Ternary Systems of Chlorine Compounds

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Graphs of 109 systems involving a compound of chlorine are presented. Most of these are ternary and show two liquid phases. Several involve chlorides of aluminum, antimony, cuprous copper, hydrogen, or mercury. Others include organic chlorine compounds. A table lists the locations of 121 published graphs of similar chlorine compounds. Mercuric chloride is much more soluble (up to 60% instead of 7%) in several organic compounds than in water. In some the maximum is in anhydrous solvents; in others, at about 90% solvent. These systems were studied extensively in the vain hope of finding some mercury salt or combination which absorbs olefins reversibly. Anhydrous cuprous chloride forms several systems with unusual types of phase diagram, some involving a complex with hydrogen chloride, postulated as $CuHCl_2$. Hydrogen chloride forms some aqueous systems having two separate binodal curves. Anhydrous systems are more likely to have island curves. The high reactivity of aluminum chloride results in graphs which are highly unconventional.

THE chlorides of aluminum, antimony, cuprous copper, hydrogen, and mercury are extremely soluble in certain mixtures of organic compounds, and show novel and perhaps useful miscibility relations. Graphs presented here include systems of several organic chlorine compounds not previously published. Some of the latter are almost equivalent to hydrocarbons in miscibility relations. Aqueous systems of ordinary salts are not listed here because of relatively little interest in solvent treatment of hydrocarbons.

ALUMINUM CHLORIDE

The more refractory Friedel-Crafts reactions—alkylation of isoparaffins with lower olefins (*5, 21*) and isomerization of normal paraffins (*5, 23*), especially *n*-butane—are catalyzed most vigorously by concentrated solutions, up to 75% of aluminum chloride, in certain oxygen-containing solvents (mixed with the hydrocarbons). Ethyl ether is probably the best. Methyl and isopropyl ethers, ethyl acetate and other esters, acetone, sulfur dioxide, Chlorex, and even acetonitrile may be used, although the last contains no oxygen.

Four aluminum chloride systems were reported earlier, with sulfur dioxide (*8*, graphs 20 to 22) and acetonitrile (*9*, graph 18). The graphs were approximations because of the rapid reaction of aluminum chloride with solvent. In two of the systems now reported, acetone (graph 1) and ethyl acetate (graph 4), rapid reaction of the solvents with aluminum chloride again makes the graphs approximate. Acetone forms a stiff gel in one area of composition. Ethyl acetate leads to graph 4 with an island curve, in turn containing an isopycnic and an iso-optic. The other graphs are more conventional. Graphs 7 and 8 include four components.

ANTIMONY CHLORIDE

Solutions of antimony chloride in water (or in aqueous concentrated hydrochloric acid) of 88 to 92% $SbCl_3$ are clear and stable though viscous. They show miscibility relations much like those of a heavy paraffin oil. Solutions of antimony chloride of lower concentrations in the same solvents are instantly hydrolyzed, giving a dense white slime. Only one aqueous system is illustrated (graph 9). It exhibited high absorption of lower olefins; but for mixtures with paraffins was almost nonselective. The same is true for 90% antimony chloride with respect to aromatic hydrocarbons over paraffins. The nonaqueous systems of antimony chloride are not unusual in type.

CUPROUS CHLORIDE

Cuprous chloride has been shown (*12, 22*) to be extremely soluble in anhydrous solutions of hydrogen chloride in alcohols, especially methanol. The methanol solutions are fairly selective for olefins in preference to paraffins. They are more suitable than ethyl alcohol solutions, which dissolve considerable amounts of the paraffin gases.

Amides and some other nitrogen compounds, with hydrogen chloride, have much higher capacity for cuprous chloride than ammonia, ammonium chloride, or hydrochloric acid; and their solutions have higher capacity for olefins (*25*). Graphs 16 to 23 and those of earlier papers (*12*, graphs 40 to 45) show a considerable variety of these systems. Those with alcohols usually have another solid phase, presumably $CuHCl_2$.

