acid and diluted with an excess of water. The product was collected; weight 9.8 grams (94%); $[\alpha]_D^{25}$ −53.2° (C = 1.0 in chloroform). On recrystallization from aqueous ethanol, the rotation remained unchanged; weight 5.9 grams; m.p. 255–257° C. decomposed; no characteristic absorption from 220 to 320 mμ, high end absorption; λ max (chloroform solution) 2.87 (s) (amino), 3.05 (s) (amino), 5.63 (m) (imide) μ.

Anal. Calcd. for $C_{24}H_{34}O_4N_2$: C, 69.54; H, 8.27; N, 6.76; O, 15.4; neutral equivalent 415. Found: C, 69.55; H, 8.39; N, 6.80; O, 15.7; neutral equivalent 414 (in ethanol).

A 3.54-gram sample of *asym*-aminomaleopimarimide was recrystallized from aqueous acetone to give 3.31 grams (85%) of acetone condensation product (VII); $[\alpha]_D^{25}$ −12.8° (C = 0.63 in chloroform), rotation unchanged on further recrystallization from acetone, m.p. 281–283° C. decomposed; no characteristic absorption from 220 to 320 mμ, high and absorption; λ max (chloroform solution) 5.66 (m) (imide), 5.88 (s) (imide) μ.

Anal. Calcd. for $C_{27}H_{38}O_4N_2$: C, 71.3; H, 8.43; N, 6.16; O, 14.1; neutral equivalent 455. Found: C, 71.2; H, 8.39; N, 6.24; O, 13.9; neutral equivalent 456 (in ethanol).

1,1-Dimethylaminomaleopimarimide (VIII). To a solution of 4.0 grams (0.01 mole) of maleopimaric acid in 15 ml. of dioxane was added slowly a solution of 1.20 grams (0.02 mole) of 1,1-dimethylhydrazine in 5 ml. of dioxane. After the solution stood overnight at room temperature, a small amount of 3*N* hydrochloric acid was added to bring the solution to pH 2. Excess water was introduced, and the solid was collected (2.16 grams) and crystallized from aqueous ethanol; yield 1.56 grams (36%) $[\alpha]_D^{25}$ −40.6° (C = 0.92 in chloroform), no change in rotation on further recrystallization; m.p. 254–257° C. decomposed; no characteristic absorption from 220 to 320 mμ, high end absorption; λ max (chloroform solution) 5.67 (m) (imide), 5.88 (s) (imide) μ, no band in 3 μ region.

Anal. Calcd. for C, 70.6; H, 8.65; N, 6.33; O, 14.5; neutral equivalent 443. Found: C, 70.5; H, 8.42; N, 6.37; O, 14.3; neutral equivalent 443 (in ethanol).

1,1-Dimethylaminopropylmaleopimarimide (IX). Preparation essentially according to Clinton and Manson (*2*). A solution of 40 grams (0.10 mole) of maleopimaric acid and 11.24 grams (0.12 mole) of 1,1-dimethylaminopropylamine in 500 ml. of benzene was set up under reflux, and in 12 minutes, a solid mass of crystals filled the flask. The theoretical amount of water was liberated in 1.5 hours, and refluxing was continued for a total of 4 hours. The crystals were collected; weight 36.5 grams. An 8.0-gram portion was extracted with ethyl acetate in a Soxhlet-type extractor for 2 hours; weight of remaining solid 7.12 grams. This product was recrystallized from 95% ethanol to give 4.63 grams (41%) of imide; m.p. 237–240° C. unchanged on further recrystallization; $[\alpha]_D^{25}$ −21.0° (C = 1.4 in chloroform); reported (*2*) for 1,1-dimethylaminopropylmaleopimarimide, m.p. 237.4–241.0° C. (corrected) and $[\alpha]_D^{25}$ = −21.8° (1% in chloroform); no characteristic absorption from 220 to 320 mμ, high end absorption; λ max (Nujol mull) 5.68 (m) (imide), 5.88 (s) (imide) μ.

