$$\gamma_i = \frac{y_i \phi_i P}{\phi_i^s x_i P_i^s \exp\left(\frac{v_i^L (P - P_i^s)}{RT}\right)} \qquad (4)$$

where for our purposes the Redlich-Kwong (*6*) equation was used to calculate values of the fugacity ratio.

From Equations 2–4 the vapor-phase composition can be computed. The consistency of the experimental data is exemplified by comparisons with the computed values as shown in Figure 1 and Tables I and II. Calculated values of the liquid-phase activity coefficients are also found in Tables I and II.

The average absolute deviations for all components on the ternary and quaternary systems are within the experimental accuracy of the data, i.e., ±0.2 mol %. These new, more accurate vapor-liquid equilibrium data show a remarkable consistency with respect to the theoretical predictions.

### Acknowledgment

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### Nomenclature

$\bar{A}$ = chromatogram area of component from liquid sample
$F$ = calibration factor of component in liquid sample
$P$ = total system pressure
$P^s$ = saturation pressure of pure component
$R$ = gas law constant
$T$ = absolute system temperature
$v^L$ = saturated liquid molar volume of pure component at solution temperature
$x$ = mole fraction of component in liquid phase
$\bar{x}$ = mole fraction of component in liquid sample
$y$ = mole fraction of component in vapor phase
$\phi$ = fugacity coefficient of component in vapor phase
$\phi^s$ = fugacity coefficient of pure vapor at solution temperature and saturation pressure $P^s$
$\gamma$ = activity coefficient of component in liquid phase
$(\lambda_{ij} - \lambda_{ii})$ = an empirically determined energy constant

*Subscripts*

$i$ = component "i" in the mixture
$j$ = component "j" in the mixture
$k$ = component "k" in the mixture
$s$ = standard component in liquid sample

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# Vapor-Liquid Equilibria in Hydrocarbon–Alcohol Systems *n*-Decane–1-Heptanol and *n*-Decane–2-Methyl-1-hexanol

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**Isobaric vapor-liquid equilibria were measured for the system *n*-decane–1-heptanol at 20 and 102 torr and for the system *n*-decane–2-methyl-1-hexanol at 100 torr. Both systems exhibited positive deviations from Raoult's law and positive azeotropes. The data were correlated by the four-parameter Wilson equation.**

Hydrocarbon–alcohol systems generally display positive deviations from Raoult's law. When the boiling points are relatively close, an azeotrope is formed. Thus, in the two systems considered here, azeotrope formation occurred. Isobaric vapor-liquid equilibrium measurements were carried out at 100 torr for both systems and at 20 torr for the *n*-decane–1-heptanol system. The data were thermodynamically consistent and were correlated by the Wilson equation by use of four parameters.

### Experimental

The *n*-decane and 1-heptanol were purchased materials. The 2-methyl-1-hexanol was made by first forming a Grignard reagent with 2-bromohexane, then reacting this with formaldehyde, and then hydrolyzing with acid to form the alcohol. The material was then purified by passing it through a preparative-scale gas chromatograph. All three materials were analyzed by gas chromatography to ensure their purity. Their boiling points checked closely against those given in the literature.

All analyses were carried out by gas-liquid chromatography. The instrument was an F&M 5754B chromatograph with thermal conductivity detector and an Infotronics CRS-100U electronic integrator. The column was 2 m long × ⅛ in. diameter and was packed with 15% XE-60 on 80/100 Chrom W high-performance support. The column was programmed up from 70°C at 4°/min. Injector temperature was 210°C. The detector was run at a current of 175 mA at a temperature of 300°C. The carrier

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gas was helium at a flow rate of 30 ml/min. Area correction factors were determined for each component over the concentration range covered. Concentration measurements were generally accurate to ±0.3%.

The vapor-liquid equilibrium studies were carried out in an Othmer still with self-lagged, heated, and insulated walls. Temperatures were measured with iron–constantan thermocouples and a Leeds and Northrup hand potentiometer. Temperature measurements were accurate to ±0.1°C. In each run, enough time was allowed at constant conditions to ensure the attainment of equilibrium.

