Effect of Polar Components on Relative Volatility of the Binary System: Normal Octane-Ethylcylohexane

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Vapor liquid equilibrium data are presented for the binary systems *n*-octane–ethylcyclohexane, *n*-octane–butyl Cellosolve, *n*-octane–2-propanol and ethylcyclohexane–2-propanol at 400 mm. Hg pressure. To determine the effect of additions of butyl Cellosolve and 2-propanol to selected compositions of the *n*-octane–ethylcyclohexane system on the relative volatility partial ternary data were determined at 400 mm. Hg. The butyl Cellosolve increased the relative volatility of the *n*-octane relative to the ethylcyclohexane to a greater extent than the 2-propanol.

THIS RESEARCH is a part of the program being conducted to study experimentally the character and the effect of polar components on the relative volatility of binary systems. Houser (*8*), Lyvers (*10*), Murthi (*11*), Roberts (*17*), and Quozati (*15*) have completed portions of this over-all study. Some other pertinent investigations in this area have been reported by Gerster (*4*), Pierotti (*13*), Prausnitz (*14*), Ralf Anderson (*16*), and Updike (*24*).

Vapor liquid equilibrium data for the *n*-octane–ethylcyclohexane, *n*-octane butyl Cellosolve, *n*-octane–2-propanol, and ethylcyclohexane–2-propanol systems have been determined at 400 mm. Hg absolute. The results are presented in tabular and graphical form.

In addition the effect of the quantity of butyl Cellosolve and 2-propanol added to mixtures of varied compositions of *n*-octane–ethylcyclohexane in modifying their relative volatilities has been investigated at 400 mm. Hg absolute. Butyl Cellosolve was found more effective than 2-propanol in changing relative volatility.

EXPERIMENTAL

Materials. The experimental and literature values of physical properties of the materials used in this investigation are given in Table I. They were of reagent or pure grade. As the physical properties of these materials checked with the literature values with the exception of 2-propanol, no attempt was made to purify them further. The maximum possible error in composition introduced by the difference in refractive index of 2-propanol is 0.0004 mole fraction.

Table I. Properties of Materials

		Normal Octane		Ethylcyclohexane	
		Exptl.	Lit.	Exptl.	Lit.
R.I. °C.					
n_D	30	1.39287	1.39268(*2*)	1.428369	1.42859(*2*)
Density					
d_4	30	0.694943	0.69438(*2*)		
	31			0.77832	0.77865(*2*)
B.P., 400 mm.		104.1	104.0(*23*)	109.2	109.1(*23*)
Antoine Constants					
A			6.92374		6.87041
B			1355.126		1384.036
C			209.517		215.128
		Butyl Cellosolve		2-Propanol	
		Exptl.	Lit.(*3*)	Exptl.	Lit.
R.I. °C.					
n_D	25	1.41746	1.4172		
	20	1.41943	1.4193	1.37672	1.37757(*9*) 1.37711(*25*)
Density					
d_4	25	0.89565	0.8958	0.780709	0.7810(*7*)
B.P., 400 mm.		149.2	149.3	67.8	67.8(*23*)
Antoine Constants					
A			7.16462		6.7392
B			1538.7		846.79
C			188.0		137.4

Log P = A – B/(C + t), where P = mm. Hg and *t* = °C.

Apparatus. The equipment used in obtaining the vapor liquid samples was a modified Colburn still similar to that described by Haynes and Van Winkle (*5*). Pressure was measured to ±0.5 mm. Hg by using a calibrated mercury manometer. A copper constantan thermocouple and a Leeds & Northrup type K potentiometer were used to measure temperature to within ±0.05° C. This arrangement was calibrated by measuring the boiling points of pure compounds. A Bausch & Lomb precision refractometer maintained at 30° C. was used to determine the index of refraction of the vapor and liquid samples. The accuracy of the refractometer was tested by the standards supplied by Bausch and Lomb.

Procedure. The procedure for determination of vapor-liquid equilibrium was essentially that described by Haynes (*5*). For each of the binary hydrocarbon systems, refractive index calibration curves were obtained with samples of different known concentrations at 30° C. The composition of vapor and liquid samples were read from the calibration curves. In the ternary systems, three mixtures of *n*-octane–ethylcyclohexane in the mole ratios of 25 to 75, 50 to 50, 75 to 25 were used; 2-propanol was added to each of the above mixtures to give equivalent mole fractions of 0.33, 0.50, 0.67, 0.75, and 0.80 in the ternary mixture. These mixtures were subjected to equilibrium distillation in the Colburn still, and vapor and liquid samples were obtained. Another set of experiments were conducted similarly using butyl Cellosolve as solvent. These samples were extracted with water to remove the added agent. After several washings, the hydrocarbon layer was transferred to 10-ml. sample bottles. To these bottles were added crystals of Drierite, which removed any traces of water remaining in the hydrocarbon mixture. The washed samples were kept overnight, and the added agent-free samples were analyzed by refractometer.