Anal. Calcd. for $C_{29}H_{44}N_2O_2$: C, 71.9; H, 9.15; N, 5.78; O, 13.2; neutral equivalent 485. Found: C, 72.0; H, 9.02; N, 5.72; O, 13.3; neutral equivalent (base) 479, acid (485) (in acetone).

***N*-methylmaleopimarimide (X).** A solution of 9.06 grams (0.03 mole) of levopimaric acid in 40 ml. of dioxane was added to a solution of 3.33 grams (0.03 mole) of *N*-methylmaleimide in 20 ml. of dioxane. After 2 days at room temperature, the specific rotation became constant and the adduct was watered out; yield 11.7 grams (94%); $[\alpha]_D^{25}$ −48° (C 1.8 in 95% ethanol). An analytical sample was recrystallized from methanol to a constant rotation of $[\alpha]_D^{25}$ −55° (C 1.15 in 95% ethanol); m.p. 254–255° C.; λ max ($CHCl_3$) 5.67 (m), 5.80–5.95(s) (both imide).

Anal. Calcd. for $C_{25}H_{35}O_4N$: C, 72.6; H, 8.53; O, 15.5; N, 3.39; neutral equivalent 414. Found: C, 72.8; H, 8.41; O, 15.5; N, 3.46; neutral equivalent 415 (in ethanol).

LITERATURE CITED

(1) Ayer, W.A., McDonald, C.E., Stothers, J.B., *Can. J. Chem.* **41**, 1113 (1963).
(2) Clinton, R.O., Manson, A.J., (to Sterling Drug Inc.), U.S. Patent **3,135,749** (June 2, 1964).
(3) Fleck, E.E., (to U. S. A. as represented by the Secretary of Agriculture), U. S. Patent **2,362,052** (Oct. 10, 1944).
(4) Graff, M.M., *J. Am. Chem. Soc.* **68**, 1937 (1946).
(5) Ruzicka, L., Ankersmit, P.J., Frank, B., *Helv. Chim. Acta* **15**, 1289 (1932).
(6) Simonsen, J., Barton, D.H.R., "The Terpenes," Vol. **III**, p. 434, The Cambridge University Press, London, England, 1952.

RECEIVED for review November 3, 1966. Accepted January 25, 1967. One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

Ternary Systems of Furfural and Several Alcohols

ALFRED W. FRANCIS
Socony Mobil Oil Co., Paulsboro, N. J.

In graphic form 26 systems of furfural, four of furfuryl alcohol, eight of ethyl alcohol, seven of isopropyl alcohol, 15 of butyl alcohols, 12 of methoxyethanol, and 17 of other higher alcohols are presented. Methanol and glycols (previously published) are not included. The graphs show two isopycnics, two twin density lines, two iso-optics, a solutrope, and four systems each having three liquid layers. Most of the other systems have two liquid phases in certain compositions.

FURFURAL (b.p. 161.7° C.) is a widely used selective solvent for hydrocarbons because of its low cost and high selectivity for the hydrocarbons of the light gas oil range (*12, 13*). The low solubility of lubricating oils in furfural makes it less applicable to them unless they are highly aromatic. Experimental studies of furfural are handicapped by its sensitivity to oxidation, causing sludge and necessitating frequent redistillation, although on exclusion of air its heat stability is high.

Critical solution temperatures (CST) of furfural have been compiled (*1*, p. 97; *11*, p. 227) for 32 lighter hydrocarbons; those for 261 pure higher hydrocarbons have been

---

[1] Present address: Mobil Chemical Co., Metuchen, N. J.

