Actually, the exact pressure at which this split commences was not determined experimentally, but extrapolation of the loci of the light liquid and heavy liquid compositions on the $P-x$ isotherm indicates that it is at about 350 p.s.i.a. At 415 p.s.i.a. the heavy liquid in the three-phase region contains 54% acetone by weight on an ethylene-free basis; the light liquid, 86%. At 515 p.s.i.a. these compositions are 41% acetone in the heavy liquid and 93% in the light liquid, respectively. At 715 p.s.i.a. they have become 21% and 95%, respectively. The ethylene content of these liquid phases decreases in the heavy liquid from 5 to 1% of ethylene and increases in the light liquid from 14 to 84% as the pressure is increased from 415 to 715 p.s.i.a.

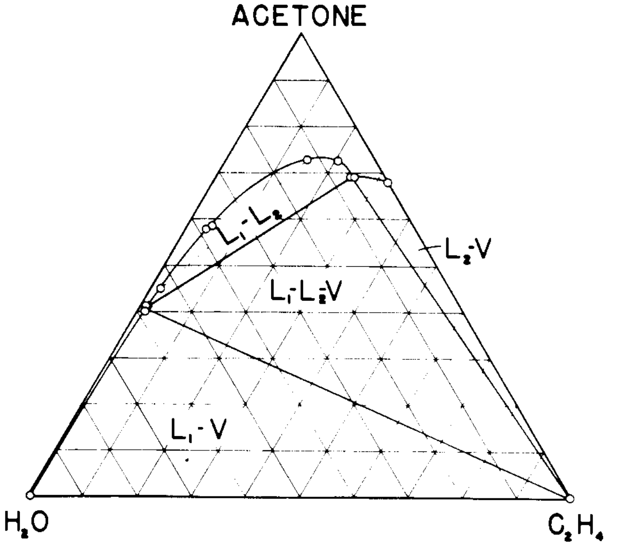

Figure 6. Phase equilibrium diagram for ethylene-water-acetone at 515 p.s.i.a. and 15.0° C.

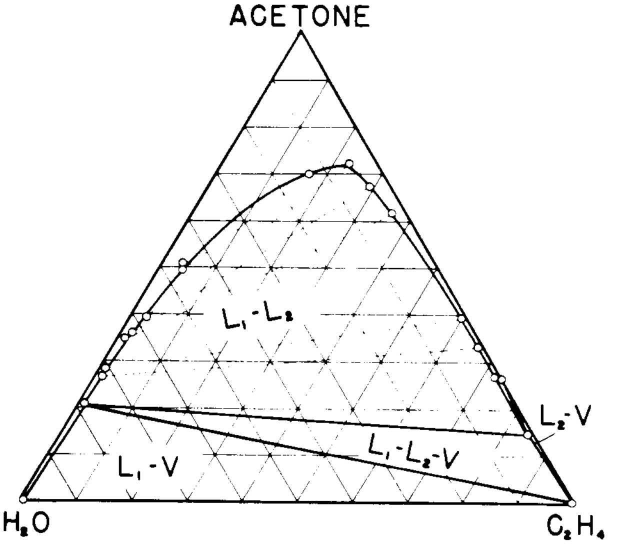

Figure 7. Phase equilibrium diagram for ethylene-water-acetone at 715 p.s.i.a. and 15.0° C.

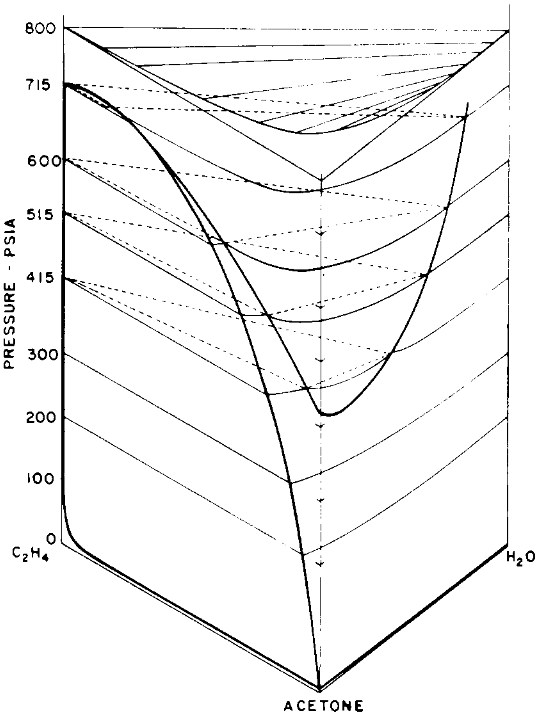

Figure 8. Pressure-composition isotherm for ethylene-water-acetone at 15.0° C.

In the acetone system, as for other systems which exhibit phase behavior of this type, the second liquid phase forms at an intermediate solvent-water composition, while the three-phase region vanishes at a point where the heavy liquid phase also has an intermediate composition.

