of the density and vapor pressure of the solution at the appropiate water jacket temperature. S is low enough that it can be converted to mole fraction, multiplying by the factor 18/22,414. Plots of S against the absolute pressure indicated that Henry's Law was satisfied in every case up to the highest pressure tested. Table I summarizes the values of S and Henry's constant H, atm/mole fraction (best slope), and Figure 2 shows some typical curves. Each value in Table I is the average of at least three measurements.

The major sources of error in this work were associated with the measurement of pressure and temperature inside the equilibrium cell and the gas and liquid volumes in the burets. The latter could be read to within 0.1 ml so that it is estimated that the data presented here are accurate to within 3-5%, the lowest inaccuracy corresponding to the lower pressures.

An examination of Table I shows that for a given concentration, hydrogen solubility increases with increasing temperature for practically every case, within the experimental error. The only significant anomaly is for xylose solutions 2*M*. Salting effects at constant temperature and pressure depend on the solute and its concentration; thus, for increased molarity the solubility of xylitol goes through a maximum, whereas that of xylose goes through a minimum.

The variation of Henry's constant with temperature does not follow a regular pattern with changes in molarity. Although this is not the expected behavior, several literature references (*1*) indicate that for light gases, the sign of the temperature derivative of Henry's constant varies with solute concentration. Apparently, for polyhydric alcohols the changes with temperature of surface tension, density, and solvation follow a more complicated pattern.

The solubility of hydrogen in pure water at 100°C and 50 atm is 0.9116 ml STP/g water (*4*); thus, it is enhanced by the solutes here considered.

Solutions of concentration 3M were extremely viscous and did not allow repetitive determination.

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Vapor-Liquid Equilibria at 1 Atm. Systems Containing *n*-Hexane, Methylcyclopentane, Ethyl Alcohol, and Benzene

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Vapor-liquid equilibrium data at 1 atm are presented for the ternary system *n*-hexane-methylcyclopentane-benzene and the quaternary system involving ethyl alcohol. The data are believed accurate to ±0.04°C and ±0.2 mol % with respect to temperature and composition, respectively. Multicomponent predictions based upon binary constants agree with the experimental data.

To study tray efficiencies in distillation columns not only requires accurate vapor-liquid equilibrium data but also a mathematical model for predicting additional values as well. Hence, prior to the determination of the reported tray efficiencies (*12, 13*) in binary, ternary, and quaternary systems containing *n*-hexane, methylcyclopentane (MCP), ethyl alcohol, and benzene, the ternary and quaternary data of Weber et al. (*1, 2, 8, 10*) were subjected to further analysis utilizing the Wilson equation (*11*) as modified by Oyre and Prausnitz (*4*). These previous investigations reported temperature and composition measurements accurate within ±0.1°C and ±0.5 mol %, respectively.

The purposes here are to present the new, more accurate data which were obtained for the tray efficiency investigation and to show the comparative results with the same analytical treatment mentioned above. These new data are believed accurate to ±0.04°C and ±0.2 mol % regarding temperature and composition, respectively.

Experimental

The benzene and MCP were pure grade (minimum 99 mol % purity) materials, and the *n*-hexane was technical grade (97.3 mol %). The major impurity (2.43%) in the straight-chain paraffin was MCP (*9*), which meant the purity was 99.7% with respect to the *n*-hexane-MCP system. These hydrocarbons were obtained from the Phillips Petroleum Co. The absolute alcohol was manufactured by USI, and glc analysis indicated only a trace amount of impurities. The chemicals were passed through a Perkin-Elmer 880 chromatograph equipped with a hot wire detector, a 194B printing integrator, and a Leeds and Northrup Speedomax G strip chart recorder. In no case did extraneous peaks appear. Within the accuracy of the glc analysis, the MCP was confirmed to be 99.8% pure with 0.2% *n*-hexane (*12*).