HYDROGEN CHLORIDE

Graphs 24 to 36 largely supplement an earlier paper (*17*). As before, the aqueous systems, graphs 24, 26, and 28, have two separate binodal curves. The lower curve in graph 28 was published (*1*), but without the upper curve. Graph 26 was included by Francis (*19*, p. 991), but without the ternary plait point, 34.5° C. (observed more recently). This graph and those of several nonaqueous systems (graphs 29 and 31 to 34) show island curves. The phenol system (graph 27) was presented in part (*27*, p. 573; *19*, p. 1025). The bismuth chloride system (graph 35) is entirely analogous to the antimony chloride system (graph 9).

MERCURIC CHLORIDE

Mercury salts were given extensive phase studies in the hope of finding some combination of reagents capable of absorbing olefins reversibly. Mercuric sulfate, with the high concentration of sulfuric acid necessary to prevent hydrolysis, serves as a reagent for gas analysis (*24*). It absorbs large quantities of olefin gases; and has complete irreversibility, contrary to definite statements (*3, 4, 26*)—

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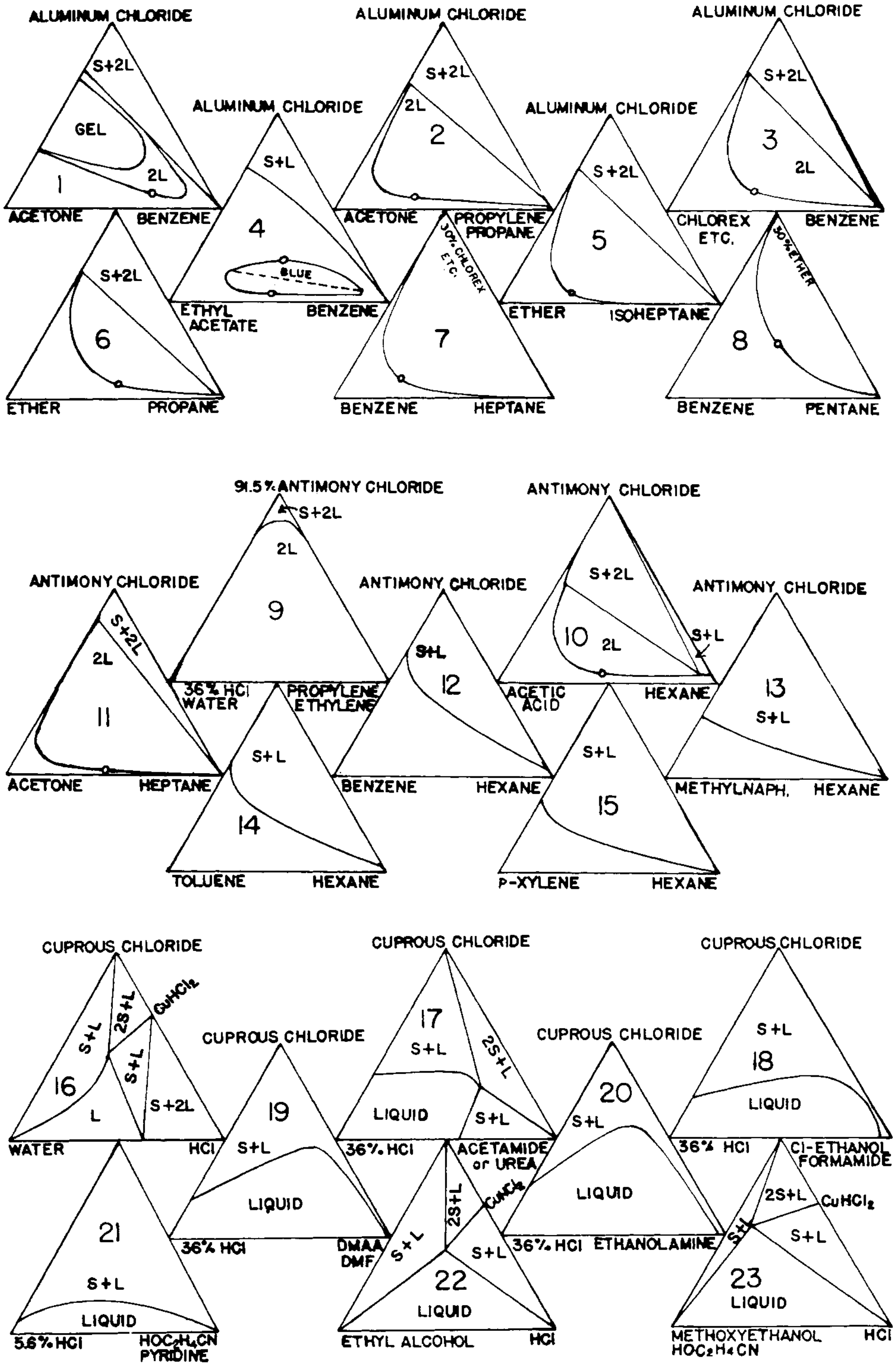

