NOMENCLATURE

d_e = equatorial diameter, cm.
d_n = outside diameter of capillary, cm.
d_s = selected plane diameter, cm.
g = acceleration due to gravity
H = shape-dependent parameter
k = exponent in surface tension equation
M = molecular weight, grams
P = parachor
x = mole fraction in liquid phase
y = mole fraction in vapor phase

Greek Symbols

γ = surface or interfacial tension, dynes/cm.
ρ = density, g./cc.

Subscripts

i = any component
L = liquid phase
V = vapor phase

LITERATURE CITED

(1) Adamson, A.W., "Physical Chemistry of Surfaces," pp. 1–44, Interscience, New York, 1960.
(2) Andreas, J.M., Hauser, E.A., Tucker, W.B., *J. Phys. Chem.* **42**, 1001 (1938).
(3) Benedict, M., Webb, G.M., Rubin, L.C., *Chem. Eng. Progr.* **47**, 419 (1951).
(4) Brauer, E.B., Hough, E.W., *Producers Monthly* **29** (8), 13 (1965).
(5) Fordham, S., *Proc. Roy. Soc. (London)* **194A**, 1 (1948).
(6) Hough, E.W., Wood, B.B., Rzasa, M.J., *J. Phys. Chem.* **56**, 996 (1952).
(7) Jasper, J.J., Kerr, E.R., Gregorich, F., *J. Am. Chem. Soc.* **75**, 5252 (1953).
(8) Jasper, J.J., Kring, E.V., *J. Phys. Chem.* **59**, 1019 (1955).
(9) Niederhauser, D.O., Bartell, F.E., "Report of Progress. Fundamental Research on Occurrence and Recovery of Petroleum," 1948–49, American Petroleum Institute, Baltimore, Md., p. 114, 1950.
(10) Pennington, B.F., Hough, E.W., *Producers Monthly* **29** (7), 4 (1965).
(11) Rackett, H.G., S.M. thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1960.
(12) Reamer, H.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **38**, 986 (1946).
(13) Savvina, Y.O., Velikovskii, A.S., *J. Phys. Chem. (USSR)* **30**, 1596 (1956).
(14) Shipman, L.M., Kohn, J.P., J. CHEM. ENG. DATA **11**, 176 (1966).
(15) Stegemeier, G.L., Ph.D. dissertation, University of Texas, Austin, Tex., 1959.
(16) Sugden, S., *J. Chem. Soc.* **858**, 30 (1922).
(17) Warren, H.G., Ph.D. dissertation, Mississippi State University, State College, Miss., 1965.
(18) Weber, J.H., "Absorption Literature Survey," prepared for Natural Gas Processors' Association, Sept. 3, 1964.
(19) Weinaug, C.F., Katz, D.L., *Ind. Eng. Chem.* **35**, 239 (1943).

RECEIVED for review February 10, 1969. Accepted February 9, 1970. Work done under a research project jointly sponsored by the Natural Gas Processors Association of Tulsa, Okla., and the Office of Engineering Research of Oklahoma State University. The Phillips Petroleum Co. provided fellowship support.

The System 2-Isopropoxypropane–2-Propanol–Water

LUCIEN A. J. VERHOEYE
State University of Ghent, Laboratory of Organic Industrial Chemistry
and Chemical Engineering, J. Plateaustraat, 22, Ghent, Belgium

The vapor-liquid equilibrium data of the ternary system and the related binary systems, including the composition of the azeotropic mixtures and liquid-liquid equilibrium at the boiling point, are reported for 760 mm. of Hg.

A STUDY of the liquid-liquid and vapor-liquid equilibria of the ternary system 2-isopropoxypropane–2-propanol–water has been made. The liquid-liquid equilibrium was studied at 25° C. and at the boiling points of the mixtures, with a constant pressure of 760 mm. of Hg. Since Frère (*4*) published data on the liquid-liquid equilibrium at 25° C. which agree very well with the present measurements, no data about this equilibrium are listed in the present work. This study does not contain new data for the 2-propanol–water system, since other sets of data are available for it (*10*). Miller and Bliss (*8*) reported data for the binary system 2-isopropoxypropane–2-propanol, and Motina and coworkers (*9*) for the ternary system 2-isopropoxypropane–2-propanol–water.

