

Vapor-liquid Equilibria and Heat of Mixing: *n*-Octane-ethylbenzene-Cellosolve System

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Vapor-liquid equilibria of the systems *n*-octane-Cellosolve, ethylbenzene-Cellosolve, and *n*-octane-ethylbenzene-Cellosolve were determined at 760 mm. Hg. The activity coefficient data of Yang and Van Winkle (23) for the system *n*-octane-ethylbenzene and the data of this work on other systems were expressed by Wohl's three-suffix Margules equations. The ternary data are predicted satisfactorily from the binary constants and no noticeable ternary effects seem to exist for this ternary system.

Heat-of-mixing data at 25°C. were determined for the ternary and the three related binary systems, and attempts were made to predict ternary heat-of-mixing data from those of the component binaries by the method of Scatchard et al. (15).

Yang and Van Winkle (23) presented vapor-liquid equilibrium data for the binary system *n*-octane-ethylbenzene at various subatmospheric pressures. Their data indicate that the relative volatility of *n*-octane with respect to ethylbenzene is very low, particularly at high concentrations of *n*-octane. This was observed in some hydrocarbon-nonhydrocarbon systems studied by Thornton and Garner (19).

The present investigation was carried out to find the influence of a third component on the relative volatility of *n*-octane with respect to ethylbenzene and to present heat-of-mixing data for the binaries and the ternary system.

PURITY OF COMPOUNDS

Pure-grade *n*-octane, supplied by Phillips Petroleum Company, was fractionated in a 4-ft. glass column packed with 1/4-in. glass helices at a reflux ratio of approximately 20:1. The first and last fractions, each approximately one-sixth of the charge, were discarded and the heart cut was used for experimental work. Ethylbenzene, supplied by the same company, was used directly without further purification. Carbide and Carbon Chemical Company Cellosolve, supplied by Baker Chemical Company, was fractionated twice in this column and a heart cut was taken for experimental work. Proper precautions minimized absorption of atmospheric moisture by cellosolve. The physical properties of the purified materials are listed in Table 1.

METHODS OF ANALYSIS

Density was used as a basis for analysis of the unknown mixtures of *n*-octane and Cellosolve, and compositions of the ethylbenzene-Cellosolve mixtures were determined at 30°C. by refractive index with a Bausch and Lomb precision refractometer using monochromatic light from a sodium lamp. The densities were determined with a 10.0-ml. pycnometer.

The analysis of the ternary system was based upon the method of Carlson, Schubert and Fenske (1), which consisted essentially

of determining one physical property of the mixture, extracting the Cellosolve with water, and finding the same or another physical property of the raffinate phase, i.e., the residual liquid. From the results of these two determinations, it is possible to fix the composition of the mixture.

Known mixtures of the three components were prepared by weighing the components and mixing them in 50-ml. conical flasks provided with ground-glass stoppers. The densities of the mixtures were determined with a 10.0-ml. pycnometer. About ten determinations were made on each mixture in which the mole percentage of *n*-octane on a Cellosolve-free basis was maintained constant, and in all about ninety determinations were made in order to describe

the entire composition range of the ternary. A plot of density vs. mole percentage of Cellosolve in the ternary with mole percentage of *n*-octane on Cellosolve-free basis as parameter was prepared. From this a cross plot of density vs. mole percentage of *n*-octane on a Cellosolve-free basis with mole percentage of Cellosolve in the ternary as a parameter was then made. This plot is shown in Figure 1.

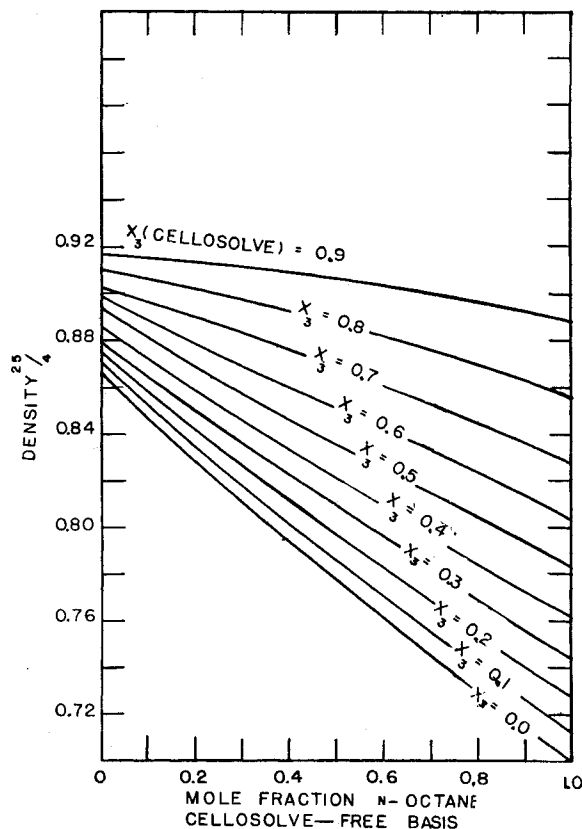
To analyze each unknown mixture, the following data were obtained: (1) the density of the mixture and (2) the refractive index of raffinate phase. From a knowledge of (2), the mole percentage of *n*-octane in the *n*-octane-ethylbenzene system on a Cellosolve-free basis was obtained from a plot of refractive index vs. composition based on the data of Yang and Van Winkle (23). With the latter information and the density of the mixture, the composition could be established by referring to Figure 1. Five determinations were made on known mixtures of the three components to test the accuracy of the method.