Methyl Ethyl Ketone. The next ketone above acetone in molecular weight, methyl ethyl ketone, exhibits Phase Behavior Pattern 3 with water and ethylene at 515 p.s.i.a. and 14.9°C. The diagram for this system is shown in Figure 9. Although the ketone-water binary still exhibits a rather wide miscibility gap, the mutual solubilities are somewhat greater than at atmospheric pressure. The im-

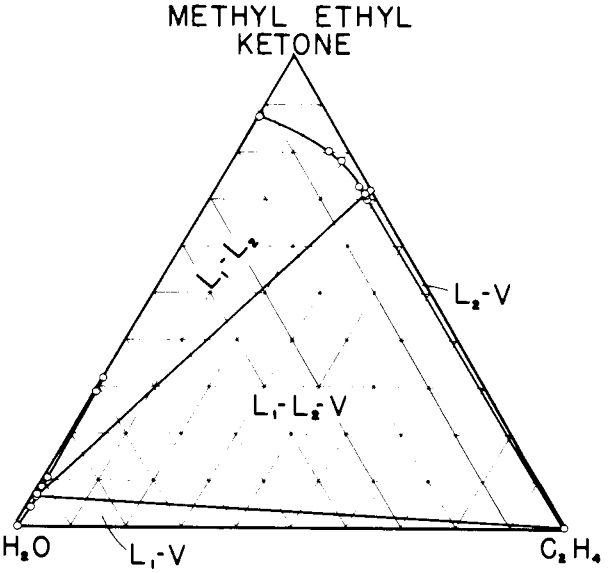

Figure 9. Phase equilibrium diagram for ethylene-water-methyl ethyl ketone at 515 p.s.i.a. and 14.9°C.

miscibility rapidly increases, however, as ethylene is added to the system. The two liquid phases which exist in the invariant three-phase region have the following ethylene-free compositions: 6.5% methyl ethyl ketone in the heavy liquid and 98% methyl ethyl ketone in the light liquid, respectively. This split will be even wider at higher pressure. The dehydration of methyl ethyl ketone to water contents below 1% by weight by this process should, therefore, be relatively easy to accomplish.

*n*-Propyl Alcohol. *n*-Propyl alcohol with ethylene and water displays Phase Behavior Pattern 2. The liquid phase split, however, does not commence until the pressure exceeds 500 p.s.i.a. Consequently, the phase diagram for this system was determined at 715 p.s.i.a. (Figure 10). The ethylene-free compositions of the liquid phases in the three-phase region are 21% *n*-propyl alcohol for the heavy liquid and 73% for the light liquid. These figures indicate the degree of separation which can be attained in a single contact at this pressure (and temperature). At higher pressures and/or lower temperatures, the separation of propyl alcohol and water is enhanced.

*tert*-Butyl Alcohol. The ternary constant pressure and temperature diagram for the *tert*-butyl alcohol-water-ethylene system, presented in Figure 11, was determined at 515 p.s.i.a. It resembles that for *n*-propyl alcohol at 715 p.s.i.a. The ethylene-free compositions of the light and heavy phases in the invariant region are 69.5 and 25% *tert*-butyl alcohol, respectively. Again, a greater separation can be attained in the three-phase region at higher pressures and/or lower temperatures. Experiment shows that a wide split between water and alcohol occurs in this system at pressures of 915 p.s.i.a. even at temperatures as high as 30°C. Visually no noticeable change in the contents of the chamber occurred when the temperature was lowered to 10°C.—i.e., the relative volumes of the phases present in the bomb changed little over this temperature range. This indicates that the liquid phase miscibility gap in this system extends to temperatures above 30°C. and that the limits of the miscibility gap do not change appreciably over this temperature range in the pressure region investigated.

Acetic Acid. The phase diagram for the acetic acid–water-ethylene system shown in Figure 12 was determined at a pressure, 783 p.s.i.a., slightly below the critical pressure for the ethylene–acetic acid binary. This system and that for acetone at 715 p.s.i.a. (Figure 7) represent the phase equilibrium occurring in Behavior Pattern 2 at pressures between $P_2$ and $P_3$ (Figure 3). It is evident that the concentration of solvent (acetic acid here) need not be low in the heavy liquid phase at pressures just below the solvent-ethylene critical point. Under the conditions of Figure 12, the ethylene-free compositions of the light and heavy liquids existing in the invariant region are 99 and 78% acetic acid, respectively.