EXPERIMENTAL

Experimental methods for the purification of materials, the determination of the liquid-liquid and vapor-liquid equilibria, and the method employed for the analysis of the samples are published (*12*). Only few remarks must be added.

The purification of 2-isopropoxypropane requires some precautions because of possible peroxidation. This was avoided by distillation under nitrogen atmosphere and keeping the samples in iron vessels.

It was impossible to purify the 2-isopropoxypropane by distillation only. Therefore, the ether was stirred thoroughly with sulfuric acid (about 65 weight %), washed, dried, and distilled.

The analysis was carried out by measurement of specific gravity and refractive index or by the Karl Fischer method of water titration (*12*). The data published by Brey (*2*) were checked and found sufficiently accurate. A diagram containing lines of constant value of refractive index and specific gravity derived from these data was used for the analysis of the present samples.

Some physical properties of the materials used in this study are listed and compared with critically chosen values from literature in Table I. There is little agreement between the published data for the listed physical properties of the pure 2-isopropoxypropane. The data listed by Weissberger and coworkers (*13*), which are the data determined by Dreisbach and Martin (*3*), seem rather unreliable (*2*). For this reason, the general range of the published values is shown in Table I.

RESULTS AND DISCUSSION

Data on the liquid-liquid equilibrium at 25° C. were published by Frère (*4*). These data for the whole concentration range are in agreement with our measurements; consequently, no data are reported here.

The importance of the liquid-liquid equilibrium of the mixtures at boiling has been indicated (*12*). The tie line data are listed in Table II and represented, together with lines of constant boiling point of homogeneous mixtures, in Figure 1. To obtain an idea of the reliability of experimental liquid-liquid equilibrium data, several correlation methods have been worked out, of which that by Othmer and Tobias (*10*) proved the most satisfactory (*1*). Figure 2 shows that the reliability of the present non-isothermal data can be ascertained by this method. The composition of the conjugate phases is correlated by the equation

$$\log \frac{b_1 + c_1}{a_1} = n \log \frac{a_2 + b_2}{c_2} + S$$

for the end points of the tie lines. The two branches of the binodal are correlated in the same diagram by plotting

$$\log \frac{b_2 + c_2}{a_2} \ vs. \log \frac{a_2 + b_2}{c_2} \text{ and } \log \frac{b_1 + c_1}{a_1} \ vs. \log \frac{a_1 + b_1}{c_1}$$

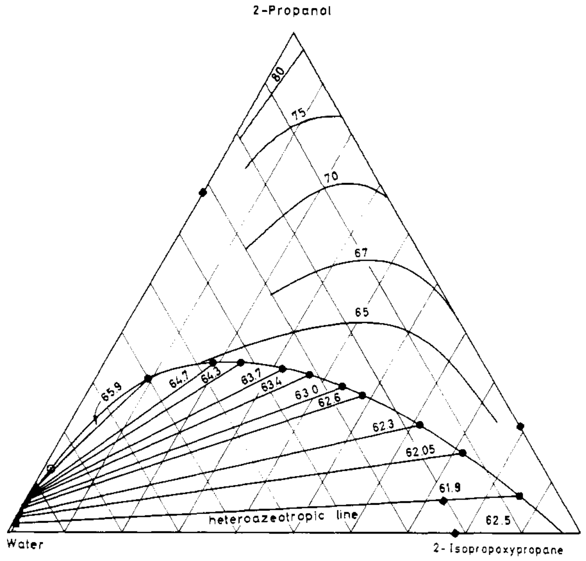

Figure 1. Boiling point diagram

● Tie lines
■ Heteroazeotropic line
● Azeotropic mixtures
⊙ Calculated plait point

The symbols a, b, and c refer to the weight % of the components: a = 2-isopropoxypropane, b = 2-propanol, and c = water. The subscript 1 refers to the 2-isopropoxypropane–rich phase and 2 to the water-rich phase.

