Solvent Effect on Relative Volatility

n-Hexane—Hexene-1 System

Y. S. SURYANARAYANA and MATTHEW VAN WINKLE

The University of Texas, Austin, Tex.

Partial vapor-liquid equilibrium data have been determined for the *n*-hexane–hexene-1–dioxane, *n*-hexane–hexene-1–Cellosolve, and *n*-hexane–hexene-1–trichloropropane ternary systems at 760 mm. of mercury pressure and complete vapor liquid equilibrium data have been determined on the binary systems at 760 mm. The effect of solvent concentration on selectivity is shown for the three solvents to be about the same. At infinite dilution, the ratios of the hexane to hexene-1 activity coefficients in the three solvents are: trichloropropane—1.41, Cellosolve—1.33, and 1,4 dioxane—1.36.

EXTRACTIVE DISTILLATION has become an important method of separating close boiling compounds of both similar and widely different chemical characteristics. The major application of this process has been in the petrochemical industry for separation of hydrocarbons such as paraffins and olefins, aromatics and parafins, cycloparaffins and aromatics, and olefins and alkynes.

Screening and selection of solvent materials to be used in extractive distillation has been and is the subject of much research both from the theoretical as well as the empirical standpoint and many investigations have been devoted to evaluation of experimental vapor-liquid equilibria to develop data to serve as bases for correlation and prediction methods. Of the lighter straight-chain alkane and alkene hydrocarbons, butane, butene, and butadiene systems have been investigated by Gerster, Mertes, and Colburn (*4*) and Hess, Naragon, and Coughland (*7*) with furfural-water and other solvents. The pentane-pentene system with various solvents has been reported on by Gerster, Gorton, and Eklund (*3*).

The present investigation was conducted to extend the data to the next higher homologous *n*-paraffin-olefin system, *n* hexane–hexene-1. Vapor-liquid equilibrium data were determined for the following systems at 760 mm. of mercury pressure: *n*-hexane-hexene-1; *n*-hexane–1, 4-dioxane; hexene-1–1, 4-dioxane; *n*-hexane–Cellosolve; hexene-1–Cellosolve; *n*-hexane–1, 2,3 trichloropropane; and hexene-1–1,2,3 trichloropropane. In addition, sufficient partial ternary data on the *n*-hexane–hexene-1–1,4 dioxane; *n*-hexane–hexene-1–Cellosolve; and the *n*-hexane–hexene-1–1,2,3 trichloropropane systems were determined to establish the effect of the solvent on the relative volatility of the hydrocarbon binary as a function of composition.

MATERIALS

Ninety-nine mole per cent minimum purity *n*-hexane and hexene-1 were analyzed using a GC-2A chromatograph at 70° C. with a column containing β-β' hydroxydipropionitrile. Both contained less than 0.05 mole % impurity. They were used without further purification. The three solvents were dried by distillation using a Soxhlet extraction unit packed with 80- to 100-mesh silica gel. The 1,4-dioxane was distilled in a glass helices–packed column at atmospheric pressure with a 15-to-1 reflux ratio. The 1,2,3-trichloropropane was distilled in the column at 100 mm. of mercury pressure, and Cellosolve was distilled in a 20-plate Oldershaw column at a reflux ratio of 20-to-1 at 100 mm. of pressure. In each case, only the constant boiling heart cut was used in the experiments. Analyses of each of these purified materials by the GC-2A chromatograph indicated no detectable impurities. Table I summarizes the properties of the materials.

APPARATUS AND PROCEDURE

The vapor-liquid equilibrium data were determined using a modified Colburn still described previously (*9*) with a special heater system added to the residue chamber of the still to simulate adiabatic operation. Equibilrium temperatures were measured by means of a copper-Constantan thermocouple, which was precalibrated using a platinum resistance thermometer and a Universal K-3 Leeds and Northrup potentiometer. The estimated accuracy of temperature measurement was ± 0.1° C. or better. The pressure in the still was indicated by an absolute mercury-in-glass manometer, and the mercury level was measured by means of a cathetometer. The pressure was controlled at 760 mm. by bleeding dry nitrogen into the system