Figure 1. Ternary systems of chlorine compounds

In graphs 1 to 36 the top corner indicates the primary component shown in the top line of each group: aluminum chloride (graphs 1 to 8), antimony chloride (graphs 9 to 15), cuprous chloride (graphs 16 to 23), and hydrogen chloride (graphs 24 to 36). However, graphs 7 and 8 are quaternary. In the former the top corner contains 30% diluent, or more properly activating solvent, which may be Chlorex, ethyl acetate, ethyl ether, ethyl formate, methyl acetate, methyl ether, or methyl formate. In graph 8 the diluent is 30% ether. In graph 37 the top corner is the cosolvent named on each curve.

The other components in these graphs, and all in the last 43 graphs, are named at the appropriate corner, except that the lower left corner in graph 3 may be any one of the components mentioned above as diluents for aluminum chloride (seven different systems). Multiple designation applies also to the top corners of graphs 62 and 63, and the lower right corner of graph 64. Graphs 9, 17 to 20, 35, 36 with "36% HCl," and graph 21 with "5.6% HCl" are quaternary. Two components named

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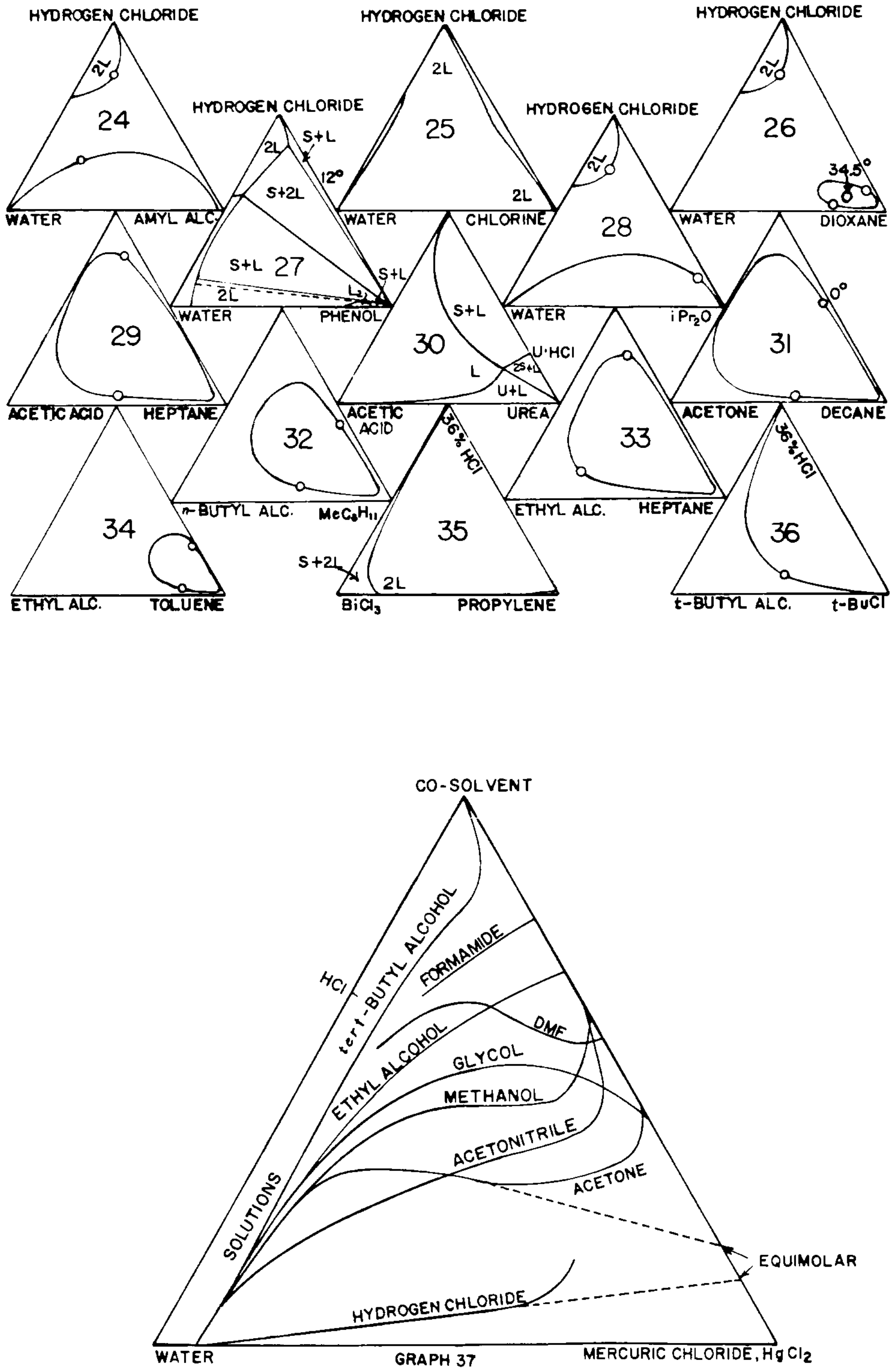

Figure 1. Ternary systems of chlorine compounds *(Continued)*

at the same corner without a plus sign (graphs 2, 9, 17, 18, 19, 21, 23, and 64) are alternative, and therefore indicate different systems.

The temperature in all graphs is 25° except where indicated otherwise above the right side line (graphs 27, 31, 51, 53, 60 to 64, and 69) or on a curve (graph 73). In some of these the purpose of the higher temperature was to avoid the complication of solid maleic or chloromaleic anhydride. In graph 69, the low temperature was used to locate the binodal curve. Plait points are indicated by small circles on the binodal curves.

A dashed tie line (graphs 4, 27, 38, 39, 41, 42, 43, and 47) shows an isopycnic or equilibrium between two liquid phases of equal density (6). A tie line marked with a color (graphs 4, 54, 55, and 56) shows iso-optics or equilibria between phases with equal refractive indices, and giving colored emulsions of the color mentioned (6). Other tie lines are omitted to avoid confusion.