Propionic Acid. Figure 13 is the phase diagram found for the propionic acid–ethylene-water system. It differs from that for the acetic acid system at the same conditions of temperature and pressure. The isobaric cross section of the $P - x$ isotherm for the propionic acid system resembles more closely the behavior of the acetone system at 715 p.s.i.a. (Figure 7). The longer carbon chain apparently hinders the hydrogen-bonding tendencies of the acid sufficiently or the hydrophobic property of the hydrocarbon portion of this compound is sufficient to produce a liquid-liquid equilibrium over a much greater range of water-acid compositions than for acetic acid. The ethylene-free composition of the heavy liquid in the invariant region is much lower in acid content, 31.5% propionic acid, and higher for the light liquid, nearly 100% propionic acid. Hence an ethylene extraction process for separating propionic acid and water should be readily

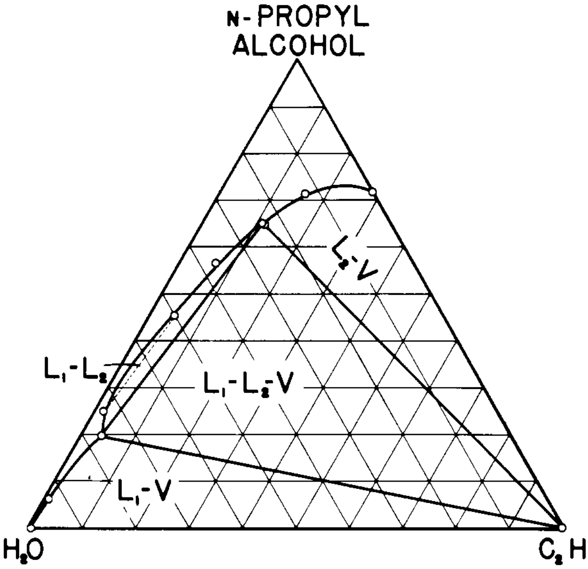

Figure 10. Phase equilibrium diagram for ethylene-water-*n*-propyl alcohol at 715 p.s.i.a. and 15.0°C.

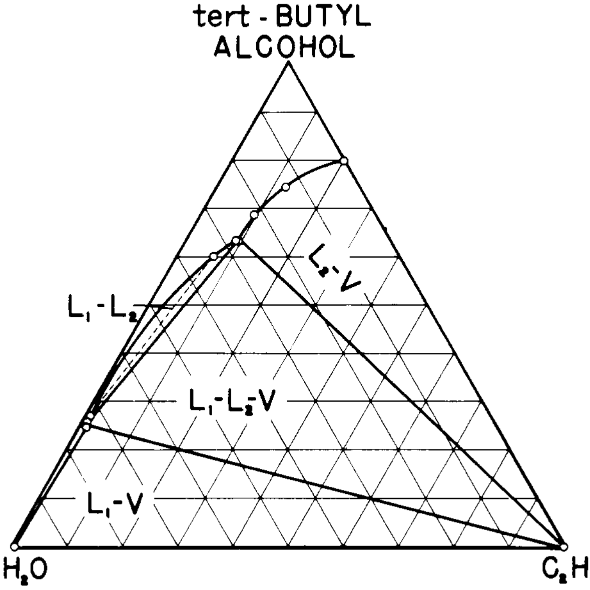

Figure 11. Phase equilibrium diagram for ethylene-water-*tert*-butyl alcohol at 515 p.s.i.a. and 15.0° C.

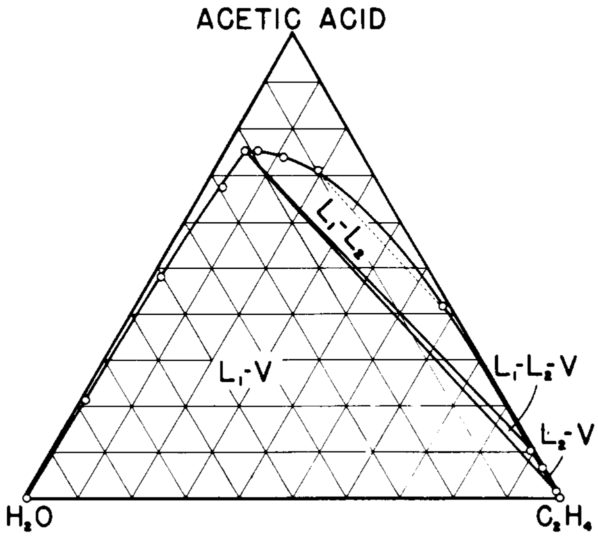

Figure 12. Phase equilibrium diagram for ethylene-water-acetic acid at 783 p.s.i.a. and 15.0° C.

feasible at or near the conditions employed. For this system (see Figure 13) the solubility of ethylene in pure propionic acid was not measured. This measurement was omitted in this case, because an analysis of the light liquid phase in the invariant region revealed essentially no water content.

Acetonitrile. The separation of water present as an impurity, from acetonitrile under ethylene pressure, was first noted in this laboratory by Sykes (9). Sykes' observations were made at the considerably lower temperature of −15°C.