Table I. Some Physical Properties of Materials

	n-Hexane	Hexene-1	1, 4-Dioxane	Cellosolve	1, 2, 3-Trichloropropane
Structural formula	$CH_3(CH_2)_4CH_3$	$CH_3(CH_2)_3CH_2{=}CH_2$	$OCH_2OCH_2OCH_2CH_2$	$C_2H_5OC_2H_4OH$	$ClCH_2CHClCH_2Cl$
Molecular weight	86.2	84.2	88.1	90.12	147.44
B. P., ° C. at 760 mm.	68.74	63.5	101.5	135.1	156.85
Antoine constants					
A	6.8778	6.8657	7.8642	8.416	6.9872
B	1171.53	1152.97	1866.7	2135.0	1502.3
C	224.366	225.85	273.0	253.0	209.0
Refractive index					
n_D^{25} Exp.	1.37234	1.38514	1.4200	1.40627	1.4816
Lit.	1.37226	1.3853	1.4202	1.4060	1.4812
Density at 25° C.	0.6548	0.6689	1.028	0.93	1.3832
Critical temperature, T° K.	507.7	510.78	584.8	570[b]	632.1[b]
Critical pressure, P_c atm.	29.92	32.10	49.4	40.5[b]	38.09[b]

[a] (*2*) (*10*) (*14*).

[b] Estimated using (*13*).

through a Nupro 4B-M fine metering valve. The pressure was maintained to within about ± 0.5 mm. of Hg.

The procedures for determining the vapor-liquid equilibrium data for the binary systems were essentially those described by Haynes and Van Winkle (*6*). In the case of the ternary systems, three mixtures of *n*-hexane and hexene-1 in the mole ratios of 25/75, 50/50, and 75/25 were used, and the solvent was added to each of the mixtures to obtain concentrations of 0.1, 0.3, 0.5, and 0.8 mole fraction. These mixtures were subjected to equilibrium distillation in the Colburn still. The vapor and liquid samples were analyzed either for refractive index, using a Bausch and Lomb precision refractometer or with a Beckmann GC-2A gas chromatograph. Table II lists the method used for each system and the estimated precision.

RESULTS AND DISCUSSION

Activity coefficients for all the components in the binary and ternary mixtures were computed from the experimental data by the relation:

$$\gamma = yP_T/xP \tag{1}$$

and Tables III and IV give the experimental vapor-liquid equilibrium data for the binary and ternary systems, respectively. Gas phase deviations were neglected in Equation 1 since they were estimated to be less than 1% of the total deviation from ideality.

CORRELATION OF DATA

The excess free energy per mole of solution in the liquid phase is given by Equation 2

$$G^E = \Sigma x_i RT \ln \gamma_i \tag{2}$$

Redlich and Kister (*12*) related the excess free energy at constant temperature and pressure to liquid composition by a series function

$$\frac{G^E_{12}}{RT} = x_1x_2[B_{12} + C_{12}(x_1 - x_2) + D_{12}(x_1 - x_2)^2 + \cdots] \tag{3}$$

for a binary mixture. For the correlation of isobaric equilibrium data, Chao and Hougen (*1*) modified the Redlich-Kister correlation by incorporating the Ibl and Dodge (*8*) modification of the Gibbs-Duhem equation. Ibl and Dodge have shown that the correct form of the Gibbs-Duhem relation for a binary solution of isobaric conditions is

$$x_1 \,d \ln \gamma_1 + x_2 \,d \ln \gamma_2 = Z_{12} \,dx_1 \tag{4}$$

Table II. Method of Analysis and Error in Composition for Systems Investigated

System	Method of Analysis	Max. Error, Mole %
n-Hexane–1, 4-dioxane	Refractive index	±0.2
Hexene-1–1, 4-dioxane	Refractive index	±0.2
n-Hexane–Cellosolve	Refractive index	±0.2
n-Hexane–1, 2, 3-trichloropropane	Refractive index	±0.2
n-Hexane–hexene-1	Gas chromatograph	±0.2
Hexene-1–Cellosolve	Gas chromatograph	±0.2
Hexene-1–1, 2, 3-trichloropropane	Gas chromatograph	±0.2
All the ternary systems	Gas chromatograph	±0.3

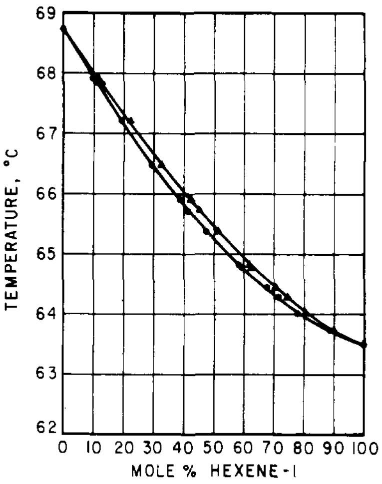

Figure 1. Equilibrium boiling point diagram for the binary system *n*-hexane–hexene-1