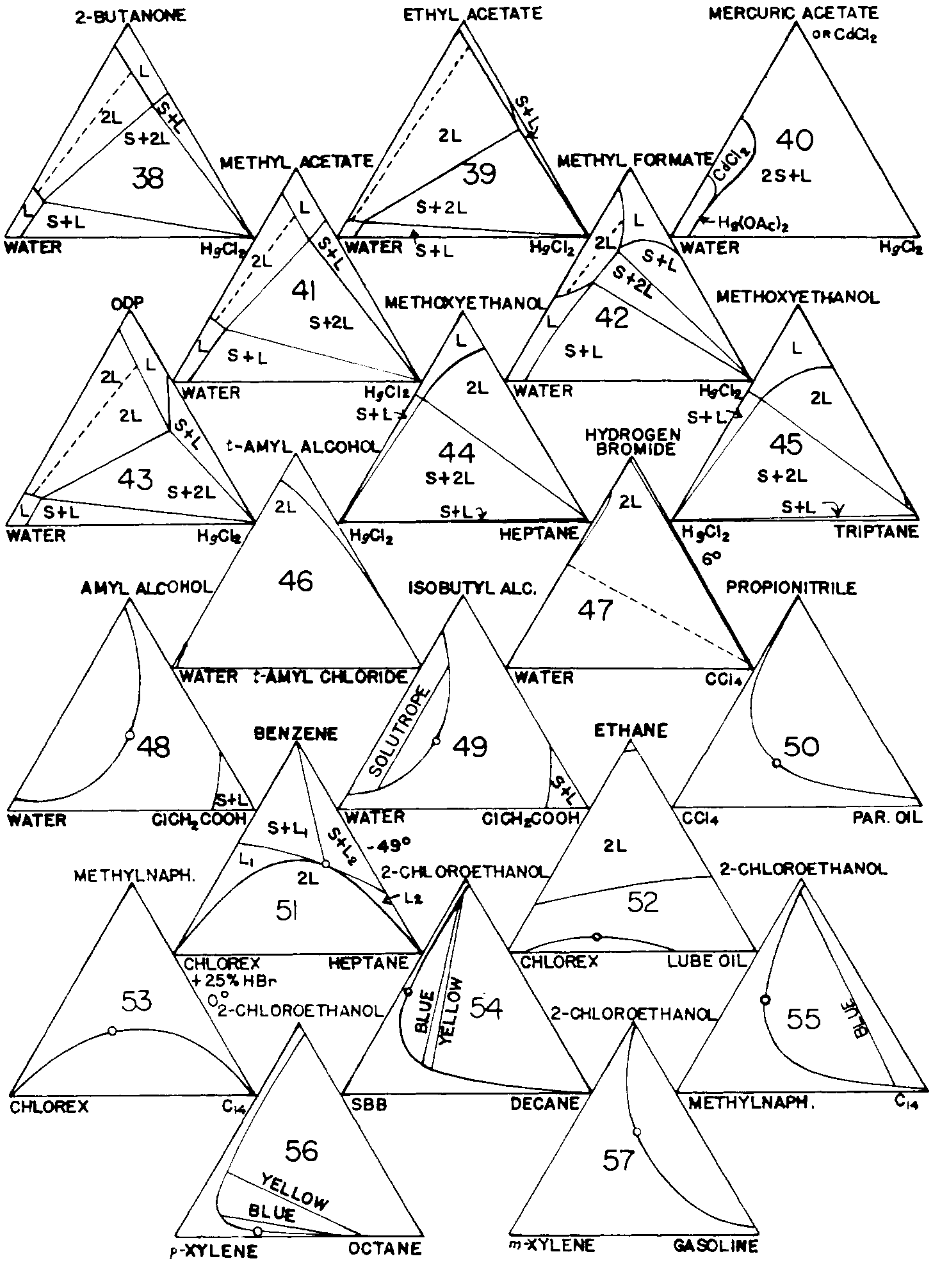

Figure 1. Ternary systems of chlorine compounds *(Continued)*

Abbreviation	Name	Graph
ALC	Alcohol	24, 32, 33, 34, 36, 49
ANH	Anhydride	61 to 64
AROM. OIL	Aromatic lubricating oil (8 or 9, Table I)	65, 70, 74, 76
t-BuCl	*tert*-Butyl chloride	36
C_{14}	*n*-Tetradecane	53, 55, 66, 69
CHLOREX	2,2′-Dichloroethyl ether	3, 7, 51, 52,53
$ClCH_2COOH$	Chloroacetic acid	48, 49
Cl-ETHANOL	2-Chloroethanol	18
$CuHCl_2$	Cuprous hydrogen chloride	16, 22, 23
DMAA	Dimethylacetamide	19
DMF	Dimethylformamide	19, 37
2,4-DMP	2,4-Dimethylpentane	58
DSBB	Di-sec-butylbenzene	64
ETHER	Ethyl ether	5, 6, 8
FREON 114	$C_2Cl_2F_4$	73