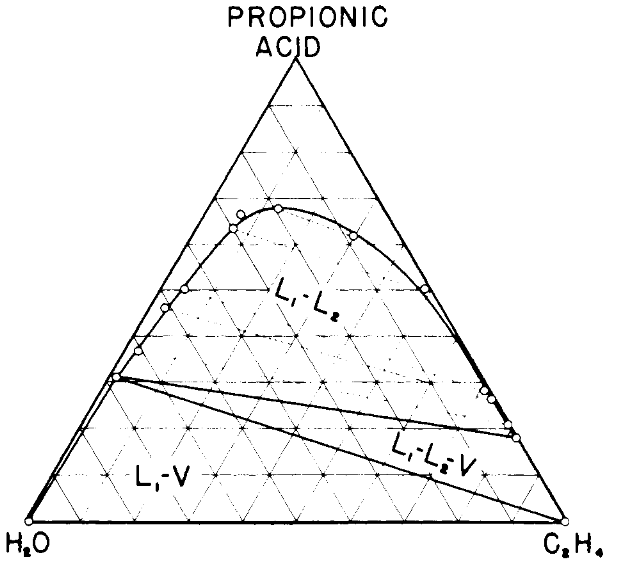

**Figure 13. Phase equilibrium diagram for ethylene-water-propionic acid at 783 p.s.i.a. and 15.0° C.**

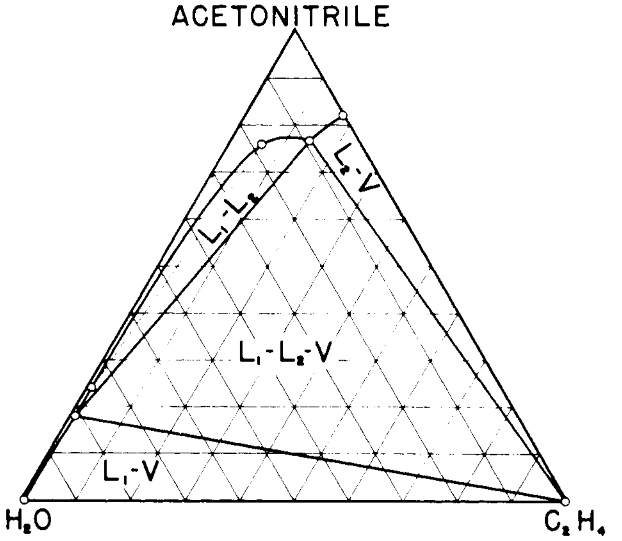

**Figure 14. Phase equilibrium diagram for ethylene-water-acetonitrile at 515 p.s.i.a. and 15.0° C.**

However, it is seen from Figure 14 that at 15°C. and 515 p.s.i.a. the completely miscible water-acetonitrile binary is readily separated by the addition of ethylene into two partially immiscible liquid phases containing 17 and 90% acetonitrile respectively, on an ethylene-free basis. At lower temperatures and/or at higher pressures the separation is more nearly complete. It is not unlikely that a 99% acetonitrile could be obtained from such an ethylene extraction process.

## QUALITATIVE STUDY OF OTHER SYSTEMS

sec-Butyl Alcohol. With water and ethylene, sec-butyl alcohol shows a behavior similar to that of methyl ethyl ketone (Pattern 3). Most of the small amount of water present in the saturated alcohol phase is precipitated into a second liquid phase on the addition of ethylene at 10°C. and 600 p.s.i.a.

**Methylal.** In the binary methylal (dimethoxymethane)-water system, water is very insoluble in the organic phase, while methylal is appreciably soluble in water. At 21°C. and 1000 p.s.i.a. a portion of this small quantity of methylal was found to be extracted from the water by ethylene with the resultant formation of a second (lighter) liquid phase.

**Triethylamine.** With ethylene and water, triethylamine follows Behavior Pattern 2 at 10.5°C. A phase separation occurs at about 450 p.s.i.a. in which the removal of water from the amine appears to be nearly quantitative. At temperatures above 19°C., the lower critical solution temperature for the triethylamine binary, $P - x$ isotherms according to Pattern 3 may be predicted for this system.

In the work subsequent to that reported here, Meter (*8*) has studied water-organic amine-supercritical ethylene systems in considerable detail. His work verifies and extends the present results.

## DISCUSSION

**Effect of Molecular Properties. Hydrogen Bonding.** It has been postulated above that the phase behavior of a system containing water, ethylene, and an organic liquid under the present conditions depends primarily on the hydrogen bond-forming tendency of the organic liquids. Those which tend to form strong hydrogen bonds also tend to be completely miscible with water. In this category are the compounds which behave as illustrated in Pattern 1. As the hydrogen bond-forming tendency of the organic compound decreases its mutual solubility with water decreases, and the phase behavior in the ternary system shifts next to that classified as Pattern 2 and with further diminution of this property to Pattern 3.

A useful classification of compounds according to their tendency to form hydrogen bonds has been proposed by Ewell, Harrison, and Berg (*4*). Their classification is as follows:

Class I. Liquids capable of forming three-dimensional networks of strong hydrogen bonds—e.g., water, glycol, glycerol, amino alcohols, hydroxylamine, hydroxyl acids, polyphenols, amides, etc. Compounds such as nitromethane and acetonitrile also form three-dimensional networks of hydrogen bonds, but the bonds are much weaker than those involving OH and NH groups. Therefore, these types of compounds are placed in Class II.

