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Phase Equilibrium in the 1-Butene-Water System and Correlation of Hydrocarbon-Water Solubility Data

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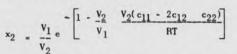
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The experimental data of this work determined the compositions of the co-existing phases in the liquid-liquid region of the 1-butene-water system in the temperature range of 130°F to 310°F and at pressures up to 10,000 psia. The experimental data are a continuation of the work of Brooks (6) who determined the phase behavior and compositions of the 1-butene-water system in the three phase region.

The data of this work have been compared with solubility data for other light hydrocarbon-water systems to illustrate the effect of molecular weight and structure upon the mutual solubilities. The effect of the double bond on solubility has been illustrated by comparing the data of this work with the data of Reamer, Sage, and Lacey (41) for the n-butane-water system.

Thermodynamic methods of interpolating and extrapolating solubility data for hydrocarbon-water systems have been investigated using the data of this work. It has been shown that for very dilute solutions a straight line should be produced by plotting $\ln \left(\frac{f}{x}\right)$ against P at a constant temperature where the term $\left(\frac{f}{x}\right)$ is the ratio of the fugacity of the solute to its mole fraction in the solution, and P is the total pressure of the system. The data of this work fit the predicted linear relationship well at pressures above about 2000 psia but show considerable deviation from linearity at lower pressures which approach the three-phase pressure.

It has also been shown that dilute solutions of structurally similar molecules should produce a straight line when constant pressure solubility data are plotted as $\ln x$ against $1/T$ where x is the mole fraction of the solute and T is the absolute temperature of the system. It was shown that water solubilities in the hydrocarbon-rich phase fit the linear relationship very well, but wide deviation from linearity exists for hydrocarbon solubilities in the water-rich phase.

A method has been proposed for estimating solubilities of water in light hydrocarbons from the volumetric and thermodynamic properties of the pure components. The method is empirical although it is based on the theoretical work of Scatchard (49) and Hildebrand (23). By making simplifying assumtions as to molecular structure it may be shown that the concentration of water in hydrocarbons may be represented as follows for very dilute solutions:

$$x_2 = \frac{V_1}{V_2} e^{-\left[1 - \frac{V_2}{V_1} \quad \frac{V_2(c_{11} - 2c_{12} \quad c_{22})}{RT}\right]}$$

where x_2 is the mole fraction of water, V_1 and V_2 are respectively the molar volumes of pure hydrocarbon and water, and the c terms are functions of the intermolecular forces between pairs of molecules.

The c_{11} and c_{22} terms which account for forces between pairs of like molecules are evaluated as follows:

$$c_{11} = \frac{(U_o - U_P)_T}{V_1}$$

where $(U_o - U_P)_T$ is the change in internal energy for an isothermal expansion of the pure component 1 from the pressure and temperature of the system to zero pressure, and V_1 is the molar volume of the pure component.

The c_{12} term which involves intermolecular forces between pairs of unlike molecules is evaluated empirically by methods suggested by the combinations of second virial coefficients in the equations of state of the pure components

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which produce the second virial coefficients in the equation of state for a bi-
nary solution. The methods found to be most effective were a linear combination:

$$c_{12} = a(c_{11} + c_{22})$$

where a is an empirical constant found to be equal to approximately 0.26 for
paraffin hydrocarbon solvents and about 0.29 for l-butene.

And also a Lorentz combination:

$$c_{12} = \frac{1}{b}(c_{11}^{1/3} + c_{22}^{1/3})^3$$

where for paraffin hydrocarbons:

$$b = 25.50 + 19.24 \, T_R^{0.2}(1 - \frac{V_2}{V_1})$$

where T_R is the reduced temperature of the pure hydrocarbon.

Using these methods solubilities of water in hydrocarbons may be estimated
with average deviations of about 20%, and maximum deviations of about 70% of ob-
served values. The constants were evaluated for liquid hydrocarbon solvents, and
the calculated solubilities become more in error as the state of the solvent
approaches that of an ideal gas.