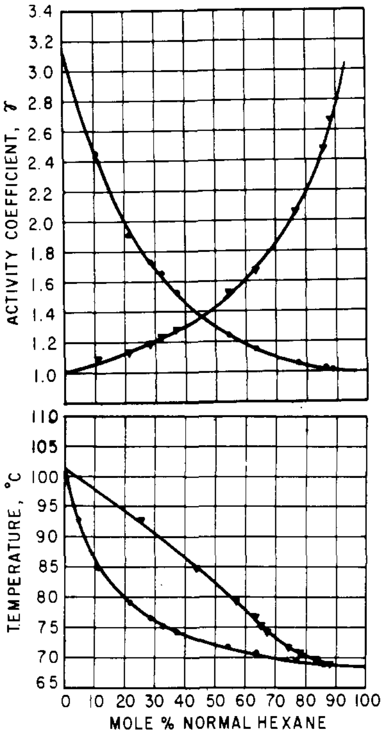

Figure 2. *n*-Hexane–1,4-dioxane system

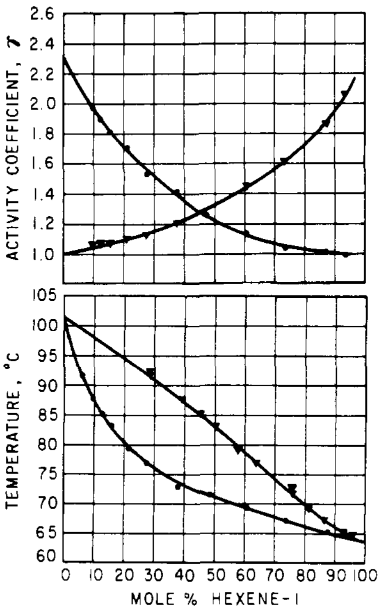

Figure 3. Hexene-1–1,4-dioxane system

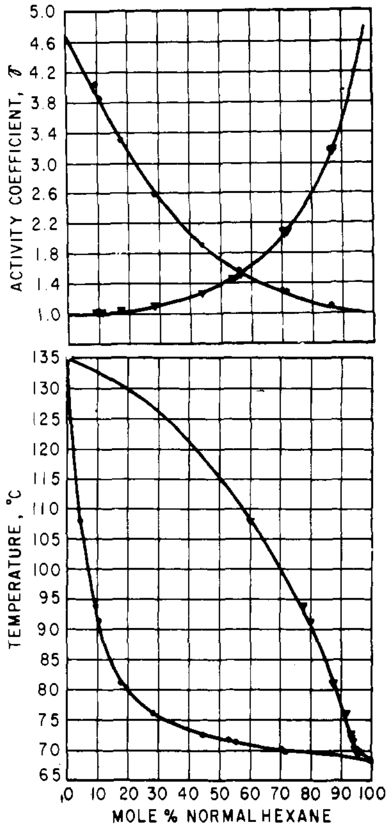

Figure 4. *n*-Hexane–Cellosolve system

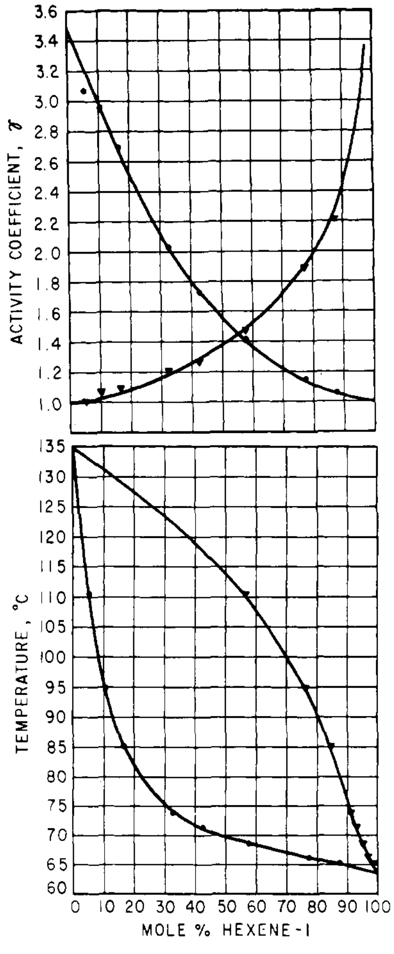

Figure 5. Hexene-1–Cellosolve system

The Z term is defined as

$$Z_{12} = \frac{-\Delta H_{12}}{RT^2}\left(\frac{dT}{dx_1}\right)_P \tag{5}$$

and

$$\Delta H_{12} = H_{12} - x_1H_1^* - x_2H_2^* \tag{6}$$

where H_{12}, H^*_1, and H^*_2 are molal enthalpies of the mixture and pure component, respectively.