DISCUSSION OF RESULTS

Experimental activity coefficients for the components in the binary mixtures were calculated using the following equation:

$$\gamma_i = \frac{\nu y_i P_T}{x_i p_i} \tag{1}$$

The fugacity coefficient $\nu = (f/p)$ is equal to unity where the ideal gas law is valid. Fugacity coefficient was assumed to be unity in all of the work reported here. The validity of the assumption was checked using the generalized f/p charts.

The vapor-liquid equilibrium data for the five binaries are reported in Table II and in Figures 1 to 4. The data were correlated by Carlson and Colburn modified van Laar equations (*1*):

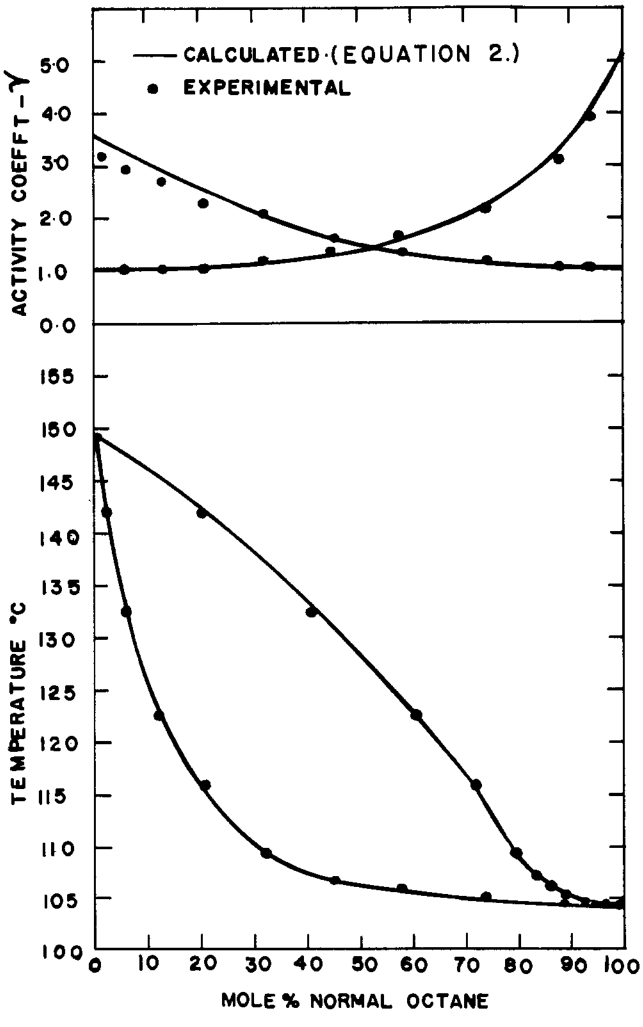

Figure 1. Normal octane-butyl Cellosolve system at 400 mm. pressure

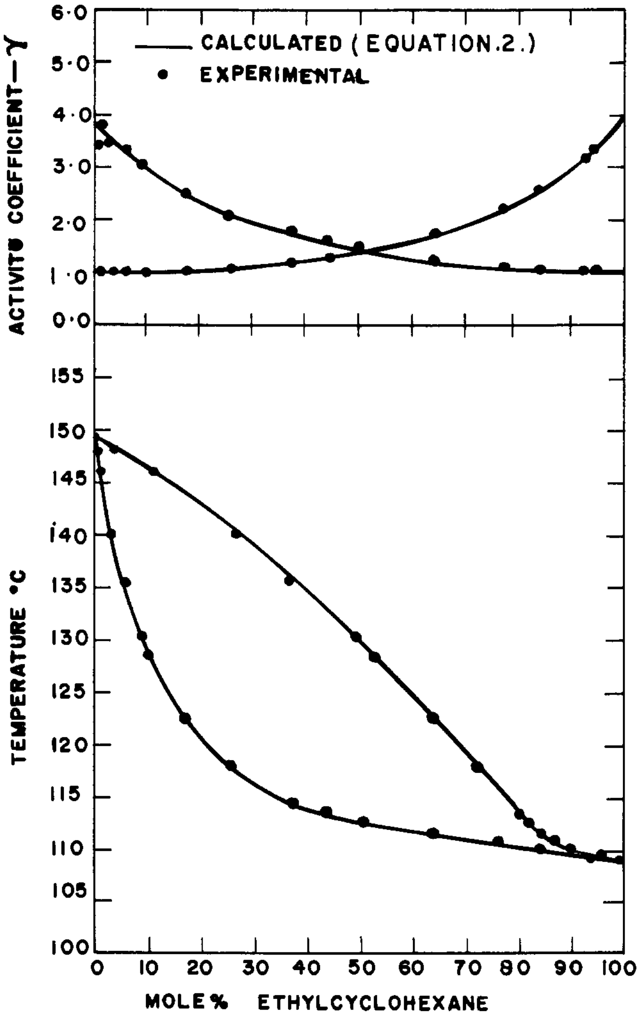

Figure 2. Ethylcyclohexane–butyl Cellosolve system at 400 mm. pressure

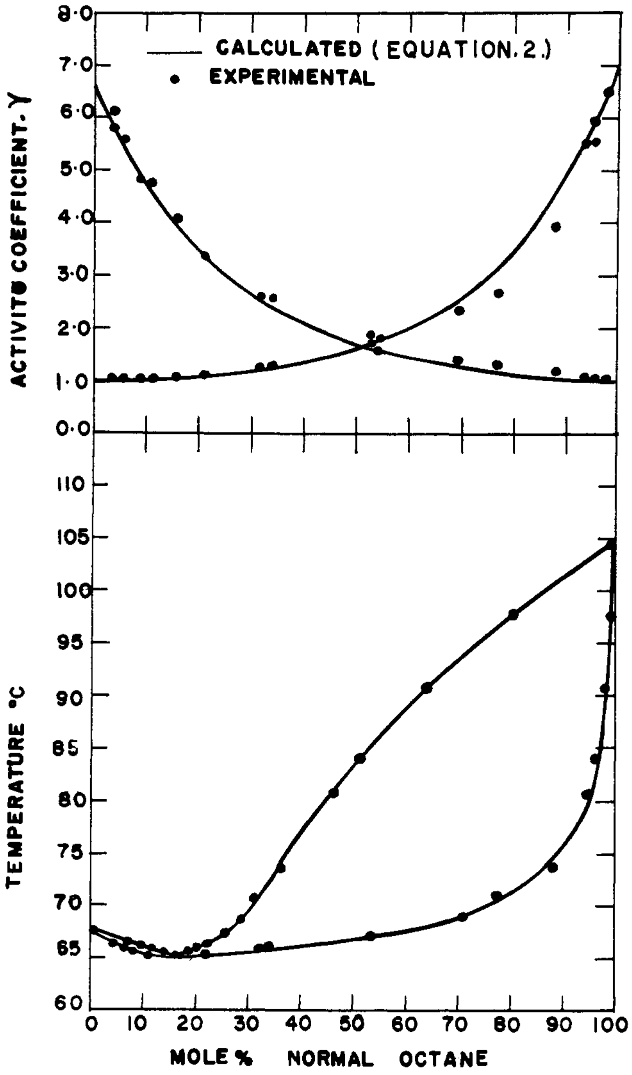

Figure 3. Normal octane–2-propanol system at 400 mm. Hg abs. pressure

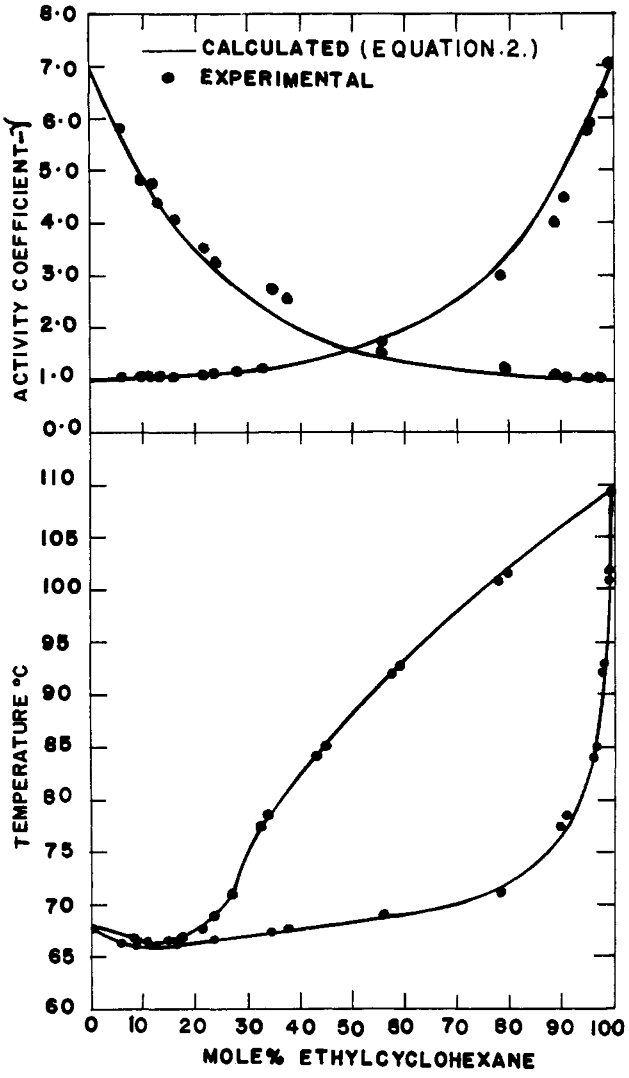

Figure 4. Ethylcyclohexane–2-propanol system at 400 mm. Hg abs. pressure

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{A}{B}\frac{x_1}{x_2}\right)^2} \qquad (2a)$$