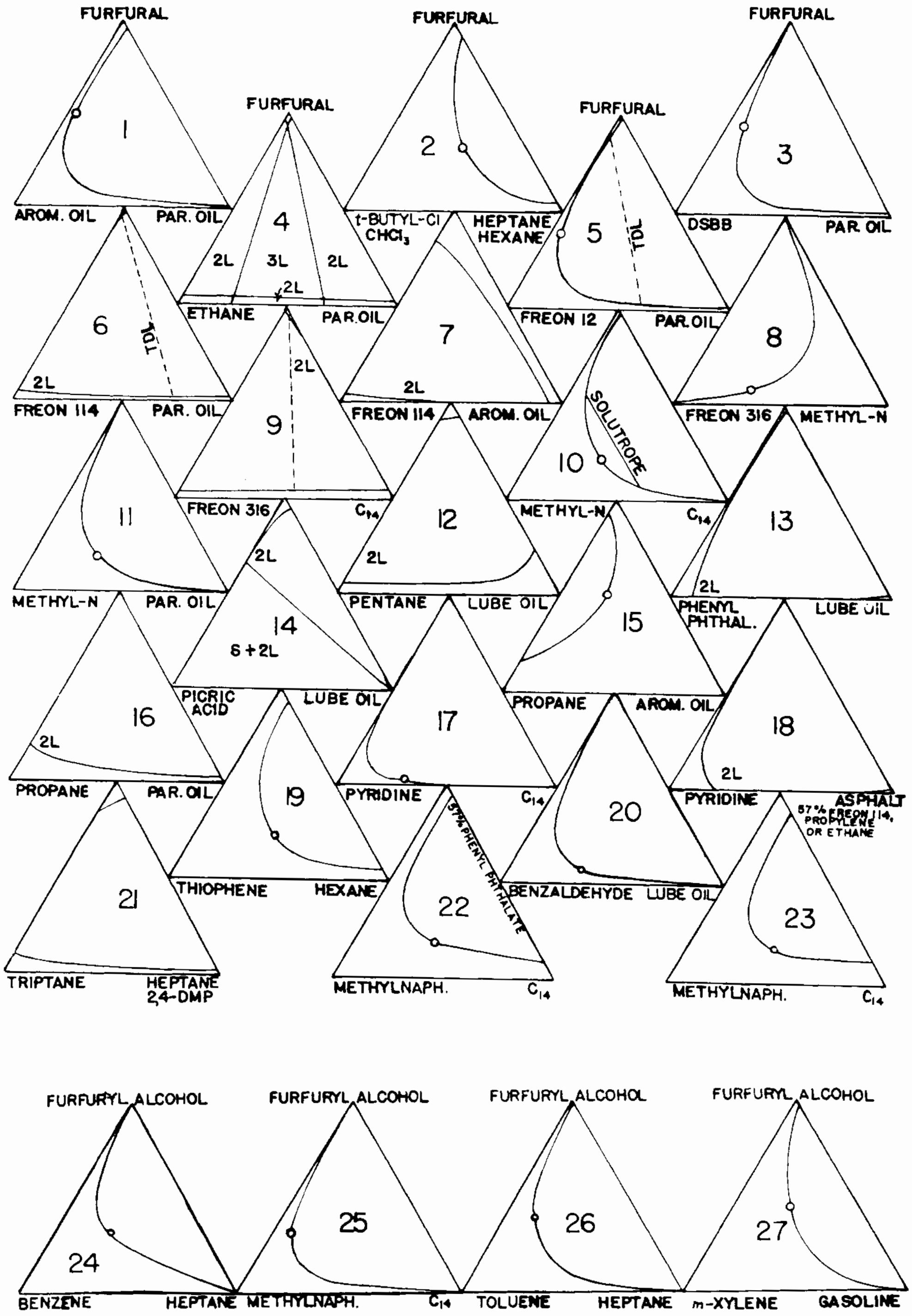

Figure 1. Ternary systems of furfural and several alcohols

Systems of furfural (graphs 1 to 24) are shown in concise arrangement; the top corner indicates furfural in each graph. The same pattern is used for aqueous systems of *tert*-butyl alcohol (graphs 51 to 58) and for the methoxyethanol group (graphs 63 to 74) but the other graphs have a slightly expanded arrangement to permit individual designation of the top component. Graphs 22 and 23 show quaternary systems with 43% furfural and 57% of a diluent, as indicated, as the top component. The other components are named below the appropriate corners in all graphs. The gasoline (graphs 27, 71, 80, 83, and 84) was straight run, aniline point 30°, indicating that it was highly naphthenic.

