# Effect of Triple-Bond Position on Thermodynamic Properties of Mixtures: Phase Equilibria For The System Acetone-3-Hexyne

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Vapor-liquid equilibrium data have recently been reported for mixtures of polar organic solvents with 1-hexyne (*1*). In order to establish how mixture properties are affected by the position of the triple bond, we have obtained experimental measurements for the system acetone-3-hexyne.

Isothermal total-pressure measurements were made using the experimental technique described previously (*1* to *3*). Acetone prepared as before (*1*), and with comparable purity, was used. The 3-hexyne was distilled at high reflux in a 10-plate Oldershaw column and dried over molecular sieves. Chromatographic analysis indicated purity to be about 99%. Vapor pressures of the pure liquids are given in Table 1. Measurements over the entire composition range were made at 0, 25 and 55°C. The data were reduced with a modification of Barker's method (*4*) as described elsewhere (*1, 5*).

Table 1. Vapor Pressures of Pure Liquids

| *T*, °C. | Vapor Pressure, mm Mercury<br>Acetone | 3-Hexyne |
|---|---|---|
| 0 | 70.05 | 22.64 |
| 25 | 230.24 | 85.35 |
| 55 | 731.1 | 306.0 |

The results are shown in Table 2 which gives coefficients for the three-parameter Redlich-Kister expansion of the excess Gibbs energy. Also shown are the limiting activity coefficients for 3-hexyne. These limiting activity coefficients are nearly twice as large as those obtained for 1-hexyne infinitely dilute in acetone (*1*).

Figure 1 compares excess Gibbs energies of acetone-3-hexyne with those for acetone-1-hexyne at 25°C.; the excess Gibbs energy of the former system is about twice that of the latter.

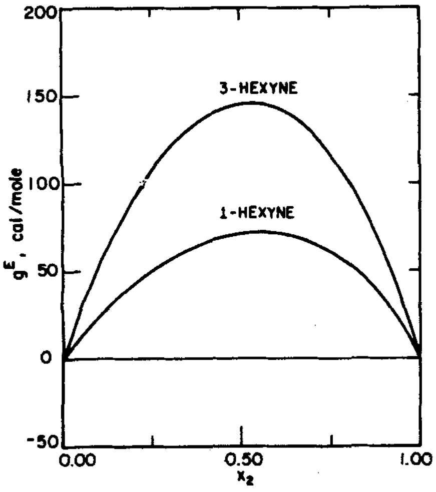

**Fig. 1. Effect of triple-bond position—Acetone(1)-Hexyne(2) at 25°C.**

Table 2. Excess Gibbs Energies for Acetone(*1*) and 3-Hexyne(*2*)

$$g^E/RT = x_1x_2[a + b(x_1 - x_2) + c(x_1 - x_2)^2]$$

| T,°C. | $a$ | $b$ | $c$ | Standard % deviation in $\left(\frac{P_{exp} - P_{calc}}{P_{exp}}\right)$ | $\gamma_2^\infty$ |
|---|---|---|---|---|---|
| 0 | 1.08621 | −0.08546 | 0.09080 | 0.95 | 2.98 |
| 25 | 0.98404 | −0.10450 | 0.06776 | 0.58 | 2.58 |
| 55 | 0.86312 | −0.16875 | 0.03026 | 0.61 | 2.06 |

Polar organic solvents tend to form charge-transfer complexes with unsaturated hydrocarbons (*6, 7*); as complex stability rises, excess Gibbs energy falls. Because of steric reasons we might expect that acetone forms a slightly more stable complex with 1-hexyne than with 3-hexyne. A more important factor, however, is likely hydrogen bonding between acetone and the hydrogen attached to the triply-bonded carbon in 1-hexyne; this possibility is excluded for 3-hexyne. Spectroscopic data and other evidence are available (*8, 9*) which support such a conclusion. Finally, the results shown in Figure 1 may follow in part from differences in polarity; the position of the triple bond in hexyne influences the molecule's symmetry and therefore, its dipole moment. The dipole moment of 3-hexyne is zero whereas that of 1-hexyne is 0.89 Debye. The dipole moment of acetone is 2.88 Debye. Therefore, since acetone and 1-hexyne are more alike than acetone and 3-hexyne, deviations from ideal behavior for that system are smaller than those for acetone-3-hexyne.

Our experimental results suggest that the position of the triple bond in alkynes may have an appreciable affect on thermodynamic properties of alkyne-polar solvent mixtures. This effect should be taken into consideration in the design of extraction or extractive distillation separations.

## ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation for financial support and to the Computer Center, University of California, Berkeley for the use of its facilities.

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