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{B}{A}\frac{x_2}{x_1}\right)^2} \qquad (2b)$$

The constants in the correlation were evaluated by trial and error to give the least deviation and are as follows:

Binary System	Modified van Laar Constants	
	A	B
NO-ECH	−0.011	0.011
NO-BC	0.56	0.74
ECH-BC	0.585	0.590
NO-2P	0.84	0.85
ECH-2P	0.845	0.865

The calculated values of activity coefficients are also given in Table II. The normal octane-ethylcyclohexane system behaves almost ideally. It was observed that the experimental values of γ_{NO} and γ_{ECH} are negative and positive respectively, though they are around unity. Such positive and negative deviations have been observed in the past for the system: naphthalene-1-octadecene (*27*) and napthalene-1-hexadecene (*26*). The variation of the gamma value from unity is probably caused by slight experimental error. A standard deviation relation is expressed in the following equation:

$$\omega = \left[\frac{(\sum k^2) - (\sum k)^2/N}{(N-1)}\right]^{1/2} \qquad (3)$$

where

k = deviation of experimental activity coefficient values from calculated values
N = Number of experimental points
ω = Average deviation.

Applying a standard deviation relation (Equation 3) to the differences between the experimental activity coefficients and those derived from the van Laar relations, the average deviations in activity coefficients are as follows:

System	Deviation	System	Deviation
NO	0.020	NO	0.1190
ECH	0.013	2P	0.229
NO	0.131	ECH	0.163
BC	0.172	2P	0.236
ECH	0.102		
BC	0.016		

Table II. Vapor-Liquid Equilibrium Data on Five Systems

Pressure. 400 mm. Hg Absolute
Correlation. Carlson and Colburn modified van Laar equation

(Normal Octane-Ethylcyclohexane)

Temp., ° C.	Exptl.				Calcd.	
	x_{NO}	y_{NO}	γ_{NO}	γ_{ECH}	γ_{NO}	γ_{ECH}
108.72	0.095	0.113	1.028	0.992	0.979	1.000
108.16	0.191	0.215	0.99	1.000	0.984	1.001
107.67	0.289	0.317	0.985	1.004	0.987	1.002
107.11	0.394	0.424	0.976	1.011	0.991	1.004
106.61	0.481	0.513	0.981	1.012	0.993	1.006
106.06	0.593	0.623	0.987	1.02	0.996	1.009
105.5	0.688	0.710	0.986	1.04	0.998	1.012
105.0	0.795	0.811	0.991	1.045	0.999	1.016
104.6	0.898	0.908	0.991	1.045	1.000	1.021

(Normal Octane-Butyl Cellosolve)

Temp., ° C.	Exptl.				Calcd.	
	x_{NO}	y_{NO}	γ_{NO}	γ_{BC}	γ_{NO}	γ_{BC}
142.0	0.022	0.204	3.17	1.03	3.48	1.00
132.5	0.060	0.407	2.96	1.09	3.23	1.00
122.7	0.128	0.606	2.71	1.11	2.84	1.02
116.0	0.210	0.722	2.39	1.11	2.44	1.05
109.3	0.322	0.796	2.10	1.23	2.03	1.13
107.04	0.450	0.828	1.68	1.41	1.64	1.28
106.0	0.580	0.862	1.40	1.54	1.36	1.56
105.0	0.738	0.886	1.17	2.13	1.14	2.20
105.0	0.744	0.882	1.15	2.25	1.13	2.24
104.5	0.882	0.928	1.04	3.04	1.03	3.42
104.3	0.938	0.952	1.01	3.90	1.01	4.23

(Ethylcyclohexane-Butyl Cellosolve)

Temp., ° C.	Exptl.				Calcd.	
	x_{ECH}	y_{ECH}	γ_{ECH}	γ_{BC}	γ_{ECH}	γ_{BC}
148.0	0.003	0.030	3.49	1.01	3.82	1.00
146.2	0.010	0.102	3.81	1.00	3.75	1.00
140.0	0.034	0.268	3.41	1.02	3.52	1.00
135.5	0.054	0.375	3.32	1.03	3.34	1.00
130.2	0.088	0.496	3.10	1.04	3.07	1.01
128.5	0.100	0.528	3.03	1.04	2.98	1.01
122.5	0.170	0.631	2.49	1.10	2.52	1.04
118.0	0.251	0.720	2.06	1.09	2.14	1.09
114.5	0.37	0.786	1.81	1.13	1.71	1.20
113.5	0.44	0.80	1.60	1.24	1.53	1.30
112.5	0.501	0.815	1.47	1.34	1.40	1.40
111.5	0.640	0.841	1.22	1.66	1.19	1.74
111.0	0.768	0.864	1.09	2.25	1.08	2.22
110.0	0.840	0.896	1.04	2.60	1.04	2.61
109.6	0.936	0.95	1.00	3.16	1.01	3.28
109.4	0.941	0.953	1.00	3.26	1.01	3.33