The Chao-Hougen relation for isobaric conditions is expressed by Equation 7,

$$\log(\gamma_1/\gamma_2) = a_{12} + b_{12}(x_2 - x_1) + c_{12}(bx_1x_2 - 1) + \cdots \tag{7}$$

When $a_{12} = 0$, the Chao-Hougen equation reduces to the Redlich-Kister equation. The constants in the equation were determined by the least-squares fit of the experimental data for each binary system. The equilibrium vapor compositions were calculated using the following equations:

$$y_1 = \gamma_1x_1P_1/E\gamma_2x_2P_2 \tag{8}$$

$$y_2 = 1/E \tag{9}$$

$$E = (\gamma_1x_1P_1/\gamma_2x_2P_2) + 1 \tag{10}$$

The average deviation of calculated vapor compositions from the experimental values is about 0.1 mole %. Figures 1 through 7 include the equilibrium boiling point diagrams and the activity coefficient versus liquid composition relations. The solid lines are those predicted by the Chao and Hougen relations with the constants reported on the tables.

The experimental data indicate that the binary system *n*-hexane–hexene-1 is nearly ideal in nature. Gerster, Mertes, and Colburn (*4*) assumed the system *n*-butane–butene-1 to be

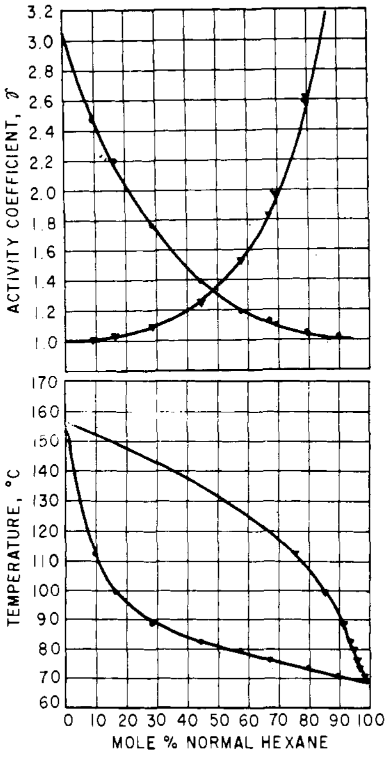

Figure 6. *n*-Hexane–1, 2, 3-trichloropropane system

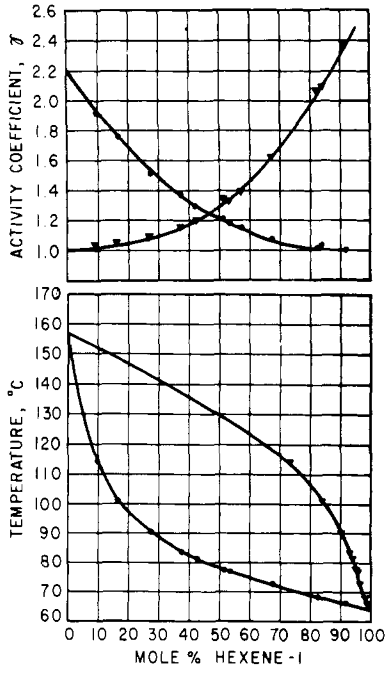

Figure 7. Hexene-1–1, 2, 3-trichloropropane system

ideal in deriving their ternary system correlations, and Randall (*11*) found that the *n*-heptane–heptene-1 system exhibited nearly ideal behavior. In all of the ternary correlations used in this work, the *n*-hexane–hexene-1 system was assumed to behave ideally.

On the other hand, the hydrocarbon-solvent binary systems studied are highly nonideal and, while there were no definite azeotropes found, the temperature-composition diagrams showed a definite pinching or approach of the saturated vapor and saturated liquid lines as the composition of the lower boiling component approached unity. The activity coefficients of the *n*-hexane were consistently higher in value then those for the hexene-1 in the hydrocarbon-solvent binary mixtures. With an increase in the value of the activity coefficient at infinite dilution γ° for *n*-hexane in the different solvents, there is a corresponding increase in the value of γ° for hexene-1 in the same solvents. Similar trends for the paraffin-olefin γ°'s were noted by Gerster, Gorton, and Eklund (*3*) in their work on the *n*-pentane–pentene-1 system.