TABLE 1
PHYSICAL PROPERTIES OF THE COMPOUNDS

Compound	Boiling point, °C.		Density ^{25/4}		Ref. Inc. 25°C.	
	Exp.	Lit. (20)	Exp.	Lit. (20)	Exp.	Lit. (20)
(1) <i>n</i> -Octane	125.7	125.665	0.69856	0.69849	1.39510	1.39505
(2) Ethylbenzene	136.2	136.187	0.86274	0.86264	1.49337	1.49330
(3) Cellosolve*	135.3	135.3†	0.92595	—	1.40812	1.4080‡

*Reference 8.
†Reference 2.
‡At 20°C.

Fig. 1. Analytical diagram for the system *n*-octane-ethylbenzene-Cellosolve.



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APPARATUS AND PROCEDURE

The modified Colburn equilibrium still (6) and its operation to obtain vapor-liquid equilibrium data were described in an earlier paper (11), and the calorimeter, its accessories and its operation to obtain heat of mixing data, was also described previously (12).

ACTIVITY COEFFICIENTS

The activity coefficients were calculated from experimental vapor-liquid equilibrium data by means of the equation

$$\log_{10} \gamma_1 = \log_{10} \frac{P_T y_1}{P_1 x_1} + \frac{(\beta_{11} - v_{11})(P_T - P_1)}{2.303RT} \quad (1)$$

(This assumes additivity of partial volumes in a gaseous mixture.) Vapor-pressure data for *n*-octane and ethylbenzene were calculated by means of the Antoine equations by Weissberger et al. (20). The vapor-pressure data available for Cellosolve were presented in the literature (2) as graphs, which could not be read with sufficient accuracy; hence, vapor pressures for this compound were determined in the Colburn still. The

TABLE 2
EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA AT 760 mm. Hg PRESSURE
SYSTEM:

(1) <i>n</i> -octane-(3) Cellosolve					
x_1	y_1	$t, ^\circ\text{C.}$	γ_1	γ_3	
0.0100	0.0640	133.6	5.161	0.997	
0.0240	0.1475	131.1	5.298	0.994	
0.0375	0.2000	129.6	4.788	0.993	
0.0535	0.2605	127.75	4.598	0.993	
0.0775	0.3300	125.5	4.278	0.996	
0.1075	0.3855	123.45	3.815	1.011	
0.1575	0.4540	121.95	3.200	1.000	
0.2230	0.4975	119.55	2.653	1.083	
0.3020	0.5395	118.4	2.196	1.150	
0.4010	0.5675	117.45	1.788	1.303	
0.5250	0.6020	117.0	1.468	1.538	
0.6510	0.6300	117.05	1.237	1.942	
0.7475	0.6625	117.25	1.123	2.430	
0.7790	0.6800	117.05	1.115	2.652	
0.8800	0.7455	119.0	1.023	3.622	
0.9475	0.8690	122.6	1.000	3.763	

x_1 = mole fraction *n*-octane in liquid.
 y_1 = mole fraction *n*-octane in vapor.
 $t, ^\circ\text{C.}$ = temperature in $^\circ\text{C.}$

Berthelot equation of state was used to calculate the second virial coefficients.

$$\beta = \frac{9RT_c}{128P_c} - \frac{27RT_c^3}{64P_cT^2} \quad (2)$$

The critical properties for *n*-octane and

TABLE 3
EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA AT 760 mm. Hg PRESSURE
SYSTEM:

(2) ethylbenzene-(3) Cellosolve					
x_3	y_3	$t, ^\circ\text{C.}$	γ_3	γ_2	
0.0460	0.1190	133.55	2.724	0.992	
0.0950	0.2028	131.9	2.372	0.990	
0.1650	0.2845	129.9	2.038	1.018	
0.2345	0.3450	129.0	1.732	1.042	
0.3345	0.4035	128.2	1.508	1.121	
0.4675	0.4730	127.8	1.283	1.247	
0.5160	0.4960	127.9	1.216	1.308	
0.6040	0.5475	128.1	1.137	1.427	
0.6715	0.5860	128.5	1.080	1.557	
0.7470	0.6400	129.2	1.037	1.723	
0.7580	0.6540	129.0	1.051	1.741	
0.8540	0.7520	131.1	1.003	1.952	
0.8825	0.7895	131.3	1.012	2.047	
0.9385	0.8725	133.2	0.992	2.248	
0.9705	0.9340	134.15	0.998	2.364	

x_3 = mole fraction cellosolve in liquid.
 y_3 = mole fraction cellosolve in vapor.
 γ_2 = activity coefficient, ethylbenzene.

ethylbenzene were obtained from the reviews of Kobe and Lynn (7) and those for cellosolve were estimated by the method of Lydersen (10). The liquid molal volumes for *n*-octane and ethylbenzene were estimated from the density-temperature data given by Rossini (14). Data for Cellosolve, which were not available in literature, were approximated by Hanson's method (4).