(Normal Octane–2-Propanol)

Temp., ° C.	Exptl.				Calcd.	
	x_{NO}	y_{NO}	γ_{NO}	γ_{2P}	γ_{NO}	γ_{2P}
66.5	0.044	0.070	6.16	1.00	5.84	1.00
66.4	0.062	0.089	5.58	1.00	5.41	1.01
66.1	0.093	0.114	4.83	1.02	4.90	1.02
65.7	0.110	0.131	4.77	1.04	4.63	1.02
65.5	0.128	0.140	4.41	1.06	4.37	1.03
65.4	0.160	0.160	4.05	1.08	3.92	1.05
65.6	0.212	0.177	3.35	1.11	3.34	1.09
65.6	0.209	0.184	3.54	1.10	3.40	1.09
65.7	0.32	0.209	2.61	1.24	2.50	1.22
65.8	0.34	0.218	2.56	1.25	2.34	1.25
67.2	0.538	0.260	1.82	1.59	1.52	1.75
66.9	0.531	0.260	1.89	1.58	1.54	1.73
70.6	0.769	0.310	1.32	2.57	1.11	3.16
68.7	0.709	0.286	1.43	2.29	1.18	2.66
73.5	0.878	0.369	1.23	3.93	1.03	4.50
84.0	0.956	0.505	1.04	5.54	1.00	5.97
80.6	0.945	0.460	1.09	5.51	1.01	5.73
90.9	0.979	0.634	1.00	6.52	1.00	6.53
97.64	0.992	0.802	1.00	6.31	1.00	6.86

(Ethylcyclohexane–2-Propanol)

Temp., ° C.	Exptl.				Calcd.	
	x_{ECH}	y_{ECH}	γ_{ECH}	γ_{2P}	γ_{ECH}	γ_{2P}
66.5	0.059	0.077	5.77	1.01	5.82	1.01
66.25	0.100	0.107	4.79	1.03	4.85	1.02
66.24	0.129	0.127	4.41	1.04	4.41	1.03
66.3	0.130	0.128	4.40	1.04	4.36	1.03
66.3	0.113	0.120	4.74	1.03	4.65	1.03
66.4	0.161	0.147	4.08	1.05	3.92	1.05
66.5	0.239	0.176	3.28	1.11	3.11	1.12
66.4	0.216	0.172	3.55	1.08	3.32	1.10
67.7	0.377	0.218	2.58	1.23	2.11	1.32
67.5	0.348	0.215	2.83	1.20	2.30	1.27
68.8	0.558	0.232	1.68	1.62	1.47	1.83
70.8	0.786	0.272	1.29	2.99	1.16	3.35
77.5	0.89	0.321	1.04	3.92	1.02	4.74
78.3	0.909	0.336	1.04	4.49	1.02	5.07
84.1	0.951	0.432	1.03	5.69	1.01	5.91
85.1	0.954	0.446	1.03	5.70	1.00	5.99
92.1	0.977	0.576	1.02	6.41	1.00	6.55
92.9	0.979	0.586	1.01	6.60	1.00	6.60
101.6	0.994	0.798	1.01	7.18	1.00	6.99
101.1	0.993	0.780	1.01	6.89	1.00	6.97

Table III. Variation of Relative Volatility with Solvent Concentration

Ternary System: Normal Octane–Ethylcyclohexane–Butyl Cellosolve
Pressure: 400 Mm. Hg Absolute

Binary Mixture[a]		Mole Fraction,	Temp.,					
x'_{NO}	x'_{ECH}	x'_{BC}	° C.	x_{NO}	y_{NO}	x_{ECH}	y_{ECH}	$\alpha_{NO/ECH}$
0.25	0.75	0.00	107.87	0.24	0.268	0.76	0.732	1.16
		0.33	111.4	0.237	0.276	0.763	0.724	1.23
		0.50	115.05	0.229	0.272	0.771	0.728	1.25
		0.67	124.0	0.220	0.268	0.780	0.732	1.30
		0.75	128.8	0.224	0.276	0.776	0.724	1.32
		0.80	131.6	0.216	0.268	0.784	0.732	1.33
0.50	0.50	0.00	106.61	0.482	0.512	0.518	0.488	1.13
		0.33	113.3	0.470	0.516	0.530	0.484	1.20
		0.50	116.3	0.432	0.487	0.568	0.513	1.25
		0.67	122.2	0.435	0.502	0.565	0.498	1.31
		0.75	127.4	0.445	0.515	0.555	0.485	1.32
		0.80	132.6	0.435	0.508	0.565	0.492	1.34
0.75	0.25	0.00	105.4	0.741	0.760	0.259	0.240	1.11
		0.33	108.8	0.732	0.769	0.268	0.231	1.22
		0.50	111.9	0.727	0.773	0.273	0.227	1.28
		0.67	122.8	0.719	0.776	0.281	0.224	1.35
		0.75	125.5	0.720	0.780	0.280	0.220	1.38
		0.80	132.4	0.718	0.781	0.282	0.219	1.40

[a] x' is solvent-free basis.

