Alteration of the Relative Volatility of *n*-Hexane–1-Hexene by Oxygenated and Chlorinated Solvents

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Vapor-liquid equilibrium data at 60° C. are reported for the binary systems 1-hexene–*n*-hexane and these hydrocarbons with 2-butanone (methyl ethyl ketone), 2-butanol, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, tetrachloroethylene, and trichloroethylene.

MEASUREMENTS were made in a glass and Teflon vapor-circulating still equipped with three guard heaters for adiabatic operation. Data were also recorded for the systems *n*-hexane–benzene at 1-atm. pressure and heptane-benzene at 60° C. to verify the experimental procedure with well known systems. Activity coefficients were corrected for vapor phase imperfections and pressure effects on liquid phase fugacity and were tested for thermodynamic consistency by the Redlich-Kister (*13*) integral test. The selectivity of the solvents was correlated with fair success by an adaptation of the polar solubility parameter method of Weimer and Prausnitz (*17*). The nonpolar, symmetrical tetrachloroethylene shows a definite selectivity for the pair but less than that expected from its calculated polar solubility parameter. The selectivity of the alcohol is much less than predicted from its large polar solubility parameter but about the same as an ether of the same molecular weight.

A program was initiated to determine the effect of oxygenated and chlorinated solvents on the relative volatility of *n*-hexane and 1-hexene. Vapor-liquid measurements were made over the full composition range at 60° C. for binary mixtures of the hydrocarbons with 2-butanone, 2-butanol, and five chloroethanes and chloroethylenes. The alcohol and ketone are similar in structure but the alcohol is strongly intermolecularly hydrogen-bonded. The chlorine compounds were chosen to show the effect of chlorine substitution and "active hydrogens" on solvent selectivity. The selectivity of the solvents for the *n*-hexane with respect to 1-hexene was reasonably well correlated by the polar solubility parameter method of Weimer and Prausnitz (*17*).

EQUIPMENT AND METHOD

The vapor-circulating equilibrium still used throughout the investigation was an adaptation of the still described by Stephenson (*14*). Three guard heaters were added to improve the approach to adiabatic operation, and a Teflon-stemmed valve replaced the greased stopcock. Details of the experimental apparatus and technique are given in the original work (*9*).

Thermocouples were calibrated from 25° to 130° C. against a set of National Bureau of Standards certified mercury-in-glass thermometers. Pressure measurement was by mercury manometer and a cathetometer with a reading precision of ±0.05 mm. Pressure was controlled manually to ±0.2 mm. of Hg with the aid of a temperature-controlled ballast. Analysis of the liquid and vapor phases was either by refractive index (Bausch and Lomb Precision Refractometer Style 33-45-03) or by gas-liquid chromatography (Beckman Instruments Type GC-2). Precision of the analytical methods was ±0.002 mole fraction or better.

MATERIALS

The hydrocarbons were Phillips pure grade materials used without further purification except for *n*-heptane, which was dried by refluxing over silica gel and then distilled to obtain an overhead product. Commercially available solvents were dried by refluxing over silica gel and then distilled in at least a 15-plate Oldershaw column at high reflux ratios. The refractive indices and typical vapor pressures (measured in the equilibrium still) are listed in Table I.

EXPERIMENTAL RESULTS

The binary liquid phase activity coefficients referred to the pure liquids at the temperature and pressure of the system were obtained by Equation 1 (written for component 1), as presented by Van Ness (*16*)

$$\ln \gamma_1^L = \ln \frac{y_1 P}{x_1 P_1'} + \frac{(B_{11} \times V_1^L)(P - P_1')}{RT} + \frac{P\delta_{12} y_2^2}{RT} \qquad (1)$$

where subscripts 1 and 2 refer to components 1 and 2 of the binary, γ_1^L is the liquid phase activity coefficient, x_1 and y_1 are liquid and vapor phase compositions, respectively, P is the total pressure, P_1' is the vapor pressure at temperature T, and V_1^L is saturated liquid volume. The term $\delta_{12} = 2B_{12} - B_{11} - B_{12}$, where B_{11} and B_{22} are pure component second virial coefficients and B_{12} is the interaction virial coefficient. The second virial coefficients for the pure compounds were obtained from *PVT* or latent heat of vaporization measurements except for the chlorinated compounds, for which very few data were found. Some data for trichloroethylene and *cis*- and *trans*-dichloroethylene (*6*) were correlated by the law of corresponding states and the second virial coefficients for the remaining chlorinated compounds obtained from this correlation.

The interaction second virial coefficient, B_{12}, was set equal to the arithmetic average of the pure component second virials for hydrocarbon-hydrocarbon and hydrocarbon-chlorocompound mixtures, implying that $\delta_{12} = 0$. This assumption is supported for the latter mixtures by measurements of virial coefficients in the *n*-hexane-chloroform (*7*) and the *n*-pentane–methyl bromide and the *n*-pentane–ethyl bromide systems (*12*). The assumption does not, however, hold for the hydrocarbon-ketone and hydrocarbon-alcohol systems where the vapor mixtures show positive deviations from the simple arithmetic averaging rule. In these systems, the interaction second virial coefficient was set equal to

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Table I. Refractive Indices and Boiling Points of Materials