Table I. Physical Properties of Materials

Materials	Specific Gravity, d_4^{25}		Refractive Index, n_D^{25}		Boiling Point, 760 Mm. of Hg, ° C.	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
2-Isopropoxypropane	0.7187	0.7187–0.7195	1.3662	1.3656–1.3662	67.5	67.5–68.3
2-Propanol	0.7808	0.78095 (*11*)	1.3749	1.3747 (*11*)	80.4	80.40 (*11*)

Table II. Liquid-Liquid Equilibrium at the Boiling Point of the Mixtures at 760 Mm. of Hg, Mole Fraction, Tie Lines

	2-Isopropoxypropane–Rich Phase			Water-Rich Phase		
Temp., ° C.	2-Isopropoxy-propane	2-Propanol	Water	2-Isopropoxy-propane	2-Propanol	Water
65.9	0.090	0.308	0.601	0.003	0.093	0.905
64.7	0.191	0.340	0.470	0.002	0.075	0.923
64.3	0.240	0.340	0.420	0.002	0.071	0.927
63.7	0.320	0.328	0.352	0.001	0.068	0.930
63.4	0.370	0.314	0.316	0.001	0.062	0.937
63.0	0.445	0.292	0.263	0.001	0.052	0.947
62.6	0.488	0.277	0.236	0.000	0.049	0.951
62.3	0.628	0.217	0.155	0.000	0.038	0.962
62.05	0.717	0.160	0.123	0.000	0.031	0.968
61.9[a]	0.862	0.070	0.067	0.000	0.018	0.982
62.5	0.972	0.000	0.028	0.000	0.000	1.000

Calculated Plait Point. 2-Isopropoxypropane 0.009
2-Propanol 0.150
Water 0.841

[a] Heteroazeotropic line.

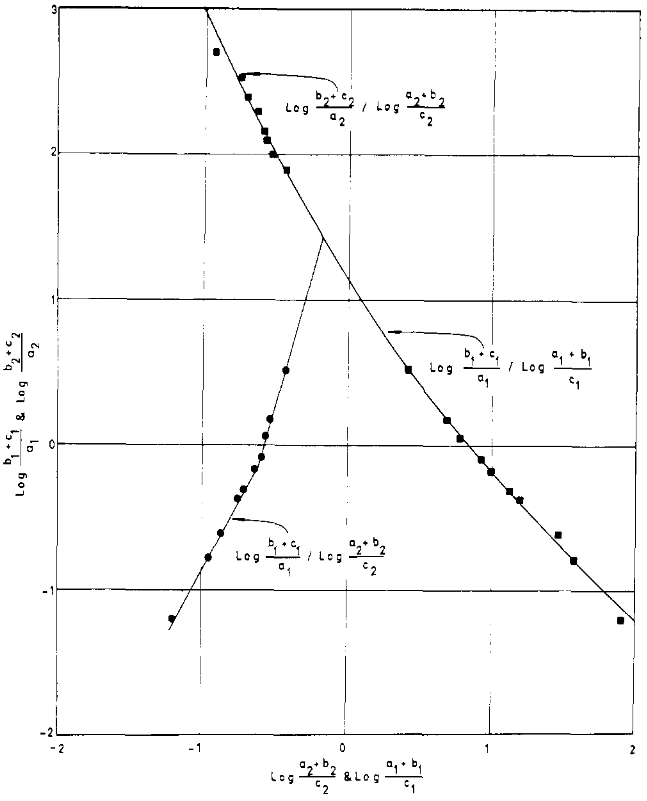

Figure 2. Correlation of the liquid-liquid equilibrium data at boiling point by the method of Othmer and Tobias