TERNARY SYSTEMS—SELECTIVITY

The relative volatility of *n*-hexane to hexene-1 is expressed by the relation

$$\alpha_{12} = \left[\left(\frac{\gamma_1}{\gamma_2}\right)\left(\frac{P_1}{P_2}\right)\right]_{12} \tag{11}$$

Table III. Binary Vapor-Liquid Equilibrium Data at 760 mm. of Hg Pressure

System: (1) hexene-1–(2) *n*-hexane: $a_{12} = -0.0063$; $b_{12} = 0.01$; $c_{12} = 0.0007$

Temp., °C.	x_{HA}	γ_{HE}	γ_{HA}	Expt. γ_{HA}	Calcd. y_{HA}
67.9	0.903	1.014	1.008	0.887	0.887
67.8	0.895	1.022	1.008	0.877	0.878
67.2	0.807	1.015	1.015	0.780	0.781
66.5	0.708	1.016	1.023	0.674	0.671
65.9	0.614	1.016	1.029	0.577	0.576
65.7	0.588	1.017	1.030	0.550	0.549
65.4	0.523	1.016	1.034	0.485	0.484
64.8	0.413	1.016	1.039	0.378	0.376
64.8	0.408	1.015	1.039	0.374	0.373
64.7	0.397	1.016	1.038	0.373	0.374
64.4	0.324	1.015	1.037	0.293	0.293
64.3	0.285	1.014	1.035	0.256	0.257
64.1	0.220	1.011	1.040	0.197	0.197
64.0	0.214	1.011	1.043	0.192	0.194
63.7	0.116	1.007	1.042	0.103	0.103
63.7	0.108	1.006	1.043	0.100	0.095

System: (1) *n*-hexane–(2) 1, 4-dioxane: $a_{12} = -0.035$; $b_{12} = 0.484$; $c_{12} = -0.021$

Temp., °C.	x_{DIO}	γ_{HA}	γ_{DIO}	Expt. y_{DIO}	Calcd. y_{DIO}
84.9	0.890	2.447	1.084	0.565	0.566
79.2	0.783	1.915	1.138	0.429	0.427
76.5	0.713	1.730	1.183	0.370	0.369
75.3	0.676	1.649	1.226	0.348	0.348
74.3	0.627	1.528	1.278	0.325	0.324
71.7	0.457	1.243	1.537	0.260	0.258
70.8	0.363	1.152	1.671	0.217	0.222
69.6	0.230	1.060	2.060	0.163	0.165
68.9	0.138	1.024	2.474	0.114	0.113
68.8	0.113	1.013	2.670	0.100	0.096

System: (1) hexene-1–(2) 1, 4-dioxane: $a_{12} = -0.019$; $b_{12} = 0.355$; $c_{12} = -0.014$

		γ_{HE}			
87.6	0.902	1.973	1.054	0.610	0.610
85.2	0.875	1.891	1.062	0.550	0.549
83.1	0.845	1.809	1.066	0.498	0.498
79.3	0.790	1.706	1.110	0.424	0.424
76.9	0.723	1.529	1.126	0.363	0.361
72.9	0.624	1.415	1.205	0.290	0.293
71.6	0.530	1.251	1.255	0.245	0.246
69.0	0.393	1.125	1.447	0.190	0.187
67.4	0.265	1.042	1.615	0.135	0.134
65.2	0.128	1.009	1.884	0.070	0.071
64.8	0.068	0.990	2.070	0.040	0.039

System: (1) *n*-hexane–(2) Cellosolve: $a_{12} = 0.059$; $b_{12} = 0.683$; $c_{12} = 0.061$

Temp., °C.	x_{CEL}	γ_{HE}	γ_{CEL}	Expt. y_{CEL}	Calcd. y_{CEL}
94.0	0.905	3.940	1.022	0.223	0.224
91.4	0.893	3.863	1.033	0.200	0.201
82.1	0.822	3.295	1.043	0.125	0.127

System: (1) *n*-hexane–(2) Cellosolve: $a_{12} = 0.059$; $b_{12} = 0.683$; $c_{12} = 0.061$

Temp., °C.	x_{CEL}	γ_{HE}	γ_{CEL}	Expt. y_{CEL}	Calcd. y_{CEL}
76.1	0.717	2.578	1.101	0.088	0.089
72.5	0.558	1.880	1.269	0.067	0.068
71.7	0.469	1.610	1.476	0.063	0.062
71.4	0.447	1.561	1.515	0.061	0.061
70.2	0.296	1.288	2.070	0.052	0.052
69.9	0.287	1.283	2.075	0.050	0.051
69.7	0.133	1.080	3.166	0.035	0.035
69.7	0.133	1.080	3.170	0.035	0.345