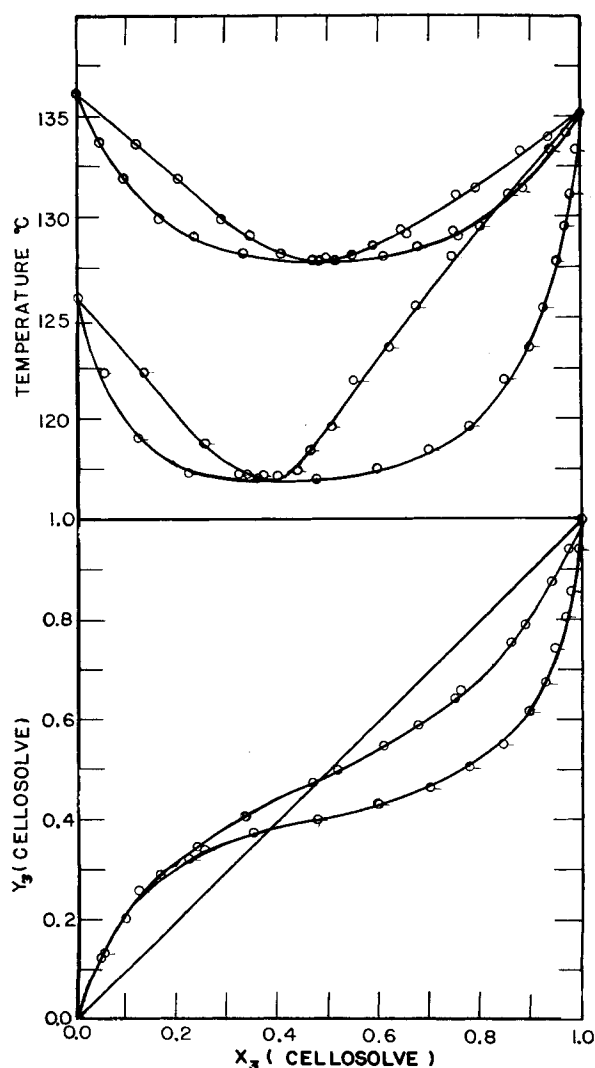


Fig. 2. Boiling-point and equilibrium diagrams: o, ethylbenzene-Cellosolve; o-, octane-Cellosolve.

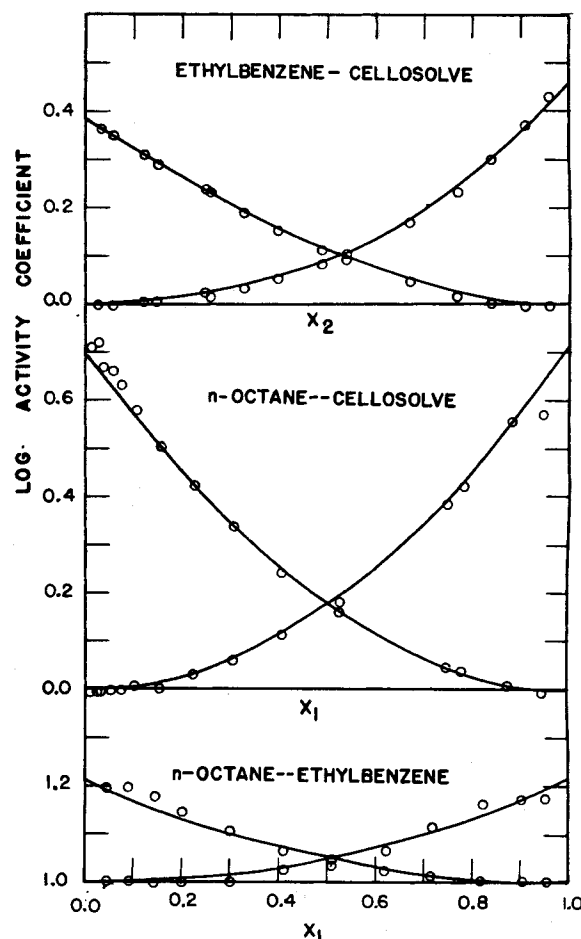


Fig. 3. Activity coefficients.

CORRELATIONS OF VAPOR-LIQUID EQUILIBRIUM DATA

The experimental activity-coefficient data for the binary systems were related by the Margules three-suffix equations modified by Wohl (21).

$$\log \gamma_1 = x_2^2[A + 2(B - A)x_1] \quad (3)$$

$$\log \gamma_2 = x_1^2[B + 2(A - B)x_2] \quad (4)$$

Therefore

$$\lim_{x_1 \rightarrow 0} \log \gamma_1 = A \quad (5)$$

and

$$\lim_{x_2 \rightarrow 0} \log \gamma_2 = B \quad (6)$$

The values for A and B were obtained by extrapolating the $\log\gamma$ -vs.- x curves.

Wohl (21) developed Equation (7) as a means of representing ternary activity-coefficient data:

$$\begin{aligned} \log \gamma_1 = & x_2^2[A_{12} + 2x_1(A_{21} - A_{12})] \\ & + x_3^2[A_{13} + 2x_1(A_{31} - A_{13})] \\ & + x_2x_3[A_{21} + A_{13} - A_{32} \\ & + 2x_1(A_{31} - A_{13}) \\ & + 2x_3(A_{32} - A_{23}) - C(1 - 2x_1)] \end{aligned} \quad (7)$$

The rotation principle can be used to express the constants for the other two components. He (22) modified his original equations and developed Equation (8).

$$\begin{aligned} \log \gamma_1 = & x_2^2[A_{12} + 2x_1(A_{21} - A_{12})] \\ & + x_3^2[A_{13} + 2x_1(A_{31} - A_{13})] \\ & + x_2x_3[\frac{1}{2}(A_{21} + A_{12} + A_{31} \\ & + A_{13} - A_{23} - A_{32}) \\ & + x_1(A_{21} - A_{12} + A_{31} - A_{13}) \\ & + (x_2 - x_3)(A_{23} - A_{32}) \\ & - (1 - 2x_1)C^*] \end{aligned} \quad (8)$$

where the A 's are the end values in $\log\gamma$ -vs.- x plots of the component binary systems, and C and C^* are the ternary constants.

The relation between C and C^* was shown by Severens, Sesonske, Perry, and Pigford (17) to be

$$\begin{aligned} C^* = & C + \frac{1}{2}(A_{12} - A_{21} + A_{23} \\ & - A_{32} + A_{31} - A_{13}) \end{aligned} \quad (9)$$

Equation (8) was used to correlate the ternary vapor-liquid equilibrium data.