Table III. Composition of Azeotropic Mixtures

	Mole %		Boiling Point at 760 Mm. of Hg, ° C.	
	Exptl.	Lit.	Exptl.	Lit.
	2-Propanol–Water[a]			
2-Propanol	68.34	68.7 (*5*)	80.20	80.10 (*5*)
	2-Isopropoxypropane–2-Propanol[a]			
2-Isopropoxypropane	78.70	75.1 (*4*)	66.20	66.2 (*4*)
	2-Isopropoxypropane–Water[b]			
2-Isopropoxypropane, vapor phase	78.0	78.9 (*4*)	62.50	62.2 (*4*)
2-Isopropoxypropane, liquid phase[c]	97.2			
2-Isopropoxypropane, liquid phase[d]	0.0			
	2-Isopropoxypropane–2-Propanol–Water[e]			
2-Isopropoxypropane, vapor phase	73.1	72.1 (*5*)	61.9	61.8 (*5*)
2-Propanol, vapor phase	6.1	5.4 (*5*)		
2-Isopropoxypropane, liquid phase[c]	86.2			
2-Propanol, liquid phase[c]	7.0			
2-Isopropoxypropane, liquid phase[d]	0.0			
2-Propanol, liquid phase[d]	1.8			

[a] Homogeneous binary mixture. [b] Heterogeneous binary mixture. [c] 2-Isopropoxypropane-rich phase. [d] Water-rich phase. [e] Heterogeneous ternary mixture.

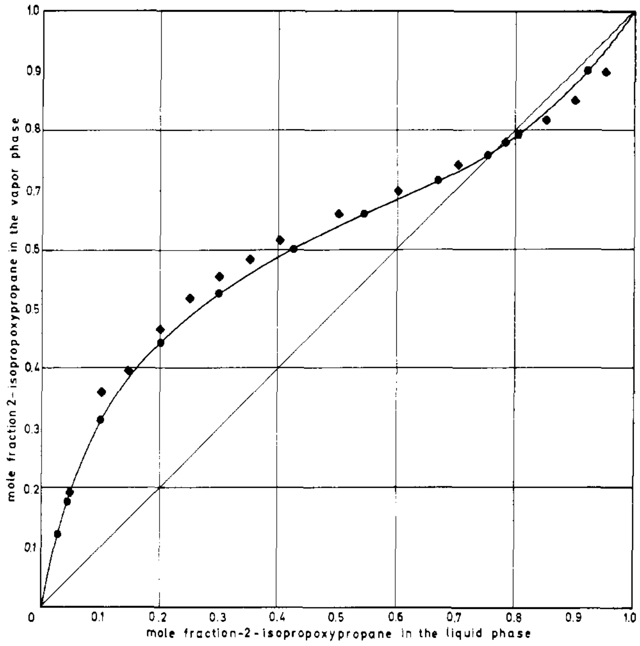

Figure 3. The vapor-liquid equilibrium of the binary system 2-isopropoxypropane–2-propanol

◆ Data of present work
● Data of Miller and Bliss

Table IV. Vapor-Liquid Equilibrium Data of the Binary System 2-Isopropoxypropane–2-Propanol

	Mole Fraction 2-Isopropoxypane		Activity Coefficients	
Temp., ° C.	Liquid Phase	Vapor Phase	2-Isopropoxypropane	2-Propanol
80.0	0.028	0.118	2.780	1.000
78.8	0.046	0.175	2.616	1.000
75.6	0.099	0.315	2.435	1.005
72.6	0.200	0.443	1.871	1.042
70.1	0.300	0.528	1.614	1.124
68.6	0.422	0.602	1.374	1.227
67.5	0.542	0.659	1.217	1.395
66.8	0.664	0.717	1.105	1.628
65.6	0.750	0.759	1.076	1.963
65.5	0.800	0.796	1.062	2.087
65.9	0.918	0.902	1.032	2.400

The intersection of the straight line correlating the end points of the tie lines and the line correlating the binodal determines the composition of the plait point.