Material	Refractive Index, n_D^{25}		Normal (760 Mm. Hg) Boiling Point, ° C.	
	Observed	Literature	Observed	Literature
Heptane	1.38524	1.38511 (5)	98.44	98.43 (5)
Benzene	1.4980	1.4979 (4)	80.03	80.10 (4)
1,1,1-Trichloroethane	1.43525	1.4352 (5)	74.05	74.1 (5)
1,1,2-Trichloroethane	1.4689	1.4687 (5)	113.63	113.77 (5)
			Vapor Pressure at 60° C. Mm. Hg	
1-Hexene	1.3851	1.3850 (5)	679.7	679.7 (5)
n-Hexane	1.3724	1.37226 (5)	573.4	572.2 (5)
2-Butanone	1.3762	1.3761 (3)	389.9	389.9 (3)
2-Butanol	1.39525	1.3950 (1)	136.1	136.6 (1)
1,1,2,2-Tetrachloroethane	1.4981	1.4915[a] (15)	34.3	[b]
Tetrachloroethylene	1.5032	1.5028 (5)	94.4	96.6[c] (5)
Trichloroethylene	1.4748	1.4746 (5)	312.6	311.6[c] (5)

[a] Estimated. [b] Not known. [c] Calculated.

the arithmetic average of the hydrocarbon second virial coefficient and the second virial coefficient of the nonpolar homomorph of the alcohol or ketone, determined at the same temperature. In effect, we say that the interaction between the hydrocarbon and polar molecule is merely the interaction between nonpolar molecules, with methyl or methylene groups substituted for the polar groups of the alcohol or ketone. This is an empirical method which gave better agreement with experiment than the true homomorphic method (homomorph at the same reduced temperature as the polar compound) when tested with mixture virial coefficients for the acetone-cyclohexane system reported by Lambert, Murphy, and Sanday (*10*).

The size of the imperfection correction is indicated in Table II where the sum of the two rightmost terms of Equation 1, evaluated at the boundaries and raised to the power e, is listed for the 15 systems containing either *n*-hexane or 1-hexene. This number is a multiplier which corrects the apparent limiting activity coefficient, $[yP/xP']^0$, to the true limiting liquid phase activity coefficient. The corrections cannot be ignored in many cases and consequently have been applied for all cases. The effect of these corrections on the apparent consistency of the data will be discussed.

To test the thermodynamic consistency of each data set and to obtain the limiting activity coefficients, the function ln (γ_1/γ_2) was fitted by least squares to the empirical equation

$$\ln(\gamma_1/\gamma_2) = \sum_{n=0}^{N} A_n(x_1 - 0.5)^n \tag{2}$$

The systems containing 2-butanone, 2-butanol, 1,1,1-trichloroethane, and 1,1,2-trichloroethane were treated by regression analysis to obtain the power series of maximum degree at which all variables were significant. Variables were tested at the 95% confidence level by the t test and removed one at a time if shown to be nonsignificant. The degree of the power series is indicated in Table III where regression coefficients and standard deviations for each system are listed for all systems. The remaining systems were not subjected to analysis but were adjudged by inspection to be adequately fitted by the quadratic form of Equation 2.

The function ln (γ_1/γ_2) was integrated over the limits of concentration to provide a measure of consistency by the well known Redlich-Kister test (*13*). A consistency index, defined as

$$\text{C.I.} = \frac{I_p + I_m}{|I_p| + |I_m|} \tag{3}$$

where I_p is the positive integrated area and I_m the negative integrated area, less in magnitude than 0.05 was considered excellent evidence of thermodynamic consistency. Of the 17 systems measured, |C.I.| for 12 was 0.05 or less, for

Table II. Size of Imperfection Correction to Limiting Activity Coefficient

System	$\exp\left[\frac{(B_{11} - V_1^L)(P_2' - P_1') + P_2'\delta_{12}}{RT}\right]$	$\exp\left[\frac{(B_{22} - V_2^L)(P_1' - P_2') + P_1'\delta_{12}}{RT}\right]$
1-Hexene–*n*-hexane	1.0072	0.9922
1-Hexene–2-butanone	1.0556	0.9925
n-Hexane–2-butanone	1.0443	1.0027
1-Hexene–2-butanol	1.0946	0.9455
n-Hexene–2-butanol	1.0784	0.990
1-Hexene–1,1,1-trichloroethane	1.0136	0.988
n-Hexane–1,1,1,-trichloroethane	1.0068	0.9945
1-Hexene–1,1,2-trichloroethane	1.0391	0.9565
n-Hexane–1,1,2-trichloroethane	1.0342	0.965
1-Hexene–1,1,2,2-tetrachloroethane	1.0449	0.932
n-Hexane–1,1,2,2-tetrachloroethane	1.0405	0.943
1-Hexene–trichloroethylene	1.0253	0.975
n-Hexane–trichloroethylene	1.0194	0.982
1-Hexene–tetrachloroethylene	1.0406	0.944
n-Hexane–tetrachloroethylene	1.0360	0.954

Table III. Coefficients of Equation 2

System	A_0	A_1	A_2	A_3	A_4	Standard Deviation of Correlation
Hexane-benzene	−0.039595	−0.852177	0.499219			0.0056
Hexane-benzene[a]	−0.041674	−0.862399	0.551323			0.0160
Benzene-heptane	0.045420	−0.822371	−0.694080			0.0088
Benzene-heptane[b]	0.031051	−0.807114	−0.731529			0.0107
Hexene-hexane	0.001599	−0.055782	−0.017090			0.0044
Hexene-MEK	0.028361	−1.613355	−0.250400	−1.235992		0.0106
Hexene-MEK	0.041389	−2.158113	−0.363789	−1.641533		0.0119
Hexene-butanol	0.094692	−2.3360	−0.51786	−3.5123	−4.9428	0.0076
Hexane-butanol	0.15526	−2.5383	−0.89723	−4.0023	−4.8580	0.0120
Hexene-1,1,1-trichloroethane	−0.000664	−0.348935	0.094489			0.0061
Hexane-1,1,1-trichloroethane	−0.007546	−0.603861	−0.125751			0.0064
Hexene-1,1,2-trichloroethane	−0.034799	−1.24616	0.438318			0.0080
Hexane-1,1,2-trichloroethane	−0.046000	−1.98362	0.498931			0.0219
Hexene-1,1,2,2-tetrachloroethane	−0.012311	−1.11862	−0.017350			0.0244
Hexane-1,1,2,2-tetrachloroethane	−0.043042	−1.89118	0.218279			0.0172
Hexene-trichloroethylene	−0.004518	−0.352921	0.114399			0.0036
Hexane-trichloroethylene	−0.012711	−0.658315	0.237759			0.0044
Hexene-tetrachloroethylene	−0.007230	−0.557856	0.083491			0.0005
Hexane-tetrachloroethylene	−0.028439	−0.717746	0.211123			0.0017