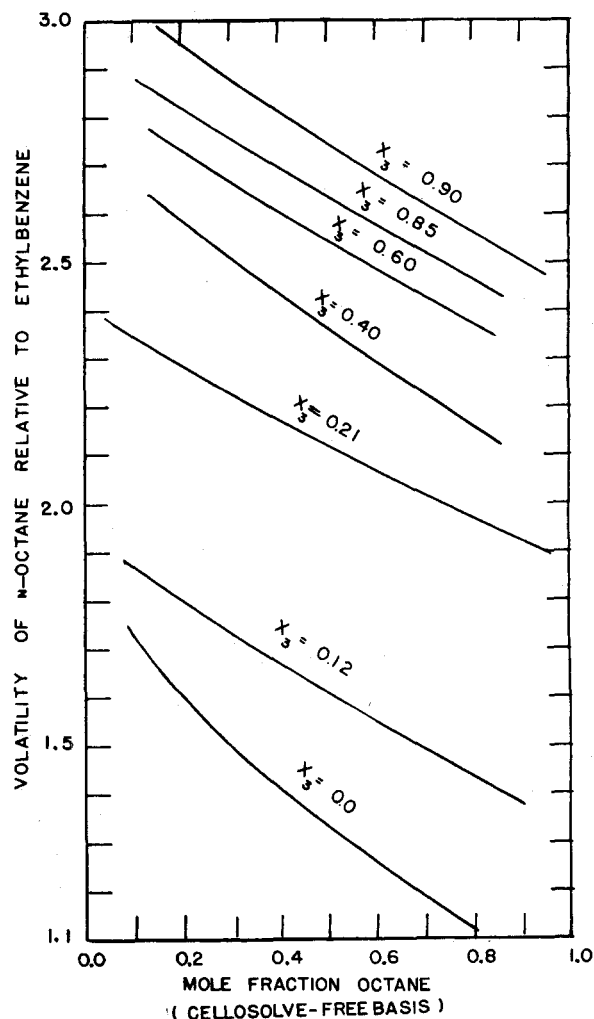
CORRELATIONS OF HEAT-OF-MIXING DATA

The heat-of-mixing data for binary systems were satisfactorily correlated by means of the empirical expressions of the type used by Scatchard et al. (15):

$$\begin{aligned} \Delta H_x^M = & x_1x_2[A_0 + A_1(x_1 - x_2) \\ & + A_2(x_1 - x_2)^2 + \dots] \end{aligned} \quad (10)$$

The choice of the number of constants depends upon the accuracy of the experi-

Fig. 4. Relative volatility. Parameter: mole fraction Cellosolve in ternary mixture.



mental data and the dissymmetry of the system under investigation.

It is desirable to predict the ternary heat-of-mixing data from the component binary heat-of-mixing data if possible. Based on free-energy analogy, Scatchard et al. proposed an equation of the type:

$$\begin{aligned} \Delta H_{x_{1,2}}^M = & x_1x_2[A_{0,1,2} + A_{1,1,2}(x_1 - x_2) \\ & + A_{2,1,2}(x_1 - x_2)^2 + \dots] \end{aligned}$$

$$\begin{aligned} & + x_1x_3[A_{0,1,3} + A_{1,1,3}(x_1 - x_3) \\ & + A_{2,1,3}(x_1 - x_3)^2 + \dots] \\ & + x_2x_3[A_{0,2,3} + A_{1,2,3}(x_2 - x_3) \\ & + A_{2,2,3}(x_2 - x_3)^2 + \dots] \end{aligned} \quad (11)$$

Equation (11) involved the assumption that the heat of mixing of a ternary mixture could be expressed as a sum of

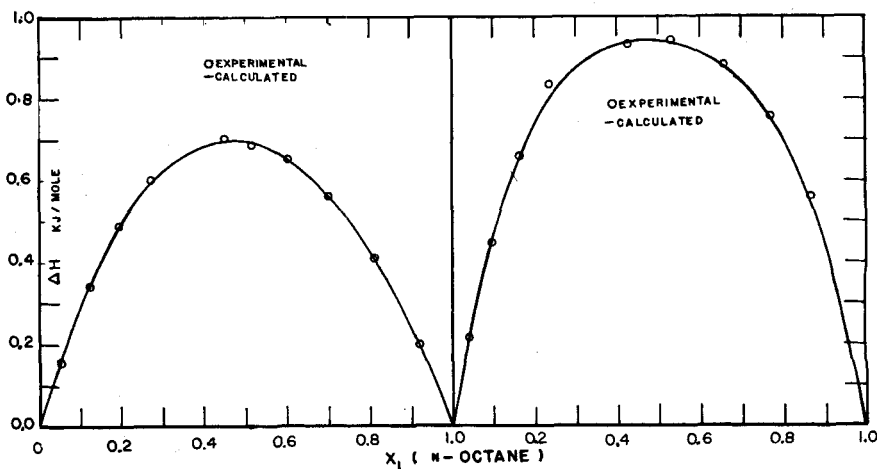


Fig. 5. Heat of mixing at 25°C., n-octane-ethylbenzene.