The vapor pressures and Antoine constants used in the calculations were taken from Wilhoit and Zwolinski (*3*) for the two alcohols and from an American Petroleum Institute report (*2*) for *n*-decane. The following form of the Antoine equation was used. The constants are given in Table I.

$$\ln P_v = A + \frac{B}{C + T} \tag{1}$$

Vapor-liquid equilibrium measurements were taken on the *n*-decane–1-heptanol system at pressures of 102 and 20 torr and on the *n*-decane–2-methyl-1-hexanol system at 100 torr. Each set of data was tested by the method of Herington (*1*) and was thermodynamically consistent. The factor $J$ was 5.8, 6.3, and 3.6, respectively, for the three sets of data. The factor $D$ was 1.6, 2.9, and 1.8, all of which satisfy Herington's criteria for consistency, $D < J$.

## Results

Experimental data for the *n*-decane–1-heptanol system are given in Table II and for the *n*-decane–2-methyl-1-hexanol system in Table III. As would be expected for alcohol–hydrocarbon systems, both systems show positive deviations from Raoult's law. All experimental activity coefficients are either unity or larger.

Each table of data contains the azeotrope point at or near atmospheric pressure. These were determined by fractionation of an appropriate mixture through a batch distillation column. In each case, the charge to the still-pot was sufficiently close to the azeotrope concentration, and the separating power of the column was sufficient to ensure that the first distillates from the column were at the azeotrope concentration.

The data for each system were best correlated by the four-parameter Wilson equation (*4*) which follows:

$$\ln \gamma_i = 1 - \ln (X_i + A_{ij}X_j) - \frac{X_i}{X_i + A_{ij}X_j} - \frac{A_{ji}X_j}{A_{ji}X_i + X_j} \tag{2}$$

where

$$\ln A_{ij} = a_i + \frac{b_i}{T} \tag{3}$$

and

$$\ln A_{ji} = a_j + \frac{b_j}{T} \tag{4}$$

The values of the selected parameters are given in Table IV. All data points from Tables II and III were used in the correlations. With the exception of the 712 torr

**Table I. Antoine Constants**

| | A | B | C |
|---|---|---|---|
| *n*-Decane | 9.35592 | −3439.7 | −79.46 |
| 1-Heptanol | 8.67352 | −2626.4 | −146.4 |
| 2-Methyl-1-hexanol | 14.712 | −6433. | 0.0 |