Class II. Other liquids composed of molecules containing both active hydrogen atoms and donor atoms (oxygen, nitrogen, and fluorine)—e.g., alcohols, acids, phenols, primary and secondary amines, oximes, nitro compounds with α-hydrogen atoms, nitriles with α-hydrogen atoms, ammonia, hydrazine, hydrogen fluoride, hydrogen cyanide, etc.

Class III. Liquids composed of molecules containing donor atoms, but no active hydrogen atoms—e.g., ethers, aldehydes, ketones, esters, tertiary amines (including pyridine type), nitro compounds and nitriles without α-hydrogen atoms, etc.

Class IV. Liquids composed of molecules containing active hydrogen atoms but no donor atoms. These are molecules having two or three chlorine atoms on the same carbon atom as a hydrogen atom, or one chlorine atom on the same carbon atom and one or more chlorine atoms on adjacent carbon atoms—e.g., $CHCl_3$, $CH_2Cl_2$, $CH_3CHCl_2$, $CH_2Cl—CH_2Cl$, $CH_2Cl—CHCl—CH_2Cl$, $CH_2Cl—CHCl_2$, etc.

Class V. All other liquids—i.e., liquids having no hydrogen bond-forming capabilities, such as hydrocarbons, carbon disulfide, sulfides, mercaptans, halohydrocarbons not in Class IV, nonmetallic elements such as iodine, sulfur, phosphorus, etc.

The phase equilibrium behavior pattern with ethylene and water of the compounds studied in the present work are compared in Table II with their hydrogen bond classification in this system. It is seen that the hydrogen bond-forming class of the compounds and their phase behavior pattern with ethylene and water are closely related. This

**Table II. Comparison of Hydrogen Bond-Forming Tendency with Phase Behavior Classification**

| Compound | Hydrogen-Bonding Classification | Phase Behavior Classification |
|---|---|---|
| Acetaldehyde | 2 | 1[a] |
| Ethyl alcohol | 2 | 1[a] |
| Ethylenediamine | 1 | 1 |
| Ethylene glycol | 1 | 1 |
| Glyoxal | 1 | 1 |
| Isopropyl alcohol | 2 | 1[a] |
| Methanol | 2 | 1[a] |
| Methyl Cellosolve | 1 | 1 |
| Morpholine | 1 | 1 |
| Triethanolamine | 1 | 1 |
| Acetone | 2 | 2 |
| Acetonitrile | 2 | 2 |
| Formic acid | 2 | 2 |
| Acetic acid | 2 | 2 |
| Propionic acid | 2 | 2 |
| Formaldehyde | 2 | 2 |
| *n*-Propyl alcohol | 2 | 2 |
| *tert*-Butyl alcohol | 2 | 2 |
| Pyridine | 3 | 2 |
| Triethylamine | 3 | 2 |
| Triethyl phosphate | 3 | 2 |
| Ethyl acetate | 3 | 3 |
| *sec*-Butyl alcohol | 3 | 3 |
| Methylal | 3 | 3 |
| Methyl ethyl ketone | 3 | 3 |
| Propionaldehyde | 3 | 3 |

[a] Classification uncertain.

agreement indicates that the hydrogen-bonding property of an organic compound is a primary factor in determining its phase equilibrium behavior under the present circumstances.

In the cases where the classifications do not appear to correspond in Table II, uncertainty as to the proper classification with respect to one of the other properties exists. For acetaldehyde, ethyl alcohol, and isopropyl alcohol, it is possible that a small two-liquid phase region exists, which may not have been detected in the preliminary qualitative explorations before the experimental sophistication of the later work was developed. This also probably explains the apparent discrepancy for the case of methanol between the results reported by Jaglom (*7*) and the present work. Jaglom reports a narrow three-phase region for the methanol-water-ethylene system at 10.5°C. In this system, the upper critical solution temperature (ternary) appears to be within the range of temperatures studied, so that a small disappearing three-phase region could have failed to be detected because of the small number of water-solvent binary compositions included in the qualitative explorations.

It is probable that the types of phase behavior encountered in the present work are representative of those which will be exhibited by a wide variety of systems and that the primary factor which determines the particular phase behavior pattern exhibited by a given system is the extent of similarity in the intermolecular attractive forces of the two solvents used and the chemical nature of the gaseous component relative to that of the solvent.