Fig. 6. Heat of mixing at 25°C., n-octane-cellosolve.

the heats of mixing of the related binary systems. This is true only when the contribution from the triple interactions is very small or negligible. To account for the effect of one or more polar liquids in the mixture and at the same time to eliminate the necessity for a ternary constant, Scatchard et al. (16) proposed a form of Equation (12) in terms of volume fractions (Redlich and Kister (13) expressed it in terms of mole fraction) and found fairly good agreement with experimental data:

$$\Delta H_{x_{123}}^M = x_1 x_2 [A_{012} + A_{112}(x_1 - x_2) + A_{212}(x_1 - x_2)^2 + \dots] + x_1 x_3 [A_{013} + A_{113}(1 - 2x_3) + A_{213}(1 - 2x_3)^2 + \dots] + x_2 x_3 [A_{023} + A_{123}(1 - 2x_3) + A_{223}(1 - 2x_3)^2 + \dots] \quad (12)$$

They also suggested that it might be advantageous to replace $(x_1 - x_2)$ by $(1 - 2x_2)$ for certain cases. This results in Equation (13):

$$\Delta H_{x_{123}}^M = x_1 x_2 [A_{012} + A_{112}(1 - 2x_2) + A_{212}(1 - 2x_2)^2 + \dots] + x_1 x_3 [A_{013} + A_{113}(1 - 2x_3) + A_{213}(1 - 2x_3)^2 + \dots] + x_2 x_3 [A_{023} + A_{123}(1 - 2x_3) + A_{223}(1 - 2x_3)^2 + \dots] \quad (13)$$

Prediction of ternary heat-of-mixing data through binary data was attempted by use of Equations (11) and (13) and the following Equation (14):

$$\Delta H_{x_{123}}^M = x_1 x_2 [A_{012} + A_{112}(x_1 - x_2) + A_{212}(x_1 - x_2)^2 + \dots] + x_1 x_3 [A_{013} + A_{113}(1 - 2x_3) + A_{213}(1 - 2x_3)^2 + \dots] + x_2 x_3 [A_{023} + A_{123}(x_2 - x_3) + A_{223}(x_2 - x_3)^2 + \dots] \quad (14)$$

When none of these equations adequately represent the ternary heat-of-mixing data, probably because of extreme dissymmetry of the system, it is necessary to introduce one or more ternary constants.

$$\Delta H_{x_{123}}^M = \text{Equation (11)} + Cx_1 x_2 x_3 \quad (15)$$

RESULTS AND DISCUSSION

Vapor-liquid Equilibria

The vapor-liquid equilibrium data of the binary and ternary systems are given in Tables 2 through 4 and the boiling-point diagrams and the equilibrium

TABLE 4
EXPERIMENTAL VAPOR-LIQUID-EQUILIBRIUM DATA AT 760 mm. HG PRESSURE SYSTEM:
(1) *n*-Octane-(2) ethylbenzene-(3) Cellosolve
Composition on Mole-fraction Basis