**Table II. Vapor-Liquid Equilibrium Data for *n*-Decane–1-Heptanol**

| | *n*-Decane mole fraction | | | Activity coefficients | | | |
|---|---|---|---|---|---|---|---|
| Temp, °C | $X_1$ | $Y_1$, exptl | $Y_1$, calcd | $\gamma_1$, exptl | $\gamma_1$, calcd | $\gamma_2$, exptl | $\gamma_2$, calcd |
| | | Pressure = 102 torr | | | | | |
| 106.0 | 0.898 | 0.812 | 0.818 | 0.992 | 1.026 | 3.305 | 3.280 |
| 106.6 | 0.901 | 0.813 | 0.821 | 0.967 | 1.025 | 3.289 | 3.307 |
| 105.5 | 0.696 | 0.708 | 0.711 | 1.165 | 1.186 | 1.806 | 1.818 |
| 105.5 | 0.698 | 0.708 | 0.712 | 1.161 | 1.184 | 1.817 | 1.825 |
| 106.0 | 0.496 | 0.646 | 0.643 | 1.508 | 1.471 | 1.329 | 1.315 |
| 106.4 | 0.477 | 0.638 | 0.586 | 1.529 | 1.437 | 1.288 | 1.269 |
| 107.5 | 0.334 | 0.583 | 0.567 | 1.949 | 1.821 | 1.125 | 1.125 |
| 107.5 | 0.334 | 0.571 | 0.567 | 1.904 | 1.821 | 1.155 | 1.215 |
| 109.3 | 0.193 | 0.484 | 0.452 | 2.636 | 2.260 | 1.063 | 1.039 |
| 109.7 | 0.192 | 0.478 | 0.449 | 2.575 | 2.260 | 1.053 | 1.039 |
| 112.5 | 0.103 | 0.349 | 0.314 | 3.130 | 2.618 | 1.028 | 1.011 |
| 113.0 | 0.101 | 0.327 | 0.308 | 2.924 | 2.623 | 1.032 | 1.010 |
| 118.0 | 0.022 | 0.106 | 0.090 | 3.528 | 2.993 | 0.978 | 1.000 |
| 118.7 | 0.019 | 0.092 | 0.078 | 3.451 | 3.003 | 0.958 | 1.000 |
| 105.4 | 0.710 | 0.710 | Azeotrope point by interpolation | | | | |
| | | Pressure = 20 torr | | | | | |
| 70.6 | 0.872 | 0.840 | 0.844 | 0.977 | 1.058 | 3.372 | 3.545 |
| 70.0 | 0.900 | 0.857 | 0.865 | 1.170 | 1.040 | 5.032 | 4.204 |
| 71.5 | 0.714 | 0.801 | 0.799 | 1.119 | 1.219 | 1.817 | 2.010 |
| 68.9 | 0.756 | 0.815 | 0.815 | 1.215 | 1.172 | 2.346 | 2.272 |
| 71.7 | 0.329 | 0.726 | 0.696 | 2.332 | 2.010 | 1.125 | 1.128 |
| 69.4 | 0.426 | 0.740 | 0.742 | 2.020 | 1.747 | 1.433 | 1.233 |
| 82.7 | 0.059 | 0.306 | 0.300 | 3.153 | 3.146 | 0.977 | 1.004 |
| 86.5 | 0.007 | 0.041 | 0.048 | 2.879 | 3.459 | 0.980 | 1.000 |
| 68.5 | 0.822 | 0.822 | Azeotrope point by interpolation | | | | |
| | | Pressure = 760 torr | | | | | |
| 166.0 | 0.553 | 0.553 | 0.557 | 1.240 | 1.223 | 1.355 | 1.319 |

**Table III. Vapor-Liquid Equilibrium Data for *n*-Decane–2-Methyl-1-hexanol**

| | *n*-Decane mole fraction | | | Activity coefficients | | | |
|---|---|---|---|---|---|---|---|
| Temp, °C | $X_1$ | $Y_1$, exptl | $Y_1$, calcd | $\gamma_1$, exptl | $\gamma_1$, calcd | $\gamma_2$, exptl | $\gamma_2$, calcd |
| | | Pressure = 100 torr | | | | | |
| 107.1 | 0.093 | 0.260 | 0.236 | 3.046 | 2.705 | 1.002 | 1.011 |
| 107.0 | 0.093 | 0.259 | 0.238 | 3.045 | 2.699 | 1.008 | 1.010 |
| 103.9 | 0.261 | 0.441 | 0.421 | 2.090 | 1.911 | 1.077 | 1.071 |
| 103.9 | 0.261 | 0.449 | 0.421 | 2.132 | 1.911 | 1.064 | 1.071 |
| 103.0 | 0.441 | 0.541 | 0.528 | 1.546 | 1.492 | 1.198 | 1.217 |
| 103.1 | 0.440 | 0.542 | 0.528 | 1.547 | 1.494 | 1.189 | 1.215 |
| 102.7 | 0.638 | 0.604 | 0.616 | 1.172 | 1.213 | 1.571 | 1.549 |
| 102.7 | 0.637 | 0.607 | 0.615 | 1.181 | 1.214 | 1.556 | 1.547 |
| 103.9 | 0.869 | 0.716 | 0.752 | 0.947 | 1.032 | 2.867 | 2.601 |
| 104.0 | 0.871 | 0.718 | 0.754 | 0.943 | 1.031 | 2.878 | 2.618 |
| 102.5 | 0.592 | 0.592 | Azeotrope point by interpolation | | | | |
| | | Pressure = 712 torr | | | | | |
| 160.5 | 0.386 | 0.386 | 0.308 | 1.348 | 1.072 | 1.058 | 1.194 |

**Table IV. Wilson Equation Coefficients**

| | *a* | *b* |
|---|---|---|
| *n*-Decane–1-heptanol system | | |
| *n*-Decane | −0.30913 | −53.517 |
| 1-Heptanol | +3.5132 | −1837.4 |
| *n*-Decane–2-methyl-1-hexanol system | | |
| *n*-Decane | −17.747 | +6518.6 |
| 2-Methyl-1-hexanol | +12.208 | −5001.3 |

point in Table III, the largest deviation between experimental and calculated values is about 10%.