One of the tie lines is the heteroazeotropic line, which corresponds to the ternary heterogeneous azeotropic mixture. This line is indicated on Figure 1; the composition of the vapor phase and both liquid phases is listed in Table III, which also contains the composition of the binary azeotropic mixtures. Some data from literature (*5*, *6*) are added for comparison.

Miller and Bliss (*8*) reported data on the vapor-liquid equilibrium of the binary system 2-isopropoxypropane–2-propanol. These data are represented in Figure 3, together with the data of the present work, listed in Table IV. The two sets of data do not agree. The most important source of error connected with an Othmer still is rectification of the vapor phase in the upper part of the still, necessitated by partial condensation on the wall because of heat loss. In that case, the results plotted in Figure 4 are too far from the diagonal. Results too near the diagonal are caused by entrainment of small droplets of the liquid phase by the rising vapor. The latter was controlled by carrying

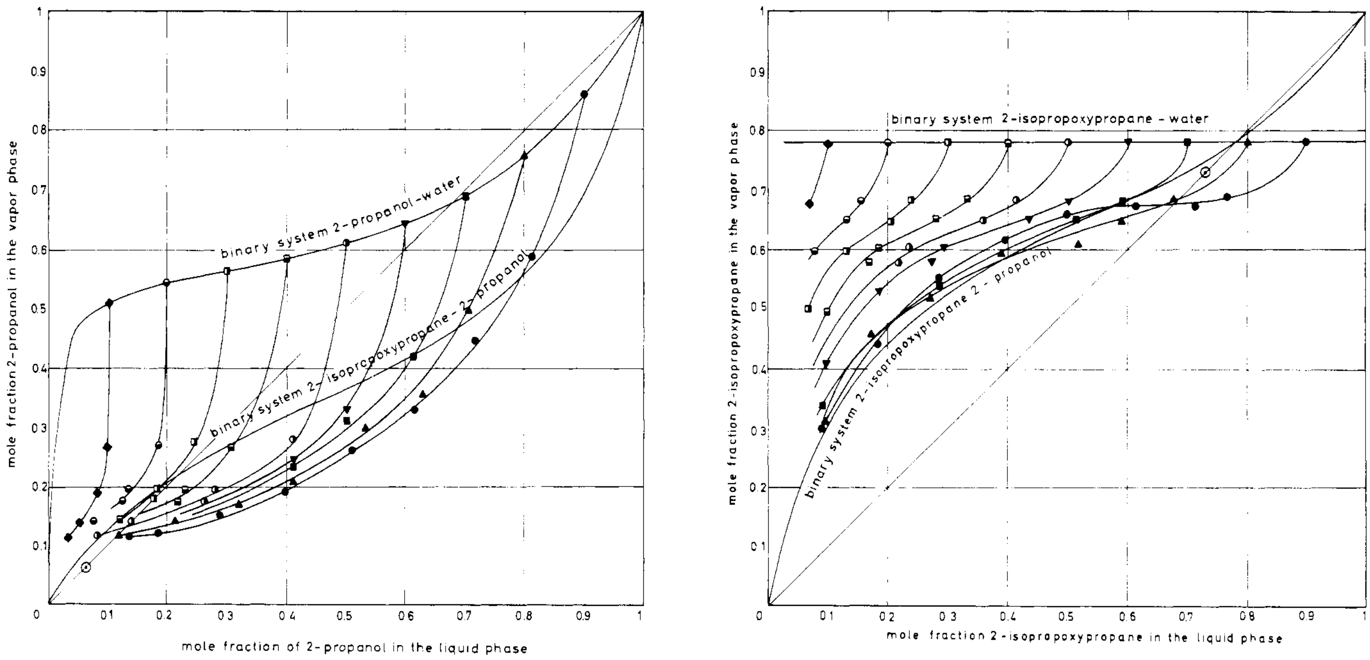

Figure 4. The vapor-liquid equilibrium of the ternary system 2-isopropoxypropane–2-propanol–water