<i>t</i> , °C.	<i>x</i> ₁	<i>x</i> ₂	<i>y</i> ₁	<i>y</i> ₂	(γ) ₁		(γ) ₂		(γ) ₃	
					Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
125.35	0.4116	0.5061	0.4442	0.3753	1.089	1.077	1.0001	1.027	2.955	2.835
123.00	0.3289	0.4541	0.3835	0.3300	1.252	1.221	1.027	1.043	1.950	2.087
122.35	0.2515	0.3734	0.3386	0.2799	1.471	1.459	1.092	1.125	1.531	1.571
122.75	0.1673	0.2831	0.3071	0.2492	1.984	1.909	1.267	1.305	1.202	1.250
124.00	0.1218	0.2120	0.2642	0.2119	2.267	2.369	1.387	1.486	1.234	1.127
125.25	0.0786	0.1483	0.2250	0.1797	2.896	2.947	1.623	1.711	1.055	1.055
128.15	0.0448	0.0985	0.1711	0.1389	3.581	3.562	1.729	1.935	1.003	1.021
130.70	0.0230	0.0529	0.1094	0.0904	4.179	4.168	1.972	2.147	1.000	1.006
123.7	0.4724	0.4046	0.4866	0.2872	1.086	1.102	1.005	1.037	2.652	2.702
122.0	0.4154	0.3738	0.4470	0.2603	1.187	1.180	1.039	1.045	2.115	2.205
121.3	0.3137	0.2984	0.4007	0.2200	1.436	1.436	1.109	1.127	1.525	1.585
121.8	0.2158	0.2296	0.3609	0.1905	1.854	1.865	1.232	1.295	1.243	1.264
123.2	0.1411	0.1698	0.3208	0.1670	2.428	2.417	1.400	1.513	1.093	1.116
125.5	0.0791	0.1163	0.2663	0.1443	3.389	3.119	1.646	1.777	1.005	1.042
127.7	0.0431	0.0732	0.2012	0.1033	3.967	3.707	1.856	1.989	1.000	1.017
130.4	0.0264	0.0429	0.1347	0.0751	4.513	4.397	2.041	2.162	0.999	1.003
122.2	0.5633	0.3037	0.5492	0.2160	1.063	1.079	1.032	1.050	2.360	2.831
120.7	0.4917	0.2735	0.4965	0.1860	1.154	1.171	1.049	1.056	2.156	2.199
120.1	0.3695	0.2229	0.4550	0.1630	1.430	1.429	1.140	1.135	1.523	1.583
120.7	0.2486	0.1718	0.4132	0.1433	1.899	1.892	1.203	1.314	1.220	1.249
122.1	0.1638	0.1256	0.3603	0.1242	2.419	2.461	1.454	1.536	1.104	1.107
124.1	0.1008	0.0874	0.3037	0.1051	3.141	3.102	1.668	1.776	1.037	1.043
121.3	0.6636	0.2022	0.6201	0.1454	1.050	1.061	1.082	1.069	2.730	2.974
119.7	0.6072	0.1928	0.5562	0.1267	1.077	1.110	1.037	1.065	2.619	2.508
119.2	0.4443	0.1494	0.5036	0.1037	1.349	1.399	1.157	1.132	1.566	1.640
119.85	0.2918	0.1118	0.4575	0.0945	1.833	1.884	1.327	1.320	1.234	1.248
121.35	0.1845	0.0798	0.4016	0.0815	2.440	2.530	1.534	1.466	1.097	1.097
123.75	0.1067	0.0541	0.3420	0.0683	3.370	3.247	1.795	1.833	1.016	1.034
126.8	0.0625	0.0341	0.2544	0.0525	3.951	3.837	1.977	2.039	1.000	1.012
120.1	0.7366	0.1186	0.6496	0.0897	1.024	1.052	1.174	1.094	2.928	3.043
118.65	0.6519	0.1084	0.6002	0.0754	1.113	1.124	1.127	1.074	2.304	2.393
118.2	0.4866	0.0875	0.5497	0.0679	1.383	1.374	1.274	1.138	1.461	1.631
118.85	0.3338	0.0662	0.5065	0.0563	1.824	1.843	1.370	1.310	1.237	1.259
120.75	0.2006	0.0463	0.4460	0.0490	2.535	2.566	1.611	1.585	1.068	1.069
123.2	0.1254	0.0317	0.3763	0.0413	3.204	3.212	1.850	1.823	1.011	1.035
119.65	0.8267	0.0528	0.7265	0.0303	1.031	1.029	1.167	1.111	3.193	3.418
117.75	0.6963	0.0464	0.6344	0.0320	1.129	1.122	1.147	1.083	2.291	2.384
117.5	0.5284	0.0367	0.5756	0.0286	1.361	1.368	1.306	1.141	1.624	1.645
125.5	0.0769	0.0675	0.1437	0.4090	1.877	1.769	1.160	1.225	1.334	1.336
124.25	0.1241	0.4759	0.2146	0.3765	1.796	1.603	1.09	1.163	1.447	1.449
122.9	0.2115	0.4014	0.3011	0.3134	1.532	1.514	1.117	1.142	1.474	1.564
118.65	0.5119	0.1289	0.5440	0.0919	1.284	1.320	1.155	1.102	1.735	1.814
119.9	0.4711	0.2309	0.4961	0.1601	1.230	1.238	1.081	1.076	1.884	1.952
121.5	0.4100	0.3341	0.4492	0.2366	1.224	1.221	1.054	1.053	1.904	2.030
126.45	0.3092	0.5918	0.3623	0.4555	1.150	1.142	1.007	1.017	2.394	2.598
124.4	0.2558	0.5249	0.3177	0.3923	1.234	1.257	1.001	1.043	1.858	1.996
123.3	0.1982	0.4351	0.2834	0.3493	1.522	1.483	1.140	1.125	1.476	1.556
123.1	0.1367	0.3347	0.2510	0.2964	1.966	1.889	1.260	1.289	1.254	1.263
124.65	0.0905	0.2458	0.2193	0.2589	2.493	2.409	1.435	1.499	1.098	1.120
126.4	0.0668	0.1783	0.1775	0.2148	2.604	2.880	1.564	1.682	1.060	1.061
128.5	0.0350	0.1083	0.1393	0.1686	3.696	3.596	1.905	1.953	1.000	1.061
127.0	0.2227	0.6507	0.2762	0.5045	1.198	1.192	1.000	1.017	2.234	2.360
125.6	0.1914	0.4860	0.2485	0.4515	1.266	1.293	1.033	1.045	1.826	1.941
124.4	0.1490	0.4962	0.2228	0.3896	1.547	1.497	1.043	1.123	1.541	1.554
124.65	0.1029	0.3844	0.1970	0.3441	1.967	1.898	1.222	1.283	1.244	1.269
125.7	0.0680	0.2794	0.1706	0.3101	2.503	2.405	1.469	1.493	1.074	1.123
127.0	0.0455	0.2036	0.1422	0.2483	3.017	2.912	1.561	1.690	1.046	1.059
128.8	0.0262	0.1234	0.1092	0.1984	3.841	3.582	1.956	1.938	0.9982	1.020
128.6	0.1441	0.7429	0.1978	0.5966	1.224	1.217	0.988	1.012	2.224	2.344
126.9	0.1300	0.6769	0.1771	0.5315	1.351	1.299	1.006	1.036	1.942	1.986
125.5	0.0936	0.5411	0.1547	0.4453	1.661	1.563	1.098	1.139	1.487	1.490
125.7	0.0720	0.4571	0.1422	0.4123	1.979	1.812	1.197	1.243	1.274	1.312
126.2	0.0517	0.3346	0.1245	0.3590	2.373	2.282	1.400	1.438	1.116	1.150
127.45	0.0350	0.2510	0.1021	0.2964	2.784	2.799	1.543	1.642	1.060	1.070
129.30	0.0193	0.1534	0.0738	0.2366	3.714	3.446	1.854	1.887	1.000	1.026
130.8	0.0680	0.8400	0.0984	0.7391	1.259	1.240	1.000	1.008	2.014	2.370
128.55	0.0568	0.7600	0.0833	0.6254	1.354	1.328	1.000	1.056	1.95	1.971
127.2	0.0440	0.6405	0.0753	0.5593	1.641	1.517	1.106	1.110	1.487	1.579
126.75	0.0331	0.5191	0.0652	0.4927	1.948	1.802	1.219	1.231	1.281	1.328
127.45	0.0227	0.3763	0.0558	0.4189	2.342	2.296	1.400	1.436	1.105	1.151
128.3	0.0121	0.2408	0.0447	0.3336	3.438	2.983	1.732	1.710	1.02	1.055

curves for the two binary systems studied in this work are shown in Figure 2. The activity coefficients calculated from the experimental data of the three binary systems are shown in Figure 3, in which the solid curve represents the values calculated by means of Wohl's three-suffix Margules equations.