System: (1) hexene-1–(2) Cellosolve: $a_{12} = 0.055$; $b_{12} = 0.498$; $c_{12} = 0.005$

Temp., °C.	x_{CEL}	γ_{HE}	γ_{CEL}	Expt. y_{CEL}	Calcd. y_{CEL}
110.5	0.950	3.064	1.000	0.435	—
94.7	0.895	2.958	1.067	0.237	0.234
95.0	0.833	2.688	1.087	0.150	0.152
73.9	0.672	2.036	1.205	0.082	0.082
71.2	0.573	1.726	1.274	0.065	0.065
68.5	0.423	1.410	1.476	0.049	0.049
66.2	0.227	1.151	1.885	0.030	0.030
65.1	0.124	1.064	2.214	0.018	0.018

System: (1) *n*-hexane–(2) 1, 2, 3-trichloropropane: $a_{12} = -0.047$; $b_{12} = 0.574$; $c_{12} = 0.065$

Temp., °C.	x_{TCP}	γ_{HA}	γ_{TCP}	Expt. y_{TCP}	Calc. y_{TCP}
112.6	0.908	2.47	1.00	0.247	0.249
99.3	0.837	2.199	1.021	0.146	0.145
88.7	0.713	1.771	1.086	0.089	0.089
82.6	0.553	1.387	1.246	0.062	0.062
79.7	0.427	1.188	1.525	0.052	0.051
76.4	0.330	1.130	1.829	0.042	0.043
76.3	0.308	1.100	1.971	0.040	0.042
73.8	0.203	1.038	2.624	0.033	0.032
73.4	0.202	1.053	2.58	0.032	0.032
70.7	0.105	1.030	3.50	0.020	0.020

System: (1) hexene-1–(2) 1, 2, 3-trichloropropane: $a_{12} = -0.032$; $b_{12} = 0.397$; $c_{12} = 0.046$

Temp., °C.	x_{TCP}	γ_{HE}	γ_{TCP}	Expt. y_{TCP}	Calcd. y_{TCP}
114.1	0.903	1.912	1.038	0.269	0.269
101.1	0.832	1.757	1.057	0.160	0.158
90.3	0.726	1.513	1.088	0.097	0.094
83.6	0.622	1.363	1.148	0.067	0.066
81.3	0.571	1.288	1.190	0.058	0.057
77.4	0.482	1.206	1.341	0.047	0.045
77.2	0.473	1.172	1.327	0.045	0.044
75.6	0.422	1.150	1.386	0.039	0.039
72.8	0.321	1.072	1.618	0.031	0.030
68.4	0.170	1.014	2.062	0.017	0.017
67.7	0.157	1.026	2.087	0.016	0.016
66.1	0.084	0.998	2.360	0.009	0.009

Selectivity is expressed by Equation 12

$$S = \frac{(\alpha_{12})_{123}}{(\alpha_{12})_{12}} = \frac{[(\gamma_1/\gamma_2)(P_1/P_2)]_{123}}{[(\gamma_1/\gamma_2)(P_1/P_2)]_{12}} \qquad (12)$$

The primary effect of adding the solvent to the original mixture is to modify the relative volatility of the hydrocarbons to some value different from the relative volatility in the absence of the solvent. This ratio shown in Equation 12 is a measure of the effectiveness of the solvent for the particular compounds involved.

Because the variation in the ratio of the pure component vapor pressures varies but slightly with temperature, Equation 12 will reduce to

$$S \cong \frac{(\alpha_{12})_{123}}{(\alpha_{12})_{12}} = \frac{(\gamma_1/\gamma_2)_{123}}{(\gamma_1/\gamma_2)_{12}} \qquad (13)$$

Also, since the activity coefficient ratio of the hydrocarbons in the hydrocarbon-nonsolvent binary is essentially unity, Equation 13 further reduces to

$$S \cong (\gamma_1/\gamma_2)_{123} \qquad (14)$$

Because there is a tendency in the literature to express selectivity in terms of the ratio of the activity coefficients of the two components whose separability is of principal interest, at infinite dilution,—where the concentration of the solvent approaches unity, and the temperature approaches the boiling temperature of the solvent at the pressure imposed,—Equation 15 is commonly used to express selectivity.