(continued on page 271)

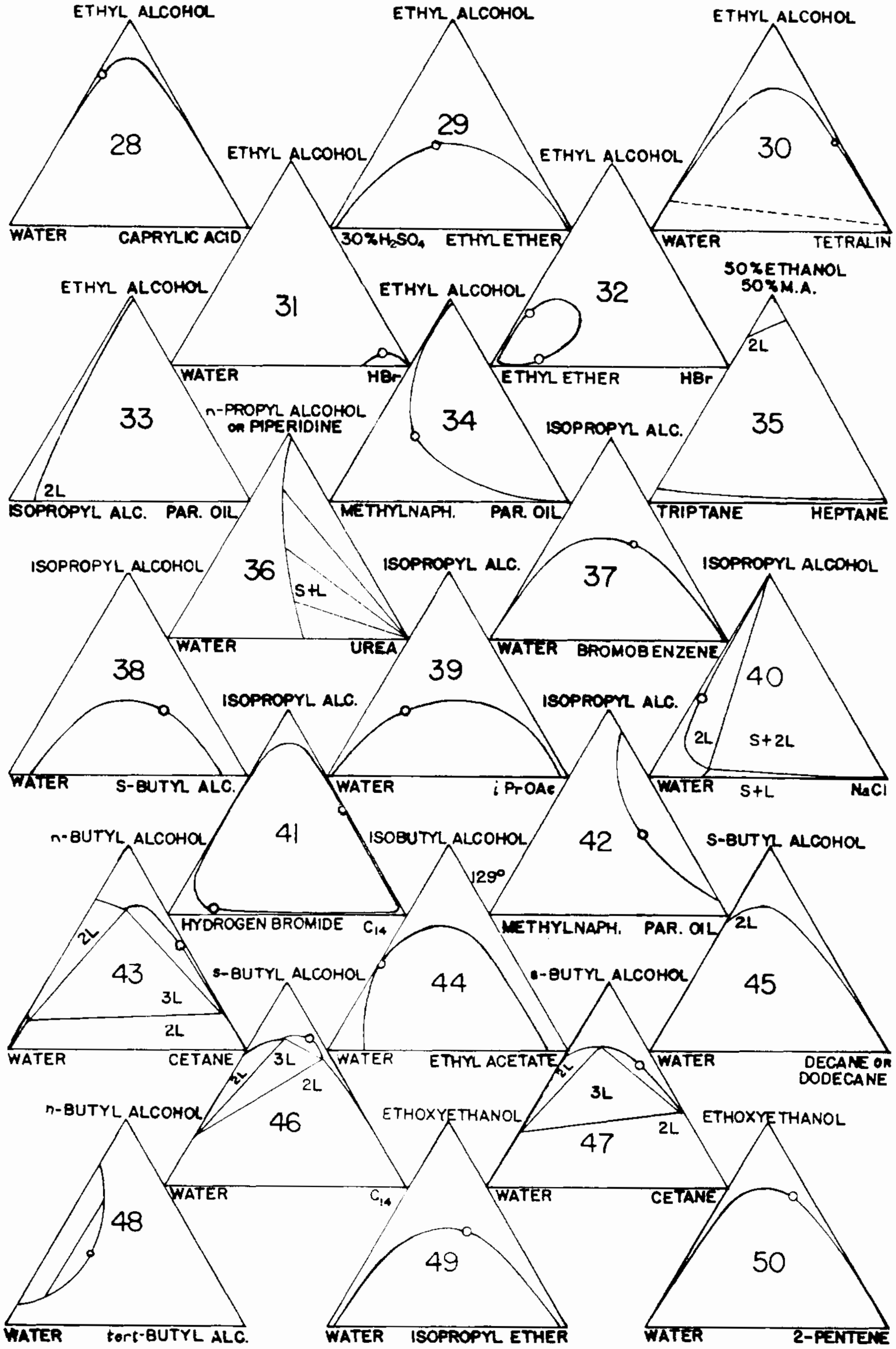

Figure 1 (*Continued*)