A modified Braun equilibrium still was used to obtain the experimental data. Equipment and procedures were similar to those of Lee (*3*). An iron-constantan thermocouple in conjunction with a Leeds and Northrup-type K potentiometer permitted temperature measurements with a probable error (*7*) of ±0.04°C.

The equilibrium pressure was measured by a manometer and was maintained at 760 ± 0.1 mm of mercury. The pressure above existing atmospheric pressure was obtained by bleeding nitrogen into the equilibrium still. The flow of nitrogen was controlled by a manostat.

Ternary and quaternary samples were analyzed by glc. Helium was the carrier gas. The ternary system was analyzed with a 10-ft column (1/8-in. o.d.) with solid support

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of 80/90 mesh-type ABS Anakrom and stationary phase of diisodecyl phthalate. The column for the quaternary system was similar, except the stationary phase was tetraethylene glycol dimethyl ether.

The instrument was calibrated with 20 samples of different, but known, compositions. We used the mean value of the calibration factors defined as

$$F_i = \frac{\bar{X}_i/\bar{X}_s}{\bar{A}_i/\bar{A}_s} \qquad (1)$$

The compositions of the calibration samples were back calculated and compared with the compositions obtained by weighing. From these comparisons, the average absolute deviation is ±0.2 mol % for the chromatographic analyses. The experimental data are included in Tables I and II.

Analysis of Data

Values of the liquid-phase activity coefficient were correlated by the Wilson equation (*11*) as discussed by Orye and Prausnitz (*4*):

$$\ln \gamma_k = 1 - \ln\left(\sum_j x_j \Lambda_{kj}\right) - \sum_i \frac{x_i \Lambda_{ik}}{\sum_j x_j \Lambda_{ij}} \qquad (2)$$

where

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp\left(-\frac{(\lambda_{ij} - \lambda_{ii})}{RT}\right) \qquad (3)$$

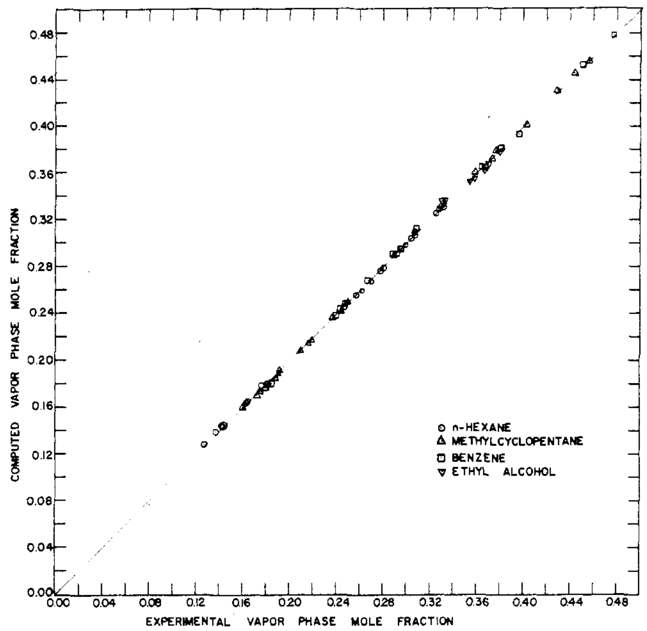

Figure 1. Comparison of experimental and computed results

Values of the Wilson parameters were those presented by Prausnitz et al. (*5*).