[a] Data of Myers (*11*). [b] Data of Brown (*2*).

16 systems, |C.I.| was 0.06 or less, and for all systems, |C.I.| was 0.083 or less (Table IV).

The experimental data are divided into two sections: binary systems measured for comparison with the results of other investigators to serve as a check on the technique, and new binary systems among the hydrocarbons and the seven solvents.

The experimentally observed temperatures, pressures, and compositions plus the calculated activity coefficient, and difference between the observed and back-calculated ln (γ_1/γ_2) function are listed for the 19 binary systems (Tables V and VI). The consistency indices, limiting activity coefficients, and volumetric data used in calculating activity coefficients are also listed (Table IV).

Systems Measured for Comparison. Our *n*-hexane–benzene data are very smooth and consistent and are fitted extremely well by quadratic form of Equation 2 (Tables III, IV, and V). The data of Myers (*11*) are also smooth and consistent (same tables) and the agreement between the two sets of data is good, as shown by the common plot (Figure 1). The system benzene-heptane (Tables III and V) was measured at 60° C. to check against the measurements of Brown (*2*). Our data are smooth but show a consistency index (Table IV) larger in absolute value (0.060) than our hexane-benzene system (0.009). Brown's data (*2*) were recalculated by Equation 1 (Tables III and V) and show a consistency index of −0.147 (Table IV). The common plot (Figure 2) shows disagreement of the benzene activity coefficients at low benzene concentration. On the basis of a smaller absolute value of consistency index, our data are the more accurate of the two sets.

New Binary Systems. Numerical data for the 15 new binary systems are listed (Tables III, IV, and VI). The *n*-hexane–1-hexene activity coefficients, despite rather small deviations

Table IV. Consistency Index, Limiting Activity Coefficients, and Volumetric Data

System	Consistency Index[a]						
	Corrected	Uncorrected	$\gamma_1^{L\circ}$	$\gamma_2^{L\circ}$	$B_{11} - V_1^L$ Cc./Mole	$B_{22} - V_2^L$ Cc./Mole	δ_{12} Cc./Mole
n-Hexane–benzene	0.009		1.667	1.406	[c]	[c]	0
n-Hexane–benzene[b]	0.020		1.694	1.398	[c]	[c]	0
Benzene–heptane	−0.060		1.327	1.715	−1212	−2202	0
Benzene–heptane[d]	−0.147		1.286	1.743	−1212	−2202	0
1-Hexene–*n*-hexane	0.013	−0.5	1.02255	1.031	−1413	−1530	0
1-Hexene–2-butanone	0.017	−0.023	2.527	2.706	−1413	−1990	1079
n-Hexane–2-butanone	0.019	0.000	3.436	3.795	−1530	−1990	1079
1-Hexene–2-butanol	−0.015	−0.061	3.537	7.034	−1413	−2530	1564
n-Hexane–2-butanol	0.026	−0.008	4.042	8.517	−1530	−2530	1564
1-Hexene–1,1,1-trichloroethane	0.083	−0.06	1.218	1.164	−1413	−1249	0
n-Hexane–1,1,1-trichloroethane	0.019	−0.019	1.385	1.321	−1530	−1249	0
1-Hexene–1,1,2-trichloroethane	0.006	−0.126	2.009	1.730	−1413	−1640	0
n-Hexane–1,1,2-trichloroethane	−0.009	−0.086	2.917	2.492	−1530	−1640	0
1-Hexene–1,1,2,2-tetrachloroethane	−0.049	−0.250	1.721	1.779	−1413	−2280	0
n-Hexane–1,1,2,2-tetrachloroethane	−0.052	−0.159	2.604	2.545	−1530	−2280	0
1-Hexene–trichloroethylene	0.057	−0.220	1.222	1.165	−1413	−1407	0
n-Hexane–trichloroethylene	0.043	−0.068	1.456	1.326	−1530	−1407	0
1-Hexene–tetrachloroethylene	−0.002	−0.331	1.340	1.304	−1413	−2042	0
n-Hexane–tetrachloroethylene	−0.060	−0.278	1.467	1.397	−1530	−2042	0

[a] Listed both for apparent activity coefficient (uncorrected) and activity coefficient corrected for vapor phase imperfection. [b] Data of Myers (*11*). [c] This data listed for constant temperature systems only. [d] Data of Brown (*2*).