**Polarity.** Ewell, Harrison, and Berg (*4*) indicate that for binary systems the second most important influence on the extent and the direction of the deviation from Raoult's law is the difference in polarities of the dipole moments of the components. Although there are no data in the present work to indicate a secondary dependence with respect to a particular phase behavior classification on a difference in dipole moment between the liquid components, such dependence probably exists. The immiscibility in the system ethylene-technical grade *o*-dichlorobenzene disclosed by Todd (*11*) may result from this effect. The impurity largely present in the *o*-dichlorobenzene was probably the para isomer. This isomer has a dipole moment of zero compared with a relatively large dipole moment of 2.3 Debye units for the ortho isomer. Todd found nonpolar ethylene to be considerably more soluble in nonpolar *p*-dichlorobenzene than in the more highly polar ortho compound (approximately 45 weight % of ethylene in *p*-dichlorobenzene at 600 p.s.i.a. compared with 18% in *o*-dichlorobenzene at this pressure). This difference in solubilities may permit a liquid-liquid separation of these two isomers through the use of ethylene at suitable conditions of temperature and pressure. A similar separation method for mixtures of other polar-nonpolar isomers may likewise be feasible using either a nonpolar or a polar gaseous "salting-out" agent.

**Functional Groups.** It appears that a functional group in the molecule affects the phase behavior with ethylene and water only to the degree that it determines the hydrogen-bonding characteristics or the dipole moment. Thus, those compounds containing either individual functional groups or arrangements of functional groups which provide both strong electron donors (O, N, F) and active hydrogen atoms (as in OH and NH) fall into Class I of the hydrogen-bonding classification and exhibit Behavior Pattern 1 with ethylene and water. Corresponding relationships appear to hold for the other classifications.

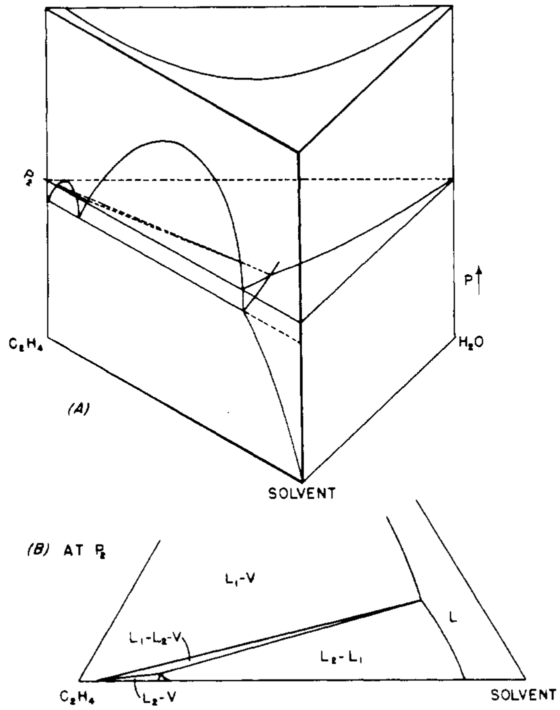

**Figure 15. Schematic isotherm showing liquid immiscibility in the solvent-ethylene binary**

Three exceptions to this solubility behavior scheme seem to be indicated by the present work—i.e., triethylamine, triethyl phosphate, and pyridine. In each of these cases, apparently, the functional group retains sufficient hydrophylic character to prevent the formation of a miscibility gap in the solvent-water binary. Thus these compounds behave according to Pattern 2 and are classified as Type 3 in hydrogen bond-forming tendency.

**Chain Length.** As its hydrocarbon chain length is increased, a compound becomes more soluble in hydrocarbons and less soluble in water. It is not, therefore, unexpected that increasing chain length results in an increased tendency toward Type 3 phase behavior in contrast to Type 1, as exemplified by acetaldehyde (Type 1) and propionaldehyde (Type 3); and by acetone (Type 2) and methyl ethyl ketone (Type 3).

**Effect of Temperature and Pressure.** The effect of pressure on the phase equilibria of the systems studied is shown quantitatively for the case of acetone in Figure 8. In all cases, the solubility of ethylene in a given organic liquid is increased by pressure until a critical solubility point is reached or a separation into two liquid layers occurs. Where the critical point is reached before liquid phase immiscibility occurs, no opportunity exists for the separation of water and the organic liquid. In Behavior Pattern 2, however, increased concentrations of dissolved ethylene in the liquid, produced by increased pressures, produce a liquid phase miscibility gap. This gap widens as the pressure is increased until, at the critical pressure of the solvent-ethylene binary, the greatest possible liquid-liquid separation between water and organic liquid is achieved. In other words, in the region of two liquid phases, higher pressure increases the separation factor. Above the solvent-ethylene critical solution pressure the separation factor continues to increase, but the phases involved are then a water-rich liquid and a supercritical fluid in which the concentration of the organic liquid is relatively low.

The effect of temperature on any specific system was not determined quantitatively in this study. It was observed, however, that for the acetic acid-water-ethylene system at one liquid binary composition at least containing approximately 20% water, no liquid miscibility gap exists at 20°C. while one does exist at 10.5°C. A further indication that the liquid miscibility gap for this system widens at lower temperatures is the result in Figure 12. The gap approaches its widest point or highest pressure at 783 p.s.i.a. at 15°C., and under these conditions covers a very narrow range of water-acetic acid compositions. On the other hand, at a temperature of 10.5°C., approximately the same degree (composition range) of immiscibility was observed qualitatively at the narrowest point (lowest pressure) of the miscibility gap.