n-Octane-ethylbenzene System

Data on this system at various pressures were reported by Yang and Van Winkle (23). No attempt was made to rerun these data as they are thermodynamically consistent and are available at the pressure required for this work. Yang and Van Winkle found that the van Laar equation fits the data more closely than the Margules or Redlich and Kister equations. However, for reasons explained earlier, the activity-coefficient data were again fitted by Wohl's three-suffix Margules equations, and it was observed that the variation of activity coefficients is symmetrical with respect to composition.

n-Octane-Cellosolve System

Data on this system were not reported in the literature. The experimental data at 760 mm. Hg total pressure show that the system is both nonideal and azeotropic in its behavior. The azeotropic conditions with regard to temperature and pressure were established by distilling a mixture of the two components of approximately the same composition as the azeotrope in a 4-ft. glass column packed with 1/4-in. glass helices with a reflux ratio of approximately 20:1. The fraction boiling at constant temperature was collected and the distillation was repeated with this heart cut. A heart cut of this distillate was analyzed by means of density and found to have the following composition:

Total pressure	Temperature, °C.	Mole % <i>n</i> -octane	Density ^{25/4}
650 mm. Hg	116.1	60.9	0.75922

Lecat's data (9) as reported by Horsley (5) show good agreement with respect to temperature (116°C.) but the composition (38% Cellosolve on weight basis) as reported by them does not seem to be correct. Streiff et al. (18) gave the composition as approximately equal to 28 wt. % Cellosolve but did not report the temperature.

Ethylbenzene-Cellosolve System

Vapor-liquid equilibrium data on this system were reported by Kieffer and Grabiell (8) at 735 mm. Hg total pressure; however, they did not report the equilibrium temperatures. Although methods are available (3) for the calculation of equilibrium temperature from a knowledge of *x-y* relations in binary systems, it was not done in this case either, as the total pressure of the present work was 760 instead of the 735 mm. Hg at

which the data were reported. In order that accurate prediction of ternary data may be made, the method should be based upon the equilibrium measurements of the binary systems under the same conditions.

TABLE 5
HEAT OF MIXING—BINARY SYSTEMS

(1) <i>n</i> -Octane-(2) ethylbenzene		(1) <i>n</i> -octane-(3) Cellosolve		(2) ethylbenzene-(3) Cellosolve	
x_1	ΔH_x^M , kjoules./mole	x_1	ΔH_x^M , kjoules./mole	x_2	ΔH_x^M , kjoules./mole
0.9210	0.2031	0.8663	0.5660	0.9120	0.3508
0.8085	0.4109	0.7684	0.7582	0.7826	0.5715
0.6985	0.5637	0.6521	0.8850	0.6604	0.6140
0.6007	0.6580	0.5297	9.9445	0.5318	0.5610
0.5143	0.6908	0.4235	0.9349	0.3911	0.4472
0.4505	0.7089	0.2387	0.8374	0.2962	0.3510
0.2703	0.6082	0.1616	0.6612	0.2121	0.2502
0.1922	0.4944	0.0956	0.4493	0.1252	0.1484
0.1262	0.3403	0.0391	0.2163	0.0636	0.0610

x_1 = mole fraction *n*-octane.
 x_2 = mole fraction ethylbenzene.

TABLE 6
EXPERIMENTAL AND CALCULATED HEAT OF MIXING AT 25°C. SYSTEM:

(1) *n*-octane-(2) ethylbenzene-(3) Cellosolve
Heat of Mixing in kilojoules/Mole

x_1	x_2	Exp.	Eq. (14)	Eq. (15)
0.0217	0.0263	0.1534	0.1662	0.1671
0.0593	0.0721	0.3996	0.3610	0.3671
0.2908	0.3536	1.0976	1.0258	1.0695
0.2378	0.2891	1.0036	0.9434	0.9891
0.0472	0.4335	0.6448	0.6435	0.6554
0.1264	0.3975	0.8368	0.8297	0.8432
0.2095	0.3597	0.9731	0.9101	0.9731
0.2884	0.3238	1.0595	0.9786	1.0465
0.3755	0.2841	1.100	1.0409	1.0747
0.4341	0.0698	0.9678	0.9688	0.9878
0.3817	0.1836	1.0138	1.0087	1.0408
0.2878	0.3844	0.9966	1.0204	1.052
0.1704	0.6355	0.8680	0.8603	0.8728
0.1192	0.7449	0.7187	0.6984	0.7040
0.0770	0.8353	0.5231	0.5115	0.5152
0.0308	0.9341	0.2610	0.2307	0.2297

x_1 = mole fraction *n*-octane.
 x_2 = mole fraction ethylbenzene.