Temperature is 25° C. except where indicated above the right side line (graphs 44 and 78) or on a curve (graph 72). Plait points are indicated by small circles on the binodal curves. A dashed tie line (graphs 9 and 30) or twin density line (graphs 5 and 6), not rigorously straight because one component is a mixture, indicates compositions separating into two layers of equal density (2). The tie line in graphs 64 and 72, which bear the legends "blue" or "yellow" indicate iso-optics, in which the two layers have equal refractive indices (2). A solutrope, or tie line parallel to the base line, is shown in graph 10. Graph 44 is the isotherm at the CST of water and isobutyl alcohol, 129° C.

(*continued on page 272*)

presented (*1*, *14*, *15*) in comparison with those for aniline as an aid to identification (*1*). About 44 ternary systems of furfural have been compiled (*11*, pp. 159–60, 207; and three additional ones are presented in the current series (*6*, graph 55; *8*, graphs 5 and 6).

EXPERIMENTAL

As in the work on acetonitrile systems (*4*), all observations except those involving liquefied gases were made in a 10-ml. graduated tube. Reagent grade chemicals were used in all cases. One reagent was pipetted into the tube with a graduated pipet and titrated with another reagent until a cloud or separate layer appeared. Enough of the third component was added to mix the layers. These alternate additions were continued until the tube was filled, or all required data were obtained. When a liquefied gas was a component—a Freon (graphs 5 to 9 and 23), propane (graphs 15 and 16), HCl (graphs 57 and 61), or HBr (graphs 31, 32, 41, 73 to 75)—observations were made in a sealed glass tube as in the sulfur dioxide systems (*3*). The temperature was controlled by immersion in a bath of water. The ethane systems (graphs 4 and 23) were studied in a visual autoclave (*9*) capable of holding the pressure necessary to keep the ethane liquid in the region near its critical temperature, 32.1° C. Ethane in this temperature range provides an exception to the generality that all liquid hydrocarbons are miscible; the system of graph 4 exhibits three liquid phases.

DISCUSSION

This paper presents in concise graphic form (graphs 1 to 23) observations on 26 new ternary systems and two quaternary systems of furfural. Since furfural is only slightly miscible with nonaromatic hydrocarbons, its ternary graphs consist mostly of binodal curves from the right side line. Systems of Freon 114 and 316 (graphs 6 to 9) are exceptional. Their high densities cause isopycnics or twin density lines in two of these systems and also in graph 5, although Freon 12 is low enough in molecular weight to mix