The liquid-phase activity coefficients were also calculated by the expression:

Table I. Vapor-Liquid Equilibrium at 760 mm Hg for *n*-Hexane(1)–Methylcyclopentane(2)–Benzene(3) System

Exptl T, °C	Experimental						Calculated					
	Liquid mole fraction			Vapor mole fraction			Vapor mole fraction			Liquid-phase activity coeff		
	Hexane	MCP	Benzene	Hexane	MCP	Benzene	Hexane	MCP	Benzene	Hexane	MCP	Benzene
72.60	0.226	0.169	0.605	0.295	0.192	0.513	0.295	0.191	0.514	1.18	1.12	1.08
72.26	0.240	0.198	0.562	0.304	0.219	0.477	0.304	0.218	0.478	1.15	1.10	1.09
71.95	0.269	0.200	0.531	0.333	0.216	0.451	0.331	0.216	0.453	1.13	1.09	1.11
71.44	0.282	0.279	0.439	0.331	0.289	0.380	0.330	0.289	0.381	1.09	1.06	1.14
71.36	0.261	0.366	0.373	0.299	0.373	0.328	0.298	0.372	0.330	1.07	1.04	1.17
71.35	0.230	0.442	0.328	0.261	0.444	0.295	0.259	0.446	0.295	1.06	1.03	1.19
71.25	0.248	0.458	0.294	0.277	0.456	0.267	0.276	0.456	0.268	1.05	1.03	1.21
71.26	0.248	0.429	0.323	0.280	0.429	0.291	0.278	0.431	0.291	1.05	1.03	1.20
71.33	0.233	0.394	0.373	0.269	0.402	0.329	0.267	0.402	0.331	1.07	1.04	1.17
71.57	0.219	0.365	0.416	0.257	0.376	0.367	0.256	0.379	0.365	1.09	1.05	1.15
71.86	0.205	0.342	0.453	0.246	0.358	0.396	0.245	0.361	0.394	1.10	1.06	1.13

Table II. Vapor-Liquid Equilibrium at 760 mm Hg for *n*-Hexane(1)–Ethyl Alcohol(2)–Methylcyclopentane(3)–Benzene(4) System

Exptl T, °C	Experimental								Calculated							
	Liquid mole fraction				Vapor mole fraction				Vapor mole fraction				Liquid-phase activity coeff			
	Hexane	EtOH	MCP	Benzene	Hexane	EtOH	MCP	Benzene	Hexane	EtOH	MCP	Benzene	Hexane	EtOH	MCP	Benzene
62.14	0.108	0.413	0.185	0.294	0.163	0.358	0.236	0.243	0.164	0.356	0.236	0.244	1.89	1.68	1.74	1.50
62.33	0.085	0.472	0.177	0.266	0.142	0.370	0.249	0.239	0.144	0.368	0.250	0.238	2.11	1.51	1.92	1.61
62.40	0.088	0.449	0.177	0.286	0.143	0.365	0.244	0.248	0.144	0.365	0.242	0.249	2.04	1.57	1.86	1.56
63.01	0.077	0.419	0.152	0.352	0.127	0.366	0.209	0.298	0.128	0.366	0.209	0.297	2.03	1.64	1.84	1.48
63.01	0.078	0.478	0.125	0.319	0.142	0.379	0.191	0.288	0.144	0.376	0.189	0.291	2.25	1.48	2.02	1.60
63.14	0.086	0.394	0.139	0.381	0.137	0.366	0.188	0.309	0.139	0.362	0.186	0.313	1.96	1.72	1.78	1.43
62.99	0.111	0.353	0.140	0.396	0.164	0.354	0.175	0.307	0.165	0.353	0.174	0.308	1.81	1.88	1.66	1.37
62.77	0.117	0.386	0.134	0.363	0.176	0.357	0.173	0.294	0.179	0.357	0.171	0.293	1.89	1.76	1.73	1.43
60.92	0.284	0.316	0.160	0.240	0.325	0.330	0.160	0.185	0.325	0.335	0.160	0.180	1.49	2.19	1.43	1.42
60.95	0.264	0.325	0.175	0.236	0.307	0.332	0.180	0.181	0.307	0.337	0.177	0.179	1.52	2.14	1.45	1.43

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

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

The methylcyclopentane was donated by the Phillips Petroleum Co.

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
ϕ = fugacity coefficient of component in vapor phase
ϕ^s = fugacity coefficient of pure vapor at solution temperature and saturation pressure P^s
γ = 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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