For the acetone system, it was also found qualitatively that at approximately the same pressure and for the same initial quantity and composition of the acetone-water mixture charged to the equilibrium chamber, a smaller quantity of aqueous phase remained as liquid phase at 10°C. than at 20°C. This indicates that more acetone was removed from the water phase at the lower temperature.

These results indicate that in these equilibria a lower temperature in general decreases the mutual liquid solubilities. Because this is the usual behavior in most liquid-liquid systems, a given system may possess complete liquid miscibility (Behavior Pattern 1) at one temperature, ternary liquid immiscibility but not solvent-water immiscibility (Behavior Pattern 2) at a lower temperature, and finally binary as well as ternary liquid immiscibility (Behavior Pattern 3) at a still lower temperature. This final temperature will be below the solvent-water critical solution temperature.

**Liquid Immiscibility in Solvent-Ethylene Binaries.** For the conditions under which the present systems were studied, partial miscibility of the ethylene-solvent binaries in the liquid phase was not observed. In a number of systems reported by Todd (*11*), Jaglom (*7*), and Gottschlich (*5*), partial miscibility in the ethylene-organic liquid binary was, however, found to exist.

A true liquid miscibility gap in the ethylene-solvent binary would produce a special case of Behavior Pattern 2 as illustrated diagrammatically in Figure 15. For such systems, the water (or similar third component) concentration at which the liquid phase immiscibility first occurs with increasing the pressure (see Figure 3, *E*) may be considered for illustration to lie outside the ethylene-solvent face of the $P-x$ prism. The three-phase region in the ternary system would then exist as shown only over a very narrow pressure range and a cross section of the isotherm at a pressure, $P_2$, within this range, would resemble Figure 15, *B*. In this diagram the liquid-liquid equilibrium envelope intersects the solvent-ethylene face of the $P-x$ prism along with the light liquid-vapor envelope. If the pressure at which the light liquid-vapor equilibrium vanishes is assumed to be the critical pressure for the solvent-ethylene binary (as in the previous discussion), there exists above the critical pressure (say at $P_1$) a fluid-liquid equilibrium in the binary system and a higher pseudo-critical pressure for the system. This pseudo-critical pressure appears to be well above 1500 p.s.i.a. for some of the systems reported by Todd and Gottschlich, and experimental determination of its exact value is difficult because of the steep slope of the surface intersected by the face of the prism. Todd and Jaglom differed on the value in the case of *n*-propyl at 10.5°C. by as much as 175 p.s.i.

It is possible that the presence of a small quantity of water or some other impurity in the organic liquid might result in an apparent immiscibility in the binary liquid system when in fact none actually exists for the pure organic compound. Measurements of this type offer many experimental complications. For example, in systems having isotherms similar to that for acetic acid (its constant-pressure cross section is shown in Figure 12), a small quantity of water could produce the liquid-liquid separation occurring at very low water concentrations. The resulting binary $P-x$ diagram would have the same general appearance as the ethylene-solvent face of Figure 15, *A*.

**Separation Factors.** The separation factor, $\alpha$, for these systems may be defined as the solvent-to-water concentration ratio in the light liquid phase divided by the same concentration ratio for the heavy liquid phase (all on an ethylene-free basis). The values of the separation factor for the equilibria existing in the three-phase regions for the systems quantitatively measured are given in Table III. Because $\alpha$ may vary appreciably over wide ranges of pressure, temperature, or composition, these values are useful mainly to indicate the degree of separation which may be expected.

**Table III. Separation Factors Calculated from Three-Phase Equilibria Compositions Using Supercritical Ethylene**

| Solvent | Pressure, P.S.I.A. | Solvent Concentration[a] | $\alpha$ |
|---|---|---|---|
| Acetone | 415 | 54–86 | 5 |
| Acetone | 515 | 41–93 | 19 |
| Acetone | 715 | 21–95 | 71 |
| Methyl ethyl ketone | 515 | 65–98 | 705 |
| *n*-Propyl alcohol | 715 | 21–73 | 10 |
| *tert*-Butyl alcohol | 515 | 25–69 | 7 |
| Acetic acid | 783 | 78–>99 | >28 |
| Propionic acid | 783 | 31–100 | ∞ |
| Acetontrile | 515 | 17–90 | 44 |

[a] Ethylene-free solvent concentration range (weight per cent) over which values of $\alpha$ were determined.

**Application of Supercritical Ethylene in a Separation Process.** The type of phase equilibrium behavior in systems of the nature studied may be made the basis for potentially important new separation methods. As an illustration, consider the dehydration of methyl ethyl ketone, and use as the basis the equilibrium observed with ethylene for the conditions studied (Figure 9). These are not necessarily optimum conditions of temperature and pressure, because the separation is limited to a residual water content of 2% of the ketone. However, they indicate the potential simplicity of such a separation scheme.