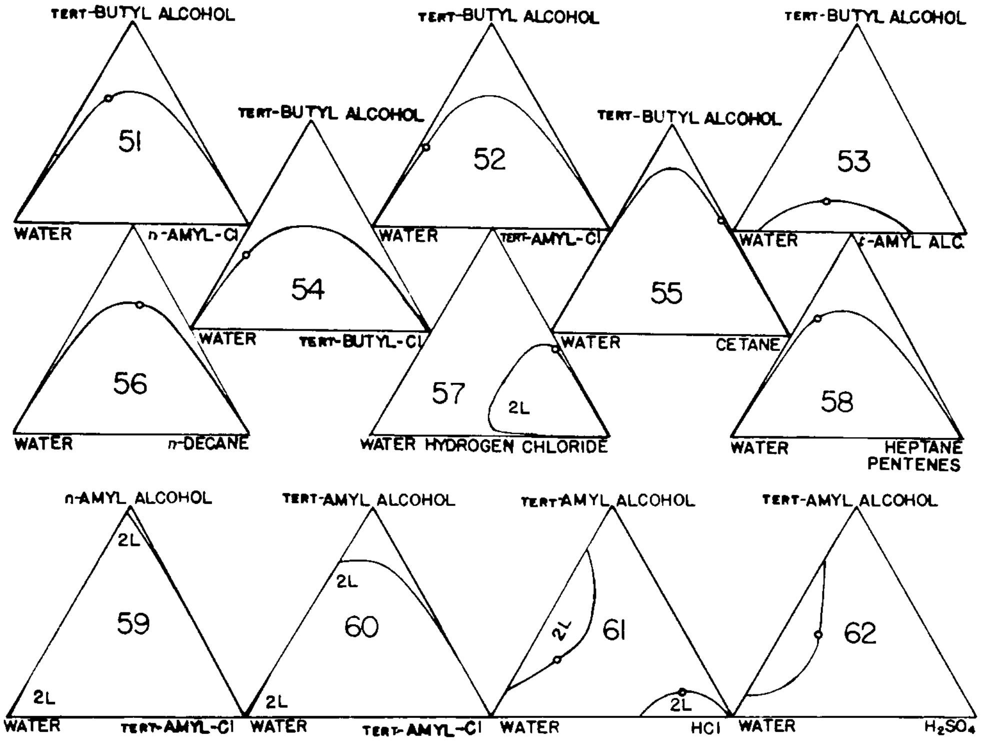

Figure 1. (*Continued*)

Abbreviation	Name	Graphs
ALC	Alcohol	33, 37–39, 41, 42, 48, 53
n-AmCl	*n*-Amyl chloride	51
tert-Amyl-Cl	*tert*-Amyl chloride	52, 59, 60
AROM. OIL	Aromatic lubricating oil (3 or 4, Table I)	1, 7, 15
t-BUTYL-Cl or tert-BUTYL-Cl	*tert*-Butyl chloride	2, 54
C_{14}	*n*-Tetradecane	9, 10, 17, 22, 23, 25, 41, 46, 66, 68, 76, 78, 79
CARBITOL	Diethylene glycol monoethyl ether	80 to 83
CETANE	*n*-Hexadecane	43, 47, 55
DMP	Dimethylpentane	21, 82
DIACETONE ALCOHOL	4-Hydroxy-4-methyl-2-pentanone	78, 79
DSBB	Di-sec-butylbenzene	3, 66, 77
ETHANOL	Ethyl alcohol	35