⊙ Azeotropic mixture

Lines of constant mole fraction of water in the liquid phase

Symbol	Mole fraction of water	Symbol	Mole fraction of water
●	0.1	⬒	0.6
▲	0.2	◘	0.7
■	0.3	◓	0.8
▼	0.4	◆	0.9
◑	0.5		

Table V. Vapor-Liquid Equilibrium Data of Ternary Mixtures

	Mole Fraction in Liquid Phase			Mole Fraction in Vapor Phase			Activity Coefficients		
Temp., ° C.	2-Isopropoxypropane	2-Propanol	Water	2-Isopropoxypropane	2-Propanol	Water	2-Isopropoxypropane	2-Propanol	Water
				Homogeneous Liquid Phase					
62.6	0.714	0.186	0.100	0.670	0.122	0.208	1.104	1.536	9.650
63.7	0.609	0.291	0.100	0.676	0.150	0.173	1.276	1.147	7.432
64.9	0.499	0.398	0.103	0.660	0.189	0.150	1.441	1.000	5.990
66.4	0.392	0.509	0.099	0.614	0.259	0.126	1.624	1.003	4.849
68.2	0.285	0.616	0.100	0.552	0.332	0.114	1.892	0.978	4.011
70.8	0.181	0.715	0.104	0.440	0.447	0.112	2.178	1.011	3.385
75.0	0.089	0.812	0.099	0.299	0.587	0.114	2.622	0.979	3.027
63.0	0.503	0.300	0.197	0.610	0.170	0.220	1.405	1.301	4.952
64.8	0.389	0.411	0.200	0.597	0.204	0.198	1.676	1.048	4.050
67.1	0.271	0.529	0.200	0.518	0.297	0.184	1.937	1.070	3.396
69.8	0.173	0.627	0.200	0.463	0.355	0.182	2.479	0.956	2.985
73.4	0.096	0.705	0.199	0.305	0.500	0.195	2.617	1.029	2.756
65.3	0.291	0.409	0.300	0.542	0.236	0.219	2.004	1.190	2.920
67.6	0.200	0.500	0.300	0.474	0.312	0.214	2.361	1.163	2.576
72.8	0.089	0.610	0.301	0.339	0.419	0.242	3.211	1.022	2.320
66.6	0.185	0.410	0.405	0.531	0.244	0.224	2.963	1.161	2.088
71.2	0.098	0.499	0.402	0.410	0.331	0.259	3.701	1.055	1.991
69.9	0.097	0.400	0.503	0.459	0.282	0.259	4.374	1.189	1.682
				Heterogeneous Liquid Phase					
61.9	0.332	0.068	0.600	0.731	0.061	0.208	2.655	2.168	1.616
62.0	0.329	0.071	0.600	0.685	0.115	0.203	2.505	3.897	1.570
62.3	0.282	0.118	0.600	0.652	0.139	0.209	2.750	2.795	1.595
63.7	0.180	0.217	0.600	0.606	0.176	0.220	3.815	1.813	1.575
64.0	0.170	0.230	0.600	0.576	0.196	0.228	3.807	1.867	1.611
65.7	0.100	0.302	0.600	0.495	0.268	0.237	5.248	1.799	1.552

out an experiment with a solution of 10% phenolphthalein in ethanol in the boiling vessel. Less than 0.01% phenolphthalein was found in the liquid of the condensate receiver. Partial condensation was avoided by applying an external heater on the upper part of the still, keeping the temperature of the space between the tube transporting the vapor to the condenser and the external wall a little higher than the temperature of the boiling liquid. Since the deviation cannot be explained by entrainment of liquid droplets, and since the present data for other binary systems agree very well with data of other authors (*12*), the most probable explanation seems to be that the data of Miller and Bliss are not correct because of insufficient insulation of their still.

The vapor-liquid equilibrium for the binary system 2-propanol–water already has been published (*12*).