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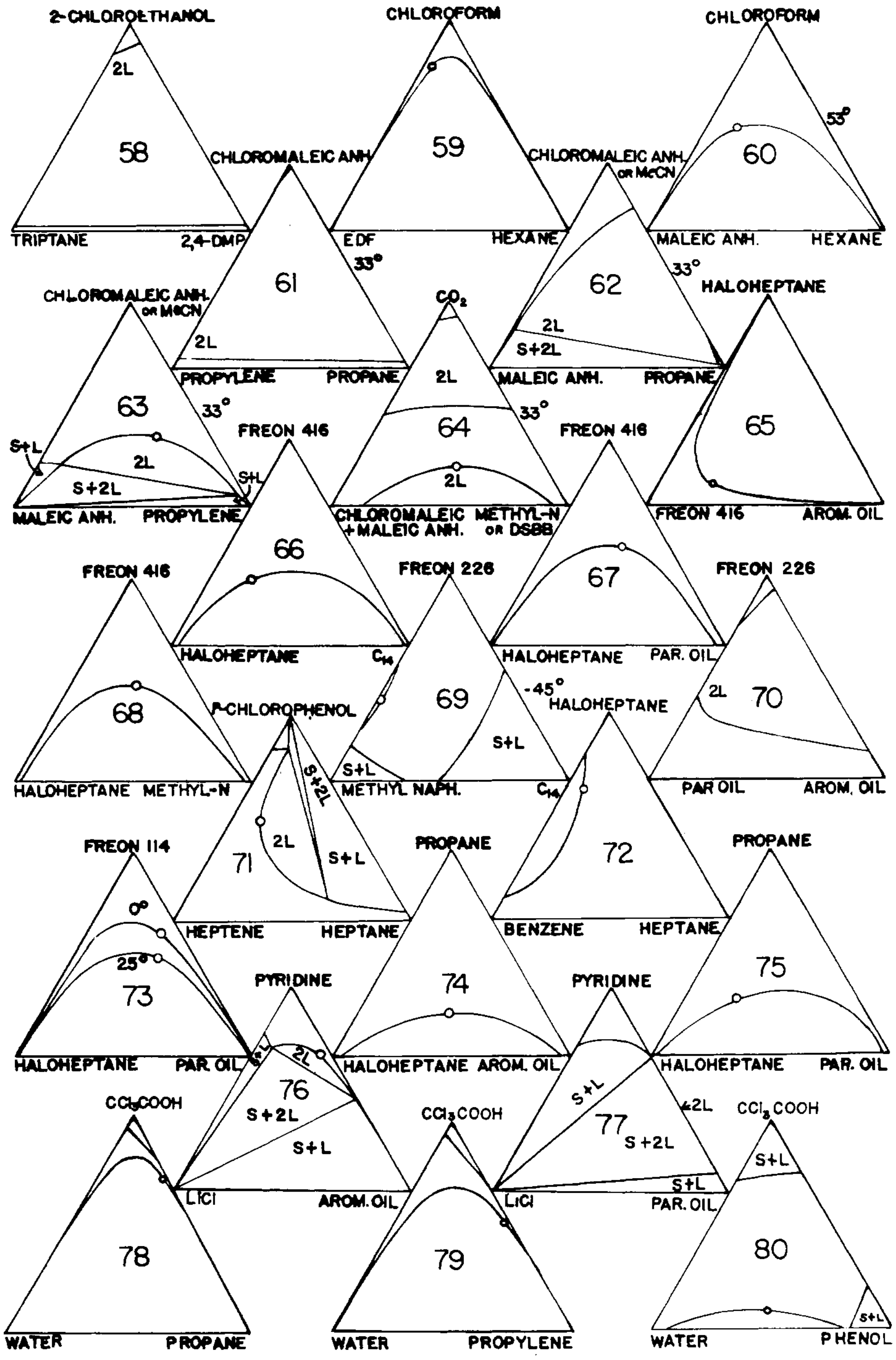