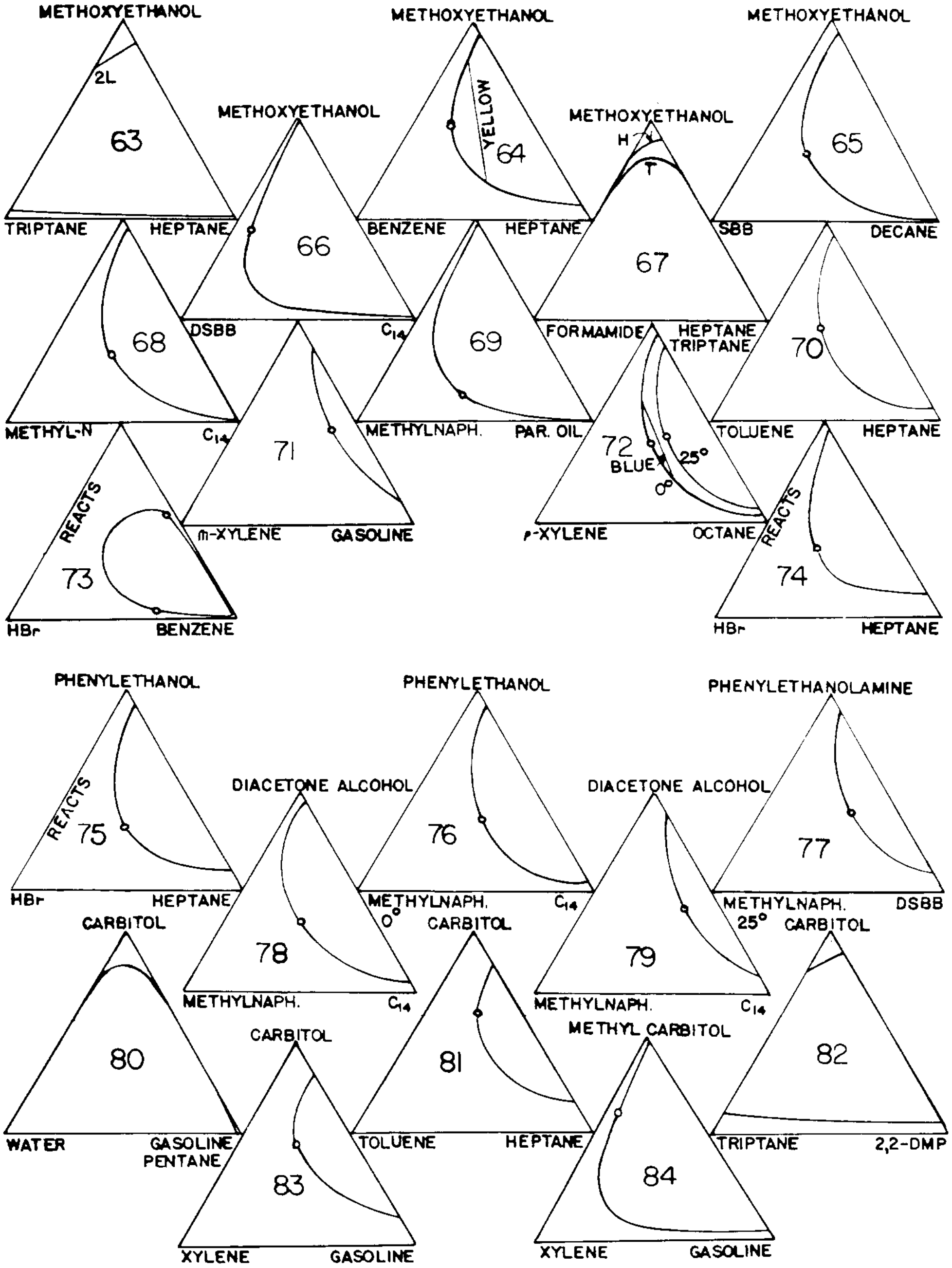

Figure 1. (*Continued*)

Abbreviation	Name	Graphs
FREON 12	CCl_2F_2	5
FREON 114	$C_2Cl_2F_4$	6, 7, 23
FREON 316	$C_4Cl_2F_6$	8, 9
HBr	Anhydrous hydrogen bromide	31, 32, 41, 73–75
HCl	Anhydrous hydrogen chloride	61
i-PrOAc	Isopropyl acetate	39
M. A.	Maleic anhydride	35
LUBE OIL	Lubricating oil (*3* or *4*, Table I)	12, 13, 14
METHYL CARBITOL	Diethylene glycol monomethyl ether	84
METHYL-N or	1-Methylnaphthalene	8, 10, 11, 68,
METHYLNAPH	1-Methylnaphthalene	22, 23, 25, 34, 42, 69, 76–79
PAR. OIL	Paraffinic lubricating oil (*3* or *4*, Table I)	1, 3, 4, 5, 6, 11, 16, 33, 34, 42, 69
PHENYL PHTHAL	Phenyl phthalate	13, 22
SBB	sec-Butylbenzene	65
TDL	Twin density line	5, 6
TETRALIN	Tetrahydronaphthalene	30
TRIPTANE	Trimethylbutane	21, 35, 63, 67, 82

with furfural. Graph 21 indicates a slight selectivity of furfural for branched-chain hydrocarbons.

Miscibility relations of furfuryl alcohol are very similar to those of furfural. CST are usually a little higher, and have been reported for 30 hydrocarbons (*1*, p. 98). Four ternary systems are now presented. However, the author is not aware of any commercial application of furfuryl alcohol for extraction. Ternary systems of methanol (*6*) and of glycols (*5*) have been presented extensively and are not repeated here.