Table V. Systems Measured to Verify Experimental Technique

x_1	y_1	T, ° C.	γ_1^L	γ_2^L	Δ ln γ_1^L/γ_2^L
n-Hexane (1) and Benzene (2) at 760 Mm. Hg					
This work					
0.052	0.108	77.9	1.584	1.004	0.014
0.055	0.112	77.9	1.565	1.004	0.006
0.122	0.216	75.9	1.436	1.013	−0.005
0.125	0.220	75.8	1.434	1.013	−0.003
0.128	0.222	75.8	1.417	1.015	−0.012
0.219	0.334	73.8	1.313	1.032	0.001
0.234	0.347	73.6	1.288	1.040	−0.008
0.311	0.422	72.4	1.218	1.060	−0.001
0.312	0.422	72.4	1.215	1.062	−0.004
0.312	0.424	72.4	1.219	1.059	0.003
0.320	0.430	72.3	1.209	1.066	−0.004
0.323	0.432	72.2	1.207	1.067	−0.003
0.381	0.483	71.5	1.168	1.086	0.004
0.387	0.487	71.5	1.162	1.088	0.002
0.499	0.577	70.4	1.101	1.137	0.006
0.503	0.579	70.4	1.096	1.141	0.002
0.603	0.657	69.7	1.060	1.191	0.005
0.606	0.659	69.7	1.058	1.195	0.002
0.717	0.746	69.1	1.030	1.260	−0.001
0.720	0.749	69.1	1.030	1.261	0.001
0.793	0.809	68.9	1.016	1.306	−0.004
0.798	0.814	68.8	1.017	1.304	0.001
0.897	0.902	68.7	1.007	1.362	−0.003
0.898	0.902	68.7	1.007	1.368	−0.007
0.937	0.939	68.6	1.006	1.368	0.009
0.940	0.942	68.6	1.006	1.386	−0.003
Data of Myers (*11*)					
0.015	0.033	79.6	1.639	0.997	−0.010
0.023	0.051	79.2	1.696	0.997	0.036
0.048	0.100	78.3	1.585	0.999	0.001
0.078	0.153	77.3	1.520	1.002	−0.003
0.082	0.156	77.2	1.490	1.003	−0.019
0.088	0.168	77.0	1.504	1.001	−0.000
0.098	0.184	76.7	1.491	1.002	0.004
0.102	0.191	76.7	1.486	1.000	0.007
0.108	0.197	76.5	1.468	1.002	0.000
0.112	0.205	76.3	1.470	1.004	0.006
0.123	0.223	76.1	1.467	1.001	0.021
0.141	0.243	75.7	1.405	1.007	−0.006
0.177	0.288	74.9	1.360	1.012	0.001
0.198	0.308	74.6	1.315	1.020	−0.015
0.215	0.330	74.2	1.308	1.023	−0.003
0.241	0.353	73.8	1.265	1.031	−0.014
0.268	0.392	73.3	1.280	1.021	0.038
0.274	0.385	73.2	1.231	1.046	−0.018
0.308	0.416	72.7	1.204	1.059	−0.016
0.310	0.418	72.6	1.204	1.060	−0.015
0.338	0.439	72.3	1.173	1.076	−0.026
0.352	0.454	72.0	1.172	1.079	−0.015
0.390	0.486	71.6	1.147	1.094	−0.013
0.451	0.539	70.9	1.120	1.111	0.005
0.511	0.586	70.5	1.089	1.137	0.007
0.532	0.603	70.3	1.082	1.146	0.011
0.566	0.629	70.2	1.066	1.160	0.011
0.608	0.661	69.8	1.052	1.185	0.009
0.650	0.692	69.6	1.039	1.218	0.000
0.688	0.725	69.4	1.034	1.224	0.016
0.743	0.770	69.2	1.024	1.254	0.016
0.795	0.815	69.0	1.017	1.271	0.025
0.872	0.878	68.6	1.013	1.362	−0.010
0.920	0.921	68.8	0.999	1.400	−0.030
0.960	0.961	68.8	1.001	1.384	−0.003
Benzene (1) and *n*-Heptane (2)					
This work					
0.087	0.187	237.6	1.316	1.003	0.005
0.088	0.188	237.9	1.313	1.004	0.001
0.180	0.340	265.2	1.286	1.011	0.003
0.280	0.463	290.8	1.232	1.022	−0.005
0.404	0.578	317.5	1.167	1.059	−0.021
0.475	0.639	332.8	1.149	1.074	0.002
0.479	0.642	333.0	1.145	1.076	0.000
0.618	0.738	355.8	1.088	1.144	0.011
0.713	0.796	368.7	1.053	1.226	0.009
0.795	0.847	377.8	1.028	1.321	0.008
0.907	0.922	387.2	1.006	1.517	−0.006
0.908	0.923	388.2	1.008	1.522	−0.007
Data of Brown (*2*) at 60° C.					
0.018	0.042	216.4	1.317	1.004	0.022
0.045	0.100	224.9	1.276	1.007	−0.010
0.093	0.193	239.7	1.285	1.011	0.002
0.188	0.342	266.9	1.249	1.023	−0.013
0.293	0.472	294.4	1.216	1.038	−0.008
0.387	0.563	315.6	1.176	1.060	−0.008
0.488	0.646	335.6	1.139	1.090	0.003
0.578	0.708	350.8	1.099	1.140	0.001
0.580	0.709	351.0	1.098	1.140	0.002
0.684	0.776	365.9	1.063	1.212	0.010
0.791	0.843	378.1	1.030	1.330	0.010
0.896	0.914	387.6	1.010	1.501	0.007
0.943	0.949	390.3	1.004	1.602	0.003
0.979	0.980	391.5	1.001	1.722	−0.019

Table VI. New Binary Systems at 60° C.