$$S \cong (\gamma_1^0/\gamma_2^0)_{x_S \to 1.0} \qquad (15)$$

These restrictions fix the comparison at a definite concentration level and pressure, but result in comparisons at tempera-

Table IV. Ternary Vapor-Liquid Equilibrium Data at 760 mm. of Hg Pressure

Temp., ° C.	x_{HA}	x_{HE}	y_{HA}	y_{HE}	γ_{HA}	γ_{HE}
System: (1) *n*-hexane–(2) hexene-1–(3) 1, 4-dioxane						
65.3	0.229	0.645	0.221	0.696	1.08	1.02
66.0	0.231	0.631	0.224	0.694	1.06	1.02
68.2	0.165	0.471	0.203	0.603	1.25	1.11
67.9	0.163	0.470	0.205	0.602	1.30	1.12
72.6	0.103	0.298	0.187	0.521	1.60	1.32
72.7	0.103	0.297	0.188	0.516	1.61	1.31
85.7	0.027	0.082	0.118	0.319	2.62	2.03
86.6	0.026	0.079	0.111	0.290	3.19	2.38
67.4	0.448	0.414	0.441	0.460	1.03	0.98
68.6	0.324	0.314	0.400	0.409	1.24	1.11
72.3	0.213	0.210	0.363	0.349	1.51	1.27
85.5	0.049	0.054	0.226	0.217	2.77	2.10
67.7	0.672	0.207	0.671	0.236	1.03	1.00
69.7	0.490	0.156	0.589	0.199	1.17	1.06
73.2	0.294	0.096	0.522	0.169	1.55	1.31
84.8	0.074	0.029	0.330	0.113	2.78	2.06
System: (1) *n*-hexane–(2) hexene-1–(3) Cellosolve						
67.7	0.443	0.405	0.470	0.487	1.10	1.06
69.4	0.306	0.294	0.466	0.475	1.49	1.35
74.5	0.167	0.163	0.468	0.447	2.35	1.96
107.9	0.027	0.028	0.320	0.286	3.98	3.03
68.5	0.659	0.205	0.706	0.249	1.11	1.04
70.3	0.468	0.149	0.700	0.239	1.42	1.30
74.9	0.237	0.080	0.683	0.224	2.39	1.98
105.5	0.043	0.015	0.488	0.148	4.08	3.03
67.0	0.227	0.633	0.238	0.723	1.11	1.04
66.6	0.229	0.619	0.241	0.719	1.13	1.05
68.5	0.160	0.439	0.244	0.701	1.53	1.36
68.8	0.151	0.441	0.235	0.708	1.55	1.36
74.5	0.082	0.230	0.247	0.667	2.52	2.08
74.4	0.078	0.229	0.240	0.675	2.55	2.11
108.8	0.014	0.043	0.160	0.430	3.74	2.88
System: (1) *n*-hexane–(2) hexene-1–(3) 1, 2, 3-trichloropropane						
70.5	0.496	0.354	0.547	0.435	1.04	0.99
77.0	0.292	0.283	0.482	0.470	1.28	1.10
129.2	0.016	0.018	0.280	0.266	3.65	2.66
71.0	0.618	0.194	0.719	0.255	1.08	1.04
72.1	0.638	0.199	0.724	0.254	1.02	0.98
77.2	0.436	0.140	0.721	0.229	1.28	1.08
78.5	0.425	0.141	0.716	0.238	1.25	1.08
88.3	0.213	0.076	0.685	0.222	1.81	1.41
88.6	0.224	0.077	0.689	0.219	1.72	1.36
127.2	0.028	0.011	0.468	0.151	3.34	2.41
69.0	0.220	0.601	0.247	0.733	1.11	1.03
69.7	0.220	0.616	0.242	0.749	1.07	1.00
76.6	0.149	0.423	0.250	0.707	1.32	1.12
89.1	0.068	0.214	0.239	0.668	1.93	1.48
127.8	0.011	0.032	0.160	0.407	3.23	2.39
129.6	0.010	0.029	0.388	0.162	3.41	2.41

tures which possibly are widely different. However, in most practical considerations, selectivity as defined by Equation 15 is sufficient to compare solvent effects if the interaction mechanism of the solvents being compared with the components in question are not too widely different in nature. In this investigation, dioxane and trichloropropane are considered to be nonhydrogen-bonding solvents and Cellosolve, a glycol-ether, can be considered a weak hydrogen-bonding agent.