Table IV. Variation of Relative Volatility with Solvent Concentration

Ternary System: Normal Octane-Ethylcyclohexane-2-propanol at 400 Mm. Hg Absolute

Binary Mixture[a]		Mole Fraction,	Temp.,					
x'_{NO}	x'_{ECH}	x_{2P}	° C.	x_{NO}	y_{NO}	x_{ECH}	y_{ECH}	$\alpha_{NO/ECH}$
0.25	0.75	0.00	107.87	0.240	0.268	0.76	0.732	1.16
		0.33	73.8	0.247	0.276	0.753	0.724	1.16
		0.50	70.0	0.244	0.272	0.756	0.728	1.16
		0.67	68.8	0.240	0.271	0.760	0.729	1.18
		0.75	68.3	0.239	0.274	0.761	0.726	1.20
		0.80	67.9	0.239	0.278	0.761	0.722	1.23
0.50	0.50	0.00	106.61	0.482	0.512	0.518	0.488	1.13
		0.33	73.2	0.492	0.520	0.508	0.480	1.12
		0.50	70.0	0.482	0.512	0.518	0.488	1.13
		0.67	68.87	0.488	0.524	0.512	0.476	1.15
		0.75	68.25	0.488	0.530	0.512	0.470	1.18
		0.80	67.75	0.496	0.540	0.504	0.460	1.19
0.75	0.25	0.00	105.4	0.741	0.760	0.259	0.240	1.11
		0.33	72.5	0.75	0.767	0.250	0.233	1.11
		0.50	69.9	0.746	0.766	0.254	0.234	1.11
		0.67	68.5	0.743	0.767	0.257	0.233	1.14
		0.75	67.5	0.741	0.769	0.259	0.231	1.16
		0.80	67.0	0.745	0.774	0.255	0.226	1.17

[a] x' is solvent -free basis.

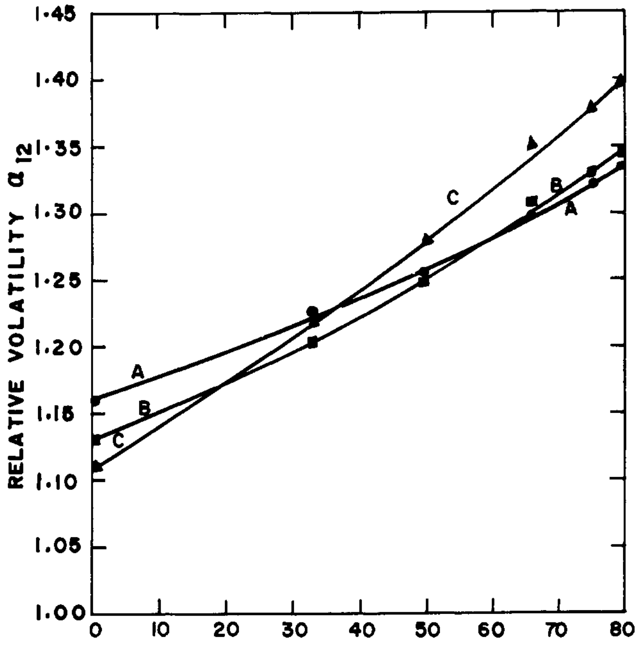

Figure 5. Effect of butyl Cellosolve on the relative-volatility of binary system *n*-octane–ethylcyclohexane at 400 mm. Hg abs.

	Mole %	
	n-octane	Ethylcyclohexane
A	25	75
B	50	50
C	75	25

The experimental data for the *n*-octane–butyl Cellosolve and ethylcyclohexane–butyl Cellosolve systems show that they are nonideal in nature and show a tendency for the formation of azeotropes at higher concentrations of the hydrocarbons. The systems behave similarly.

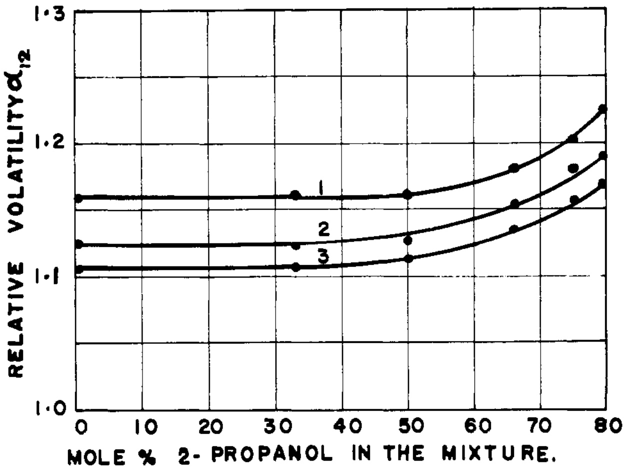

Figure 6. Effect of 2-propanol on the relative volatility of the binary system normal octane–ethylcyclohexane