Both systems exhibit positive azeotropes whose compositions vary strongly with temperature, *n*-decane concentration increasing with temperature.

**Nomenclature**

$A_{ij}$, $A_{ji}$ = Wilson equation parameters
$a_i$ = Wilson equation parameter
$b_i$ = Wilson equation parameter

$$D = \text{Herington parameter} = 100 \times \frac{\int_0^1 \frac{\gamma_1}{\gamma_2}\, dx_1}{\int_0^1 \left|\frac{\gamma_1}{\gamma_2}\right| dx_1}$$

$J$ = Herington parameter = $150\,|\theta|/T\text{min}$
ln = natural logarithm
$P_v$ = vapor pressure of pure component, atm
$T$ = temperature, K
$T_{\min}$ = lowest measured boiling point of the system, K
$X_i$ = mole fraction in the liquid of component $i$
$Y_i$ = mole fraction in the vapor of component $i$
$\gamma_i$ = activity coefficient of component $i$
$\theta$ = range of boiling points of the system, °C

*Subscripts*

$i$, $j$ = component number
1, 2 = component number. 1 is always *n*-decane

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# Vinyl Chloride Gas Compressibility and Solubility in Water and Aqueous Potassium Laurate Solutions

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**Volumetric properties of vinyl chloride gas are reported for temperatures from 0° to 75°C and for pressures from atmospheric to the saturation pressures. Solubilities in water are also reported for the same temperature range and pressures up to 6 atm. Solubilities of vinyl chloride in aqueous solutions of potassium laurate for concentrations up to 15 g/l. are reported and compared with those in water. A new solubility apparatus useful for moderate pressures and incorporating a solvent cell with an externally operated magnetic flow control valve is described.**

A knowledge of vinyl chloride volumetric properties and solubilities in water and aqueous surfactant solutions is useful when dealing with polymerization reactions of this monomer in aqueous emulsions or suspensions. Although vinyl chloride is condensable at relatively low pressures, neither gas compressibilities nor any concerted study of solubilities in water or surfactant solutions (to the authors' knowledge) has heretofore appeared in the literature.

Some vinyl chloride properties can be found in the monograph edited by Leonard (*7*) as well as an earlier publication edited by Blout et al. (*1*). These properties included vapor pressures, calculated critical properties, and saturated vapor densities.

In this work the vinyl chloride gas density was measured at 0°C and atmospheric pressure with an Anton Paar (Austria) vibrating reed densitometer and was 2.86 g/l. This density was extrapolated to other temperatures as required in the compressibility determinations. Accurate density measurements at 25°, 50°, and 75°C were unsuccessful apparently because of some chemical reaction of the gas occurring in the densitometer at the higher temperatures.

Compressibilities were measured with an accurately calibrated piston-type volumetric pump as a volume regulator in conjunction with a pressure transducer and an appropriate charging and evacuation system. The compressibility apparatus was submerged in a constant temperature bath so that once charged, direct readings of pressure and volume could be obtained at constant temperature.

Solubilities in water at atmospheric pressure were measured by a continuous solvent flow apparatus formerly described by Hayduk and Cheng (*5*) and Hayduk and Buckley (*4*). Solubilities above atmospheric pressure were obtained by means of a new apparatus by use of the volume measuring system of the compressibility apparatus in conjunction with a solvent saturation tube. A known volume of deaerated solvent initially confined in a cell was saturated by passing it dropwise over a packing in the tube. The total volume of dissolved gas required to saturate the solvent was measured at constant pressure with the calibrated volumetric pump. When operated at atmospheric pressure, this new apparatus gave nearly equivalent results to those obtained by means of the continuous solvent flow apparatus. Consequently, it was assumed that the apparatus would also give reliable results at elevated pressures.

Solubilities of vinyl chloride in potassium laurate solutions were measured with the same solubility equipment as that used for water with little added difficulty. The low solubility of potassium laurate in water at lower temperatures limited the possible surfactant concentrations for these measurements. It was possible to estimate the ex-

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