Higher alcohols are more miscible with hydrocarbons and are not very selective. Yet the number of ternary systems (about 220) of ethyl alcohol published (*11*, pp. 151–4, 204–5) is exceeded only by those of aqueous systems, and now those of methanol. Only six additional ternary and two quaternary systems of ethyl alcohol are now presented (graphs 28 to 35). When the third component is difficultly soluble in water, as with caprylic acid (graph 28) or Tetralin (graph 30), a high concentration of ethyl alcohol is required to produce a single phase. The alcohol is distributed to the acid in preference to water, but to water in preference to Tetralin. This results in an isopycnic (dashed line) (*2*) in the latter, since only a little alcohol is needed to decrease the density of the aqueous layer to that of Tetralin.

Systems of normal or isopropyl alcohols were presented (*7*, graph 41) with nitromethane and aromatic oil. Another one of *n*-propyl alcohol (graph 36) and seven more of isopropyl alcohol (graphs 33, 37 to 42) are now shown. Graphs 31, 32, and 41 show a midget curve in the aqueous system and island curves for the nonaqueous systems. Both phenomena are characteristic of hydrogen halide systems (*10*). Graphs 43, 46, and 47 show three liquid layers for aqueous systems of butyl alcohols with higher paraffin hydrocarbons. Graph 10 includes a solutrope or tie line parallel to a base line.

Aqueous systems of *tert*-butyl alcohol (graphs 51 to 58) are relatively simpler because of the mutual miscibility of the alcohol and water. However, that with hydrogen chloride (graph 57), which is similar to the one with hydrogen bromide (*11*, p. 97), is very unusual, being almost an island, but not quite so at any known temperature.

All of the alcohols except methoxyethanol (Cellosolve) and Carbitol share with furfural the low miscibility with paraffin hydrocarbons, and therefore, the position of the binodal curve at the right. Only in graph 67 does the still lower miscibility of formamide with hydrocarbons shift the position to the bottom. Iso-optics appear in graphs 64 and 72.

LITERATURE CITED

(1) Francis, A.W., *Advances in Chem. Ser.* **31**, 189–208 (1961).
(2) Francis, A.W., *Ind. Eng. Chem.* **45**, 2789 (1953).
(3) Francis, A.W., J. CHEM. ENG. DATA **10**, 45 (1965).
(4) *Ibid.*, p. 145.
(5) *Ibid.*, p. 260.
(6) *Ibid.*, **11**, 96 (1966).
(7) *Ibid.*, p. 234.
(8) *Ibid.*, p. 557.
(9) Francis, A.W., *J. Phys. Chem.* **58**, 1099 (1954).
(10) *Ibid.*, **62**, 579 (1958).
(11) Francis, A.W., "Liquid-Liquid Equilibriums," Wiley, New York, 1963.
(12) Francis, A.W., King, W.H., *Advan. Petrol. Chem. Refining* **1**, 468 (1958).
(13) Francis, A.W., King, W.H., "Chemistry of Petroleum Hydrocarbons," B.T. Brooks *et al.*, Eds., Vol. 1, Chap. 9, p. 230, Reinhold, New York, 1954.
(14) Schiessler, R.W., Dixon, J.A., others, "Properties of Hydrocarbons of High Molecular Weight," A.P.I. Research Project 42, Pennsylvania State University, September 1958.
(15) Schiessler, R.W., Whitmore, F.C., *Ind. Eng. Chem.* **47**, 1660 (1955); Document 4597, A.D.I.

RECEIVED for review December 9, 1965. Accepted March 16, 1966. Division of Physical Chemistry, 151st Meeting, ACS, Pittsburgh, Pa., March 31, 1966.

A Subject Index of Ternary Systems for papers by Alfred W. Francis has been deposited as Document number 9386 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $3.75 for photoprints, or $2.00 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.