	Mole %	
Curve No.	*n*-octane	Ethylcyclohexane
1	25	75
2	50	50
3	75	25

The *n*-octane-2-propanol and ethylcyclohexane-2-propanol systems evidence minimum boiling azeotropes. Interpolation of the data indicated that *n*-octane and 2-propanol form an azéotrope at 16 mole % *n*-octane at 65.4° C. The ethylcyclohexane and 2-propanol form an azeotrope at 12.6 mole % ethylcyclohexane at 66.2° C. The data for these two binaries calculated by means of the van Laar equations are not in good agreement with the experimental data. The attempt to correlate the data with the Scatchard and Hamer equation (*19*, *20*, *21*), taking $q_1/q_2 = V_1/V_2$, met with little success.

$$\log \gamma_1 = Z_2^2[A + 2\,(B\,\frac{V_1}{V_1} - A)\,Z_1] \tag{4a}$$

$$\log \gamma_2 = Z_1^2[B + 2\,(A\,\frac{V_2}{V_1} - B)\,Z_2] \tag{4b}$$

V_1/V_2 is the ratio of the molal volumes at the temperature of the equilibrium. Z represents the volume fraction based on the volume of pure components, neglecting the volume changes in mixing.

The disagreement is particularly evident at the higher temperatures. This may be the result of widely different boiling temperatures of the components affecting the activity coefficients or possibly the results of some type of molecular association.

Because of a wide range of temperature in the binary systems studied and because the experiments were conducted under isobaric conditions, the Herringten test *(6)* was applied to the activity coefficient composition data of the binaries. The data were found to be consistent in accordance with the criterion of this test.

Ternary Systems. The variation of relative volatility with the concentration of the solvent in the two ternary systems is reported in Tables III and IV and shown in Figures 5 and 6. Addition of 2-propanol to the binary system is not significantly effective, but the addition of butyl Cellosolve increases the relative volatility to about 1.40. However, in both the systems the greatest change in relative volatility is obtained at higher concentrations of solvent.

Because these ternary systems were extracted with water to remove the solvent, it was ensured by laboratory test and solubilities that the solvent-free hydrocarbon concentration did not change because of the different solubilities of hydrocarbon in water. Further, it was made sure that the drying agent, Drierite, had no selective absorption capacity for the hydrocarbon mixture involved.

The errors caused by the possible analytical inaccuracies were kept to a minimum by testing doubtful washing techniques with known hydrocarbon samples and by using identical procedure with all the samples from the same run.

No attempt was made to analyze the three components in the ternary vapor-liquid equilibrium samples; however, all the constants in the Wohl's Equation *(28, 29)* could be evaluated. Wohl *(28)* developed Equation 5 as a means of representing ternary activity coefficient data:

$$\begin{aligned}\log \gamma_1 = {} & x_2^2[A_{12} + 2x_1 + 2x_1\ (A_{21} - A_{12})] \\ & + x_3^2[A_{13} + 2x_1(A_{31} - A_{13})] + x_2x_3[A_{21} + A_{13} - A_{32} \\ & + 2x_1(A_{31} - A_{13}) + 2x_3(A_{32} - A_{23}) - C(1 - 2x_1)]\end{aligned} \qquad (5)$$

Wohl *(29)* modified the original equation and developed Equation 6:

$$\begin{aligned}\log \gamma_1 = {} & x_2^2[A_{12} + 2x_1(A_{21} - A_{12})] \\ & + x_3^2[A_{13} + 2x_1(A_{31} - A_{13})] + x_2x_3[\tfrac{1}{2}(A_{21} + A_{12} + A_{31} \\ & + A_{13} - A_{23} - A_{32}) + x_1(A_{21} - A_{12} + A_{31} - A_{13}) \\ & + (x_2 - x_3)(A_{23} - A_{32}) - (1 - 2x_1)\,C^*]\end{aligned} \qquad (6)$$

where A is the Margules constant of the component binary systems; C and C^* are the ternary constants. The van Laar and Margules constants were the same except for the system, *n*-octane–butyl Cellosolve. The Margules constants were $A = 0.607$ and $B = 0.793$. The relation between C and C^* was shown by Severns *(22)* to be

$$C^* = C + \tfrac{1}{2}\,(A_{12} - A_{21} + A_{23} - A_{32} + A_{31} - A_{13})$$

Assuming $C = 0$, the value of C^* for the *n*-octane–ethylcyclohexane–2-propanol system was −0.011 and for the system *n*-octane–ethylcyclohexane–butyl Cellosolve, it was 0.0745.