x_1	y_1	PT, Mm. Hg	γ_1^L	γ_1^L	Δ ln γ_1^L/γ_2^L
1-Hexene (1) and *n*-Hexane (2)					
0.121	0.142	588.3	1.022	1.000	0.001
0.123	0.143	588.1	1.015	1.001	−0.006
0.148	0.173	591.2	1.018	1.000	−0.002
0.245	0.281	602.5	1.020	0.999	0.007
0.248	0.283	602.7	1.020	0.999	0.006
0.391	0.431	619.2	1.008	1.006	−0.005
0.515	0.556	632.4	1.007	1.005	0.001
0.666	0.698	648.2	1.002	1.015	−0.005
0.825	0.845	662.7	1.000	1.016	0.002
0.874	0.889	668.3	1.001	1.019	0.004
0.877	0.891	668.5	1.000	1.026	−0.003
1-Hexene (1) and 2-Butanone (2)					
0.094	0.267	484.5	2.079	1.000	0.008
0.094	0.264	485.8	2.053	1.005	−0.010
0.201	0.417	559.1	1.740	1.034	−0.001
0.284	0.499	602.5	1.579	1.068	0.013
0.395	0.572	642.2	1.380	1.151	−0.014
0.523	0.651	677.6	1.245	1.257	0.000
0.633	0.710	697.6	1.152	1.399	−0.000
0.714	0.757	705.5	1.102	1.521	0.017
0.788	0.796	709.9	1.054	1.742	−0.015
0.903	0.886	705.2	1.017	2.125	0.005
0.905	0.886	704.3	1.015	2.149	−0.003
n-Hexane (1) and 2-Butanone (2)					
0.095	0.282	501.8	2.647	1.012	−0.004
0.098	0.288	502.7	2.632	1.009	0.002
0.197	0.419	569.1	2.133	1.044	0.007
0.282	0.484	605.9	1.824	1.102	−0.008
0.395	0.550	635.0	1.545	1.195	−0.009
0.479	0.597	648.3	1.409	1.270	0.017
0.556	0.626	656.9	1.289	1.399	−0.001
0.716	0.697	661.2	1.121	1.788	−0.009
0.803	0.748	654.4	1.058	2.132	−0.008
0.872	0.804	641.5	1.028	2.510	0.003
0.916	0.854	625.8	1.014	2.793	0.024
0.961	0.917	602.3	1.000	3.347	−0.016

(*Continued on page 323*)