Figure 1. Ternary systems of chlorine compounds *(Continued)*

Abbreviation	Name	Graph
FREON 226	C_3HClF_6	69, 70
FREON 416	$C_5Cl_2F_6$	65–68
GASOLINE	(An. pt 30% str. run)	57
HALOHEPTANE	Perfluorochloroheptane (approx. 10% Cl	65–68, 72–75
HCl	Anhydrous hydrogen chloride	16, 22, 23
36% HCl	Concentrated hydrochloric acid	9, 17–20
HOC_2H_4CN	2-Hydroxypropionitrile	21, 23
iPr_2O	Isopropyl ether	28
METHYL-N or METHYLNAP	1-Methylnaphthalene	13, 53, 55, 64, 68, 69
ODP	2,2′-Oxydipropionitrile	43
PAR, OIL	Paraffinic lube oil (8 or 9, Table I)	50, 67, 70, 73, 75, 77
SBB	sec-Butylbenzene	54
TRIPTANE	Trimethylbutane	45, 58
U· HCl	Urea hydrochloride	30

e.g., "There seems to be no doubt that the reaction is reversible..." (*2*). Reduction in pressure causes no evolution of gaseous olefins; nor does heating, unless it is sufficient to destroy the reagent. Addition of hydrochloric acid or of a soluble chloride evolves the olefin but the reagent no longer will absorb olefins.

The same statements apply to mercuric or mercurous nitrates, whose solutions also require strong acidification with nitric acid to prevent hydrolysis. In these cases the mixture with olefins becomes mildly explosive (a fizz instead of a bang unless confined).

Neutral mercuric acetate also absorbs olefins. No water is required, since propylene reacts with anhydrous crystalline mercuric acetate to form a liquid complex (*7*). Unlike the silver nitrate complex (*7*) (also anhydrous), neither this mercury acetate complex nor the solutions of propylene in aqueous mercuric acetate evolve propylene upon release of pressure or upon warming. They do so on addition of hydrochloric acid; but this changes the reagent to mercuric chloride, so that it no longer absorbs olefins. Upon heating, or upon standing for several days, the mercury solutions containing olefins deposit heavy sludge.

Table I. Ternary Graphs of Chlorine Compounds (*8* to *15*) (not including Compilation, *18*)

Chlorine Compound	Reference	Another Component	Graphs
Aluminum chloride	(*8*)	Sulfur dioxide	20, 21, 22
	(*9*)	Acetonitrile	18
	(*13*)	Nitrobenzene	7
n-Amyl chloride	(*15*)	*tert*-Butyl alcohol	51
tert-Amyl chloride	(*15*)	Alcohols	52, 59, 60
Antimony chloride	(*8*)	Sulfur dioxide	63
	(*9*)	Acetonitrile	100
	(*12*)	Methanol	20, 21
Bismuth chloride	(*9*)	Acetonitrile	102
tert-Butyl chloride	(*13*)	Dinitrochlorobenzene	66
	(*14*)	Methyl sulfate	30
	(*15*)	Furfural	2
	(*15*)	*tert*-Butyl alcohol	54
Carbon tetrachloride	(*9*)	Acetonitrile	28, 35–41, 113
	(*10*)	Glycols	38, 69
	(*12*)	Methanol	29, 37, 120
Chlorex (2,2′-Dichoroethyl ether)	(*10*)	Glycol	18
	(*11*)	Ammonia	14
	(*12*)	Methanol	38, 39, 53
	(*13*)	Nitrobenzene	10, 11
	(*13*)	*o*-Nitrobiphenyl	58
Chloroacetic acid	(*13*)	Nitrobenzene	1
2-Chloroethanol	(*13*)	Nitrobenzene	2, 12
Chloroform	(*9*)	Acetonitrile	42
	(*10*)	Diethylene glycol	38
	(*12*)	Methanol	121
	(*14*)	Methyl sulfate	32
	(*15*)	Furfural	2
Chlorosulfonic acid	(*14*)	Hydrogen chloride	27, 28
	(*14*)	