The butyl Cellosolve has higher dielectric constant and dipole moment than 2-propanol and therefore should be a better solvent for modifying the relative volatility of the binary system *n*-octane–ethylcyclohexane. This agrees with the observation made by Updike, Langdon, and Keyes *(24)*. Solubility at the boiling point is another criterion which relates to the effectiveness of a third component. Hildebrand *(7)* states that a liquid of lower vapor pressure will be less soluble than one of higher vapor pressure, other things being equal. This might explain the lower solvent action of 2-propanol. But, according to Updike and others the optimum solution abnormality (which is related to effectiveness of a solvent) is found just short of the point where two liquid phases persist at the boiling point. Although 2-propanol and hydrocarbons, unlike butyl Cellosolve, had higher differences in polarities, the latter proved to be a better solvent. For maximum change in relative volatility, an agent should be added *(18)* which differs as much as possible in polarity from the components in the binary mixture. However, this generalization on the selection of solvents did not hold true in this case. An attempt was made to calculate the relative volatility by the Robinson and Gilliland method *(18)* using the van Laar constants calculated from experimental data. Calculated values were not in agreement with experimental values. This may be the result of a number of assumptions made in the derivation of the equation.

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NOMENCLATURE

A, B = Carlson and Colburn modified van Laar constants
C^* = ternary constant in activity coefficient equation
d = density, gm./c.c.
n = refractive index
P_T = total pressure, mm. Hg
P = vapor pressure, mm. Hg
q = effective molal volume at equilibrium temperature
T = absolute temperature
V = molal volume
x_i = molal fraction of component i in liquid phase
y_i = mole fraction of component i in vapor phase
NO = normal octane
ECH = ethylcyclohexane
2P = 2-propanol
BC = butyl Cellosolve
α = relative volatility
γ = activity coefficient
ν = fugacity coefficient

Subscripts

B = binary
T = ternary
S = solvent

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The System Carbon Dioxide–Methylene Chloride

Solubility, Vapor Pressure, Liquid Density, and Activity Coefficients

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Static equilibrium measurements were made using a cell design at 70°, 100°, and 130° F., covering a pressure range from the vapor pressure of methylene chloride to 300 p.s.i.a. at each temperature. Curves of total vapor pressure and liquid density *vs.* weight per cent CO_2 in liquid are presented for these isotherms. Henry's Law was found true up to about 5.8 weight per cent CO_2 and 125 p.s.i.a. at 70° F., 5.1 weight per cent CO_2 and 156 p.s.i.a. at 100° F., and 4.4 weight per cent CO_2 and 190 p.s.i.a. at 130° F. Henry's Law constant in p.s.i.a. over these ranges is 1085 at 70°, 1505 at 100°, and 2015 at 130° F. Corresponding activity coefficient for CO_2 is 1.28 at 70°, 1.23 at 100°, and 1.18 at 130° F.

ALTHOUGH the carbon dioxide-methylene chloride system has possible propellant applications in aerosol packaging, the only equilibrium values of total vapor pressure, liquid composition, and liquid density available in the literature are those at 70° F. from 15 to 300 p.s.i.a. (*1*).

As an extension of this work, the system was investigated at 100° F. and 130° F. from the vapor pressure of pure methylene chloride to 300 p.s.i.a. at each temperature. The experimental apparatus and technique developed in the earlier work (*1*) were used in these determinations with only minor modifications.

The vapor-liquid system was brought to equilibrium in a steel chamber, or equilibrium cell, which was rocked in a constant temperature bath until constant system pressure was obtained. The construction of the cell allowed an all-liquid sample of known volume to be isolated at equilibrium conditions, and liquid densities were determined from the weight and volume of this sample. For composition determination, the liquid sample was analyzed by vaporizing it, passing the vapor through sodium hydroxide solutions which absorbed the carbon dioxide, and then titrating with standardized hydrochloric acid.

RESULTS

The liquid composition variation with total system vapor pressure is shown in Figure 1 for the 100° and 130° F. isotherms investigated. For comparison, the previously reported data at 70° F. is also included. The solubility of carbon dioxide was found to vary linearly with pressure up to approximately 5.1 weight % carbon dioxide at 100° F. and to 4.4 weight % carbon dioxide at 130° F., corresponding to total pressures of 156 and 190 p.s.i.a., respectively. Above these pressures the rate of change in carbon dioxide dissolved with increasing pressure steadily increases—i.e., the solubility of carbon dioxide increases more rapidly than predicted by Henry's Law. The experimental curves should well represent the solution characteristics since the individual data points deviated from the smoothed curve values by a maximum of only 0.2 weight %. The values of the pure methylene chloride vapor pressure indicated by extrapolation to zero weight % carbon dioxide were in close agreement with literature values. Extrapolated values: 14 p.s.i.a. at 100° F., 25 p.s.i.a. at 130° F.; literature values: 14.2 p.s.i.a. at 100° F., 25.7 p.s.i.a. at 130° F. (*2*).

The approximately linear variation of liquid density with liquid composition is shown in Figure 2. The individual data points vary a maximum of only 0.002 g./cc. from the smoothed curve values, and the density values found for pure methylene chloride, which are included in these curves, are in close agreement with literature values. Experimental values: 1.297 g./cc. at 100° F., 1.266 g./cc. at 130° F;

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