Table VI. New Binary Systems at 60° C. *(Continued)*

x_1	y_1	*PT*, Mm. Hg	γ_1^L	γ_2^L	$\Delta \ln \gamma_1^L/\gamma_2^L$
1-Hexene (1) and 2-Butanol (2)					
0.070	0.522	273.4	3.117	1.020	0.002
0.070	0.524	274.3	3.102	1.020	–0.001
0.139	0.668	368.9	2.671	1.030	0.001
0.253	0.761	477.4	2.141	1.103	–0.010
0.395	0.817	559.5	1.719	1.215	0.010
0.482	0.839	595.3	1.535	1.326	0.009
0.584	0.858	626.9	1.360	1.535	–0.012
0.696	0.879	653.5	1.218	1.855	–0.005
0.799	0.899	671.8	1.113	2.427	0.004
0.897	0.924	685.4	1.038	3.630	0.007
0.901	0.925	685.5	1.036	3.710	0.004
0.938	0.942	687.6	1.016	4.618	–0.009
n-Hexane (1) and 2-Butanol (2)					
0.094	0.579	302.4	3.313	1.020	0.005
0.097	0.585	306.2	3.289	1.022	0.004
0.186	0.700	398.8	2.651	1.062	–0.024
0.310	0.779	477.5	2.108	1.103	0.023
0.430	0.811	521.9	1.726	1.245	–0.003
0.607	0.847	563.9	1.375	1.579	–0.006
0.700	0.862	577.9	1.242	1.912	–0.003
0.795	0.877	591.5	1.138	2.554	0.002
0.888	0.899	596.2	1.052	3.858	0.009
0.897	0.902	597.0	1.046	4.078	0.005
0.931	0.918	596.3	1.024	5.104	–0.010
1-Hexene (1) and 1,1,1-Trichloroethane (2)					
0.049	0.079	496.9	1.197	0.999	0.005
0.049	0.079	497.0	1.197	1.000	0.003
0.113	0.170	515.4	1.154	1.001	–0.006
0.199	0.279	539.4	1.125	1.004	0.001
0.305	0.394	565.0	1.081	1.019	–0.013
0.412	0.502	588.6	1.062	1.031	–0.001
0.520	0.601	609.5	1.042	1.045	0.005
0.605	0.676	625.0	1.031	1.057	0.012
0.682	0.737	637.5	1.017	1.084	–0.003
0.806	0.840	655.2	1.007	1.112	–0.001
0.895	0.913	667.3	1.003	1.139	–0.004
0.948	0.957	673.9	1.002	1.149	0.001
n-Hexane (1) and 1,1,1-Trichloroethane (2)					
0.021	0.034	488.4	1.365	1.002	–0.000
0.051	0.078	496.8	1.330	1.003	–0.006
0.105	0.154	511.2	1.304	1.003	0.012
0.203	0.266	531.8	1.218	1.016	–0.002
0.291	0.354	546.4	1.164	1.031	–0.003
0.430	0.480	563.1	1.099	1.063	–0.003
0.504	0.543	570.5	1.073	1.088	–0.004
0.597	0.622	576.4	1.048	1.116	0.002
0.716	0.724	580.5	1.023	1.166	0.002
0.789	0.789	580.8	1.013	1.201	0.002
0.913	0.908	578.5	1.003	1.269	0.000
0.920	0.916	578.6	1.004	1.256	0.014
0.952	0.947	577.0	1.001	1.303	–0.009
0.975	0.972	575.7	1.001	1.312	–0.005
1-Hexene (1) and 1,1,2-Trichloroethane (2)					
0.085	0.473	209.4	1.760	1.027	–0.018
0.088	0.487	211.2	1.782	1.010	0.014
0.186	0.657	289.5	1.541	1.032	0.002
0.264	0.728	339.4	1.409	1.056	0.004
0.388	0.798	405.3	1.251	1.120	0.000
0.484	0.838	450.5	1.167	1.179	0.004
0.573	0.868	489.4	1.105	1.256	–0.005
0.714	0.913	551.0	1.045	1.389	–0.002
0.803	0.940	588.6	1.020	1.485	–0.004
0.898	0.969	632.1	1.006	1.596	0.000
0.898	0.969	632.0	1.007	1.588	0.005
n-Hexane (1) and 1,1,2-Trichloroethane (2)					
0.093	0.542	232.4	2.420	1.001	0.039
0.094	0.522	233.4	2.320	1.051	–0.049
0.185	0.670	302.6	1.951	1.040	0.002
0.107	0.561	245.3	2.310	1.026	0.000
0.106	0.560	244.3	2.316	1.023	0.003
0.192	0.681	307.3	1.947	1.028	0.026
0.285	0.738	355.3	1.635	1.098	–0.005
0.381	0.776	393.1	1.415	1.192	–0.025
0.484	0.813	426.5	1.267	1.300	–0.012
0.558	0.837	449.2	1.185	1.382	0.006
0.688	0.876	484.9	1084	1.606	0.009
0.779	0.907	510.4	1.042	1.786	0.021
0.912	0.958	546.3	1.005	2.179	0.003
0.955	0.977	560.1	1.000	2.369	–0.017
1-Hexene (1) and 1,1,2,2-Tetrachloroethane (2)					
0.098	0.758	134.4	1.608	1.056	–0.015
0.125	0.807	160.9	1.576	1.021	0.030
0.180	0.855	204.8	1.476	1.044	0.003
0.331	0.918	309.8	1.294	1.080	0.004
0.338	0.916	313.4	1.280	1.128	–0.042
0.483	0.946	395.5	1.161	1.156	–0.002
0.674	0.970	495.2	1.063	1.249	0.046
0.686	0.970	500.8	1.056	1.332	–0.012
0.897	0.990	616.7	1.006	1.590	0.001
0.908	0.991	623.2	1.005	1.634	–0.015
n-Hexane (1) and 1,1,2,2-Tetrachloroethane (2)					
0.081	0.754	137.5	2.314	1.064	–0.011
0.093	0.783	150.7	2.278	1.031	0.030
0.181	0.860	224.1	1.906	1.096	–0.029
0.331	0.913	309.9	1.520	1.136	0.008
0.491	0.937	374.3	1.266	1.296	0.002
0.683	0.959	442.8	1.095	1.600	0.003
0.902	0.985	526.5	1.008	2.155	0.008
0.902	0.985	527.0	1.008	2.194	–0.010
1-Hexene (1) and Trichloroethylene (2)					
0.100	0.216	358.9	1.169	0.997	0.004
0.196	0.366	401.6	1.122	1.006	–0.005
0.329	0.524	453.1	1.079	1.017	–0.000
0.486	0.667	510.0	1.042	1.043	–0.001
0.703	0.825	582.8	1.013	1.083	0.005
0.901	0.944	648.4	1.002	1.141	–0.002
n-Hexane (1) and Trichloroethylene (2)					
0.106	0.222	360.4	1.332	1.001	0.002
0.205	0.361	396.4	1.234	1.014	–0.006
0.336	0.504	438.1	1.157	1.038	0.007
0.493	0.634	477.0	1.077	1.090	–0.004
0.692	0.780	518.3	1.025	1.166	0.002
0.902	0.928	557.5	1.003	1.273	–0.000
1-Hexene (1) and Tetrachloroethylene (2)					
0.097	0.484	167.5	1.270	1.007	0.001
0.196	0.666	233.6	1.203	1.014	0.000
0.363	0.807	334.3	1.120	1.047	–0.003
0.539	0.886	429.7	1.057	1.093	–0.004
0.703	0.936	517.5	1.024	1.141	0.009
0.886	0.977	616.3	1.004	1.244	–0.004
n-Hexane (1) and Tetrachloroethylene (2)					
0.113	0.497	170.4	1.340	1.015	–0.002
0.196	0.638	217.1	1.267	1.025	0.003
0.346	0.771	292.1	1.161	1.063	0.001
0.478	0.840	350.9	1.094	1.108	–0.001
0.678	0.913	434.5	1.033	1.201	–0.001
0.882	0.971	521.4	1.005	1.318	0.001

from ideality, are seen to be symmetrical and consistent. The use of Equation 1 in calculating activity coefficients was essential for a meaningful Redlich-Kister consistency test. Table III lists three constants for the function ln (γ_1/γ_2) but the data can be as well represented by a single constant, as follows:

$$\ln(\gamma_1/\gamma_2) = -0.056\,(x_1 - 0.5) \tag{4}$$

The solvents 2-butanone, 2-butanol, 1,1,1-trichloroethane, and 1,1,2-trichloroethane were studied thoroughly, but the minimum of points were taken in the final six systems to describe the function ln (γ_1/γ_2) adequately. The consistency indices are 0.060 or less in absolute value for all but one system, 1-hexene–1,1,1-trichloroethane. The data are, therefore, of satisfactory thermodynamic consistency. A comparison is made (Table IV) between consistency indices of activity coefficient sets calculated by Equation 1 and of sets calculated by the first term of this equation only (apparent activity coefficient). Of the 15 new systems reported, the absolute value of C.I. of 11 systems decreased upon correction, one C.I. remained unchanged, and three increased in magnitude.