Data on the ternary system are listed in Table V and represented in Figure 4. Other data on the ternary system have been published by Motina (*9*) and coworkers. Their experiments were not carried out for a constant content of one of the components; their estimated lines for constant water content do not agree with the present results.

Experimental activity coefficients for the components are calculated neglecting vapor-phase imperfection. The vapor pressures of pure components are taken from literature (*7*). The experimental values of binary systems are correlated with the three-constant Redlich-Kister equation. Those of the ternary system are correlated with the Redlich-Kister equation containing the binary constants and one ternary constant (*11*). The ternary constants corresponding to the different components differ, and have to be retained to represent the experimental data well. The constants are listed in Table VI. All constants were considered independent of temperature. The agreement of experimental and calculated values of this coefficient is reasonable for both the binary systems and the ternary system. The root mean square deviation between the calculated logarithm of the activity coefficient and the logarithm of the experimental values of this coefficient for the homogeneous binary 2-isopropoxypropane–2-propanol is 2×10^{-2} for the 2-isopropoxypropane and 5×10^{-2} for the 2-propanol. The logarithm of the activity coefficient of the heterogeneous binary system 2-isopropoxypropane–water was correlated with a Redlich-Kister equation to obtain the third set of binary constants. The root mean square deviation is calculated for nine equidistant values of composition, and is 2×10^{-2} for the 2-isopropoxypropane and 3×10^{-2} for the water. For the ternary system, the root mean square deviation is 3×10^{-2} for the 2-isopropoxypropane, 7×10^{-2} for the 2-propanol, and 3×10^{-2} for the water.

Table VI. Constants of Redlich-Kister Equations for the System 2-Isopropoxypropane(1)–2-Propanol(2)–Water(3)

	Binary Constants	
$B_{12} = 0.387$	$C_{12} = -0.046$	$D_{12} = 0.015$
$B_{23} = 0.657$	$C_{23} = -0.244$	$D_{23} = 0.099$
$B_{31} = 1.097$	$C_{31} = 0.042$	$D_{31} = 0.287$
	Ternary Constants	
$C_1 = 0.908$	$C_2 = 0.766$	$C_3 = 0.899$

ACKNOWLEDGMENT

The author thanks Gaston Goethals, director of the Laboratory for Organic Industrial Chemistry and Chemical Engineering of the State University of Ghent, for his interest in this work.

LITERATURE CITED

(1) Alders, L., "Liquid-Liquid Extraction," p. 59, Elsevier, New York, 1955.
(2) Brey, W.S., *Anal. Chem.* **26**, 838 (1954).
(3) Dreisbach, R.R., Martin, R.A., *Ind. Eng. Chem.* **41**, 2875 (1949).
(4) Frère, F.J., *Ibid.*, **41**, 2365 (1949).
(5) Horsley, L.H., *Advan. Chem. Soc.*, No. **6**, 10, 97 (1952).
(6) Horsley, L.H., Tamplin, W.S., *Ibid.*, No. **35**, pp. 9–63 (1962).
(7) Jordan, T.E., "Vapor Pressure of Organic Compounds," pp. 75, 106, Interscience, New York, 1959.
(8) Miller, H.C., Bliss, H., *Ind. Eng. Chem.* **32**, 123 (1940).
(9) Motina, G.P., Ivannikova, A.M., Markevich, V.A., Aerov, M.E., *Tr. Nauchn. Issled. Inst. Sintet. Spirtov. Organ. Prod.* **1**, 320 (1958).
(10) Othmer, D.F., Tobias, P.E., *Ind. Eng. Chem.* **34**, 693 (1942).
(11) Redlich, O., Kister, A.T., *Ibid.*, **40**, 345 (1948).
(12) Verhoeye, L.A.J., J. Chem. Eng. Data **13**, 462 (1968).
(13) Weissberger, A., Proskauer, E.S., Riddick, E.S., Toops, E.E., "Organic Solvents," 2nd ed., pp. 93, 121, Interscience, New York, 1955.

Received for review March 3, 1969. Accepted September 28, 1969.