The system is nonideal and azeotropic in character. The azeotropic conditions were established as follows, in the manner described above:

Total pressure	Temp., °C.	Mole % ethylbenzene	Ref. index
Present work, 755 mm. Hg	127.1	52.3	1.45366
Kieffer and Grabiell, 735 mm. Hg	126.2	52.6	1.4581

n-Octane-ethylbenzene-Cellosolve System

About seventy-four runs were made to describe the vapor-liquid relationships of the ternary system at 760 mm. Hg. Wohl's three-suffix Margules equations were used to correlate the ternary data. The values of the binary constants calculated from experimental data are given in Table 7. The calculated values of γ_1 , γ_2 , and γ_3 along with the experimental data are presented in Table 4. By Equations

TABLE 7
CONSTANTS FOR VAPOR-LIQUID EQUILIBRIUM AND HEAT OF MIXING EQUATIONS

System	Margules equations		Heat-of-mixing equations	
	Binary	Ternary	Binary	Ternary
1-2	$A_{12} = 0.085$ $A_{21} = 0.085$	—	$A_{0,2} = 2.8067$ $A_{1,2} = -0.2864$ $A_{2,2} = 0.2219$	
1-3	$A_{13} = 0.700$ $A_{31} = 0.715$	—	$A_{0,3} = 3.7453$ $A_{1,3} = -0.1490$ $A_{2,3} = 2.2270$	
2-3	$A_{23} = 0.385$ $A_{32} = 0.455$	—	$A_{0,3} = 2.1780$ $A_{1,3} = 1.6497$ $A_{2,3} = 0.4239$	
1-2-3	—	$C = 0^*$ $C^* = 0.0275$	—	$C = 2.69$

(1) = *n*-Octane.
(2) = Ethylbenzene.
(3) = Cellosolve.
* Assumed for calculations.

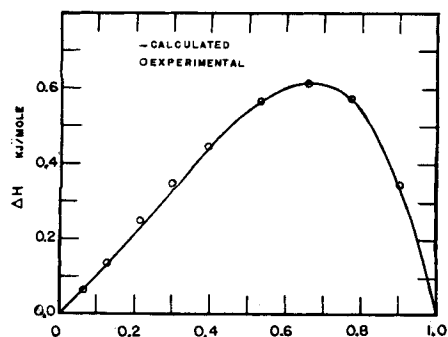


Fig. 7. Heat of mixing at 25°C., ethylbenzene-Cellosolve.

tion (9), on the assumption that $C = 0$ and that for the n -octane-ethylbenzene system $A_{12} = A_{21}$,

$$C^* = -0.0275$$

Carlson found the assumption that $C^* = 0$ was satisfactory for many of the systems which he had inspected whose deviations from ideal behavior were either zero or uniformly positive. Severns, Sesonke, Perry, and Pigford (17) also supported this view from their experimental results on acetone-methylacetate-methanol and acetone-carbon tetrachloride-methanol systems at 50°C. In the latter system a value of $C^* = -0.16$ was found. A value of $C^* = -0.0275$ from this investigation of the ternary n -octane-ethylbenzene-Cellosolve also supports the view. It is difficult to generalize, however, since in the case of the benzene-cyclohexane-methyl Cellosolve system reported by Thornton and Garner (19) the value for C^* was calculated by them (19) from the binary to be -1.582 . This value is far from zero and contributes greatly to the calculated ternary-activity-coefficient values.

The value of C^* found in this work was small, but it was retained to improve the accuracy of the fit of the data. The average deviations in γ_1 , γ_2 , and γ_3 respectively are 2.75, 3.79, and 3.18%.

Values of relative volatilities were calculated and smoothed graphically for constant percentage of Cellosolve content. These values were compared with those for the binary system n -octane-ethylbenzene reported by Yang and Van Winkle (23) and are shown in Figure 4. It is interesting to note that the relative volatility of n -octane with respect to ethylbenzene is greatly improved by the presence of cellosolve and this becomes more pronounced as the concentration of the latter increases in the liquid mixture.

There is no evidence of a ternary azeotrope in spite of the azeotropic tendency in the n -octane-ethylbenzene binary and of actual azeotropes in the other two binaries. This was confirmed by distilling a mixture of the three components in the column mentioned before and collecting the heart cuts at each

constant boiling point. These fractions were analyzed and found to correspond in composition to the binary azeotropes of n -octane-Cellosolve and ethylbenzene-Cellosolve systems respectively. Further confirmation was obtained by the analysis of the residual liquids after extraction with distilled water. The analyses showed that the residual liquids were pure n -octane and pure ethylbenzene respectively. Hence there is no ternary azeotrope.

Heat of Mixing

The experimental heat-of-mixing data at 25°C. for the three binaries and the ternary systems are given in Tables 5 and 6. The binary data were fitted with Equation (10) and the constants, evaluated by the method of least squares, are listed in Table 7. The fit of the data was examined graphically in Figures 5, 6, and 7 and found to be satisfactory. The correlation of the ternary data was tried with Equations (11), (13), (14), and (15) and the agreement of experimental and calculated values was found to be best where Equation (14) was used. Calculated values from Equations (14) and (15) are shown in Table 6. It was observed that Equations (11) and (13) do not fit the data so well as Equations (14) and (15); however, application of Equation (15) is limited because a knowledge of the ternary data is required for calculation of the constant C .

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NOTATION

- A, B = Margules constants as expressed by Wohl
 A_0, A_1 = constants in heat-of-mixing equation
 C = ternary constant in activity-coefficient expressions of Wohl (21), also ternary constant in heat-of-mixing equation
 C^* = ternary constant in activity-coefficient expressions of Wohl (22)
 d = density of the liquid, g./ml.
 g = interaction constants
 ΔH_x^M = heat of mixing in kilojoules/mole of the mixture
 P_T = total pressure
 P_1 = vapor pressure of component 1
 P_c = critical pressure
 R = gas constant
 T = absolute temperature
 V_{11} = molal volume of component 1 in pure liquid state

- x = mole fraction in the liquid
 y = mole fraction in vapor

Greek Letters

- γ = activity coefficient
 β = second virial coefficient

Subscripts

- 1 or 11 = component 1
 12 etc. = the mixture of 1 and 2 components
 123 = the mixture of the three components 1, 2, and 3
 311 = a single molecule of 3 with two molecules of 1

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