Correlation of Selectivity with Polar Solubility Parameter. Weimer and Prausnitz (*17*) have recently correlated a large number of hydrocarbon activity coefficient data at infinite dilution in a variety of polar solvents. Their expression for limiting hydrocarbon activity coefficient is

$$RT\ln\gamma^{L\circ}_{i} = V_i^L\left[(\lambda_S - \lambda_i)^2 + \tau_S^2 - 2\psi_{Si}\right] + RT\left[\ln\frac{V_i^L}{V_S^L} + 1 - \frac{V_i^L}{V_S^L}\right] \tag{5}$$

where $\gamma^{L\circ}$ is the hydrocarbon activity coefficient at infinite dilution, V^L is liquid molar volume, λ is the nonpolar part of the solubility parameter, τ_S is the solvent polar solubility parameter, and ψ_{Si} is the energy term for interaction between a polar and a nonpolar substance. The second term on the right-hand side of Equation 5 arises from the Flory-Huggins excess free energy term for mixtures of polymers. This term has been deleted. The term $V_i^L(\lambda_S - \lambda_i)^2$, which is $RT\ln\gamma^{L\circ}$ calculated from regular solution theory, is transferred to the right-hand side of the equation.

The logarithm of limiting selectivity of a solvent for a pair of hydrocarbons is obtained by taking the difference of Equation 5 for the hydrocarbons

$$\ln(\gamma_1^{L\circ}/\gamma_2^{L\circ}) - \frac{1}{RT}\left[V_1^L(\lambda_S - \lambda_1)^2 - V_2^L(\lambda_s - \lambda_2)^2\right] = \ln(\gamma_1^{L\circ}/\gamma_2^{L\circ}) - \ln S_R = \frac{1}{RT}\left[\tau_S^2(V_1^L - V_2^L) - 2V_1^L\psi_{S1} + 2V_2^L\psi_{S2}\right] \tag{6}$$

where S_R = selectivity predicted by regular theory.

Weimer and Prausnitz (*17*) found that the ψ_{Si} were constant fractions of τ_S^2 for a given class of hydrocarbons. Thus the right-hand side of Equation 6 becomes a linear function of τ_S^2. Because of the limited number of data, no attempt was made to evaluate the parameters, except to fit the data points to a straight line passing through the origin. The polar solubility parameters of the solvents were calculated by the formula

$$\tau^2 = \left(\frac{\Delta U}{V}\right)_T - \left(\frac{\Delta U}{V}\right)_{\text{Homomorph},\,T} \tag{7}$$

that is, τ^2 is the difference between the cohesive energy density of the solvent and the cohesive energy density of its polar homomorph at the same reduced temperature.

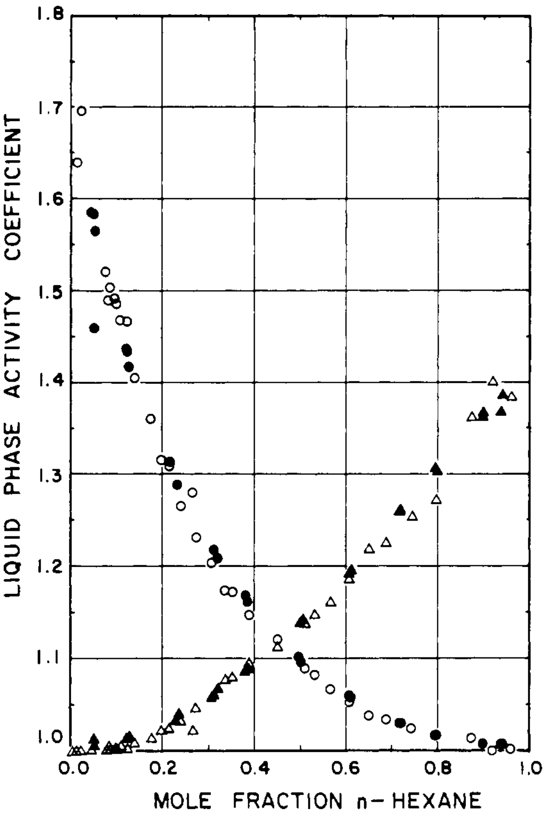

Figure 1. Activity coefficient in *n*-hexane–benzene system at 760 mm. Hg

This investigation	● *n*-Hexane	▲ Benzene
Myers (*11*)	○ *n*-Hexane	△ Benzene

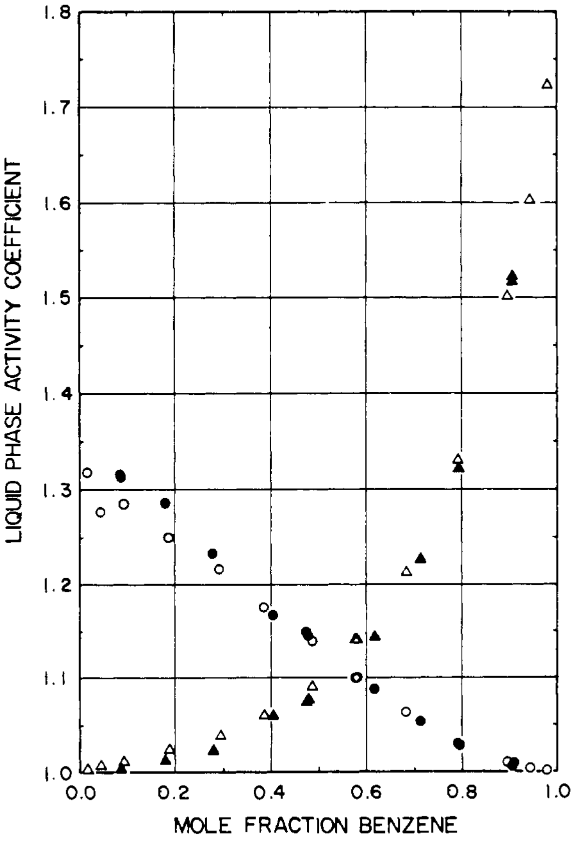

Figure 2. Activity coefficient in benzene–*n*-heptane system at 60° C.