The equipment required would be essentially that illustrated in the flow diagram of Figure 16. It consists of a high-pressure mixer-settler, flash drums for each liquid phase, a compressor for recycling ethylene, and a high-pressure pump for introducing wet solvent into the system.

On the basis of 100 pounds of actual methyl ethyl ketone plus its water content when saturated, methyl ethyl ketone at 15°C. and atmospheric pressure (11 pounds of water), the projected process using ethylene would split this feed in a single stage into two fractions: one containing 8.0

pounds of water and 0.6 pound of methyl ethyl ketone, the other containing 99.4 pounds of methyl ethyl ketone and 2.0 pounds of water. Thus approximately 90% of the water content would be removed from the methyl ethyl ketone with a loss of about 0.6% of the solvent.

The major operating cost for such a process appears to be the cost for the recompression of the recycled ethylene.

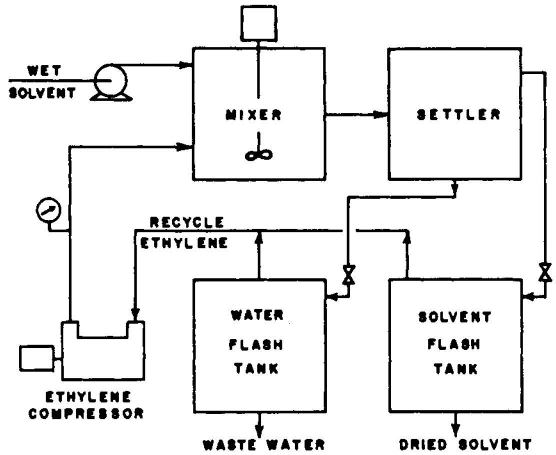

**Figure 16. Schematic flowsheet for ethylene dehydration of solvents**

For this example, the theoretical work of isothermal compression required to supply the necessary amount of ethylene (40 pounds) at the system pressure (515 p.s.i.a.) is 1.5 kw.-hr. Applying conservative values of compressor efficiency (25%) and power cost (1.0 cent per kw.-hr.) to this figure, one arrives at a magnitude for this portion of the operating cost of about 6 cents per 100 pounds of methyl ethyl ketone processed. This cost is approximately equal to the value of the methyl ethyl ketone lost with the discarded water. Undoubtedly dehydration to remarkably small water contents can be achieved by this method by suitable adjustment of temperature and pressure conditions.

## ACKNOWLEDGMENT

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## NOMENCLATURE

$F$ = fluid phase existing above critical pressure of ethylene-solvent binary at temperature of diagram
$L$ = single liquid phase existing over entire range of water-solvent compositions, usually at low ethylene concentrations
$L_1$ = water-rich or more dense liquid phase
$L_2$ = solvent-rich or less dense liquid phase
$P_1$ = low pressure, about 1 to 5 atm.
$P_2$ = moderate pressure, below critical pressure of ethylene-solvent binary
$P_3$ = high pressure, above critical pressure of ethylene-solvent binary
$S$ = solvent component of system: ethylene, water, solvent
$V$ = vapor (or gas) phase, essentially pure ethylene

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# Phase Behavior of the System $UO_2SO_4$-$CuSO_4$-$H_2SO_4$-$H_2O$ at Elevated Temperatures

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The fuel solution proposed for use in the second homogeneous reactor experiment at Oak Ridge was a heavy water solution, 0.04 molal in uranyl sulfate and 0.005 molal in copper sulfate. The purpose of the copper sulfate was to provide for the liquid-phase catalysis (*1*) of the deuterium-oxygen recombination reaction, thus eliminating problems associated with handling large volumes of an explosive mixture of radiolytic gas in the reactor system. Earlier experience with dilute uranyl sulfate solutions had indicated that increases in temperature promoted hydrolysis of the uranyl ion to such an extent that basic salts or hydrated oxides of uranium precipitated. In concentration regions where a hydrolytic precipitate was not encountered, the temperature limit of homogeneity was fixed by the appearance of a second liquid phase (*3*). Posnjak and Tunell (*2*) have reported studies of the copper sulfate system to 200°C. in which analogous promotion of hydrolysis by increased temperatures was indicated, the predominant solid phase encountered being the basic copper sulfate, $3CuO.SO_3.2H_2O$.

The addition of sulfuric acid to such solutions would be expected to oppose and retard the hydrolysis reaction. Furthermore, the addition of acid to uranyl sulfate solutions was known to cause the liquid miscibility gap (two-liquid phase region) to shrink in scope. The effect of sulfuric acid in either case was to elevate the temperature ceiling on the region of one liquid phase homogeneity. However, use of an excessive amount of acid in the reactor system was objectionable primarily because it would increase the corrosiveness of the solution and secondarily because it would increase the neutron losses in the reactor. The work reported here is a systematic determination of this temperature ceiling for a single liquid phase homogeneity as a function of the copper sulfate concentration, the uranyl sulfate

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