Vapor-liquid equilibrium data for the ternary, solvent-containing systems were measured in such a way as to find the effect of solvent concentration on the ratio of $(\gamma_1/\gamma_2)_{123}$ in the solvent-free binary systems as shown in Equation 12.

The following observations result from examination of the data.

Selectivity (Equation 14) increases steadily with solvent concentration and it varies but little with the relative proportion of *n*-hexane to hexene-1 in the mixture. This was also noted by Gerster, Mertes, and Colburn (*4*) in the case of *n*-butane and butene-1. In many cases (*5*), it has been assumed that the relative volatility of the *n*-butane to butene-1 was independent of the proportion of paraffin to olefin in computing efficiencies of fractionating towers using furfural-water as a solvent.

Cellosolve produces the largest individual values of activity coefficient but does not produce the correspondingly greatest value of selectivity, $(\gamma_1/\gamma_2)_{123}$. Solvents capable of internal hydrogen bonding have been observed in some cases to cause lower selectivity than those which do not (*3*). The selectivity of the three solvents expressed as the ratio of the hydrocarbon activity coefficients at infinite dilution, Equation 15, is as follows: trichloropropane, 1.41; Cellosolve, 1.33; 1,4-dioxane, 1.36.

$$G^E_{123} = G^E_{12} + G^E_{23} + G^E_{31} + RTx_1x_2x_3[B_{123} + C_1(x_2 - x_3) + C_2(x_3 - x_1) + C_3(x_1 - x_2) + \cdots] \qquad (16)$$

$$\frac{G^E_{123}}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_3 \ln \gamma_3 \qquad (17)$$

Using Equations 16 and 17 and the Ibl and Dodge form of the Gibbs-Duhem equation, Chao and Hougen derived the activity-coefficient ratio equation, 18, for a ternary system. This equation was used to correlate selectivity $(\gamma_1/\gamma_2)_{123}$ in the ternary mixtures.

$$\log (\gamma_1/\gamma_2)_{123} = a_{12} - b_{12}(x_1 - x_2) + c_{12}[2x_1x_2 - (x_1 - x_2)^2] + x_3[b_{31} + b_{23} - c_{23}(2x_2 - x_3) + c_{31}(x_3 - 2x_1) - b_{123}(x_1 - x_2)] \qquad (18)$$

For the nearly ideal system: *n*-hexane–hexene-1

$$\log (\gamma_1/\gamma_2)_{123} = x_3[b_{31} - b_{23} - c_{23}(2x_2 - x_3) + c_{31}(x_3 - 2x_1) - b_{123}(x_1 - x_2)] \qquad (19)$$

In the case of 1,4-dioxane and 1,2,3-trichloropropane, selectivity data were very well correlated by assuming the ternary constant to be zero. The average deviation of calculated and experimental values of selectivity were 0.7% and 2.9% for 1,4-dioxane and 1,2,3-trichloropropane, respectively. A small ternary constant, −0.1, enabled satisfactory correlation of selectivity in the case of the Cellosolve ternary system. The average deviation in this case was about 3%.

CONCLUSIONS

The binary system *n*-hexane–hexene-1 exhibits nearly ideal behavior—i.e., $(\gamma_1/\gamma_2)_{12} = 1.0$. Selectivity and the relative volatility of *n*-hexane to hexene-1 is enhanced by the addition of any of the three solvents investigated. Selectivity varies only slightly with changing the hydrocarbon composition ratio, and it increases essentially linearly with solvent concentration. The three solvents proved to be about equally effective in increasing selectivity, and their value as extractive agents for the hexane–hexene-1 system can only be considered fair.

NOMENCLATURE

a, b, c, d = constants in Chao-Hougen equation
$B_{12}, C_{12}, D_{12}, B_{123}, C_1, C_2, C_3$ = constants in Redlich-Kister equation
CEL = Cellosolve
Calc = calculated
DIO = 1, 4-dioxane
E = defined by Equation10
Expt = experimental
G^E = excess free energy
H^* = enthalpy of pure component
H_{12} = enthalpy of binary liquid mixture
HA = *n*-hexane
HE = nexene-1
n = normal
P = vapor pressure of liquid component
P_T = total system pressure
x = liquid phase mole fraction
y = vapor phase mole fraction
R = gas-law proportionality factor
S = selectivity
T = temperature, absolute
Z = defined by Equation 5

Greek letters

α_{12} = relative volatility of *n*-hexane to hexene-1
γ = liquid phase activity coefficient
γ° = liquid phase activity coefficient at infinite dilution
Δ = difference

Subscripts

1 = *n*-hexane
2 = hexene-1
3 = solvent

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