This investigation	● Benzene	▲ *n*-Heptane
Brown (2)	○ Benzene	△ *n*-Heptane

To obtain the homomorph, a methyl group was substituted for a chlorine or —OH group and a methylene for a =O group. The CED's of solvents and homomorphs and the polar solubility parameters are listed in Table VII.

Using this scheme alone, it was not possible to correlate the alcohol selectivity with that of the other solvents, the actual selectivity being far less than that expected on the basis of the alcohol polar solubility. The alcohols are strongly intermolecularly hydrogen-bonded in the pure state. A study by Gerster, Gorton, and Eklund (*8*) of the selectivity of a large number of both polar and hydrogen-bonded solvents toward the *n*-pentane-1-pentene pair showed the hydrogen-bonded to be inferior in selectivity. The high cohesive energy density of the hydrogen-bonded substances is not effective in creating selectivity among paraffin-olefin pairs.

The selectivity function for the seven solvents is plotted against the polar solubility parameter (Figure 3). A straight line passing through the origin was fitted to the data, tetrachloroethylene and 2-butanol omitted, by least squares. The standard deviation of the correlated points is ±0.045 with a maximum deviation of 0.062. The selectivity of the chlorinated solvents is well correlated with polar solubility parameter, indicating polar interaction with the olefinic double bond rather than a specific interaction of the active hydrogens with the double bond. The tetrachloroethylene is an exception, with a selectivity 0.104 unit less than that expected from the general correlation. This solvent is unique in that it has no hydrogens and a zero dipole moment. The low selectivity is probably due to the zero dipole moment and resulting reduced inductive effect on the π-electron of the olefinic double bond.

Table VII. Cohesive Energy and Its Polar Part (τ^2) for the Solvents at 60° C.

Solvent-Homomorph	(U/V) Cal./Cc.	τ^2 (Polar)
2-Butanone	76.2	22.8
2-Methyl-1-butene	53.4	
2-Butanol	108.0	60.0
Methyl *n*-propyl ether	60.6	12.6
2-Methylbutane	48.0	
1,1,1-Trichloroethane	62.6	17.2
neo-Pentane	45.4	
1,1,2-Trichloroethane	87.2	32.7
2-Methylbutane	54.5	
1,1,2,2-Tetrachloroethane	91.3	35.0
2,3-Dimethylbutane	56.3	
Trichloroethylene	75.3	15.5
2-Methyl-2-butene	59.8	
Tetrachloroethylene	78.9	14.7
2,3-Dimethyl-2-butene	64.2	

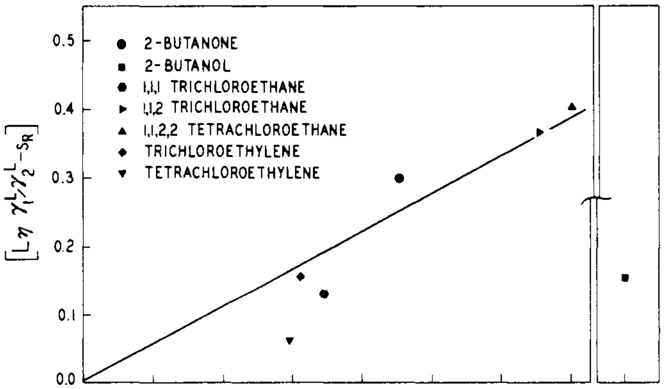

Figure 3. Selectivity as a function of solvent polar solubility parameter

By substituting the observed selectivity function for 2-butanol into the linear equation for the nonhydrogen-bonded solvents (Figure 3), a polar solubility parameter of 13.5 is calculated. The polar solubility of *n*-propyl ether, structurally similar to the alcohol, but not hydrogen-bonded, is 12.6 (Table VII). In this case, the alcohol has nearly the same selectivity toward the olefin as the structurally similar ether. If generally true, this observation would be a useful method for predicting the selectivity of hydrogen-bonded substances using the Weimer-Prausnitz method.

NOMENCLATURE

A_n = empirical coefficient
B_{11} = component 1 second virial coefficient, cc./mole
B_{22} = component 2 second virial coefficient
B_{12} = interaction virial coefficient
ln = logarithm to base *e*
P = total pressure, mm. Hg
P' = vapor pressure, mm. Hg
R = gas law constant
S_R = selectivity calculated by regular theory
U = internal energy, cal./mole
V^L = liquid volume, cc./mole
x = mole fraction, liquid phase
y = mole fraction, vapor phase
γ^L = liquid phase activity coefficient
γ^{L° = activity coefficient in limit of zero concentration
δ_{12} = $2B_{12} - B_{11} - B_{22}$
λ = nonpolar part of solubility parameter
τ = polar part of the solubility parameter
ψ = energy interaction term
$\Delta \ln \gamma_1^L/\gamma_2^L$ = $\ln (\gamma_1^L/\gamma_2^L)_{\text{obsd.}} - \ln (\gamma_1^L/\gamma_2^L)_{\text{calcd.}}$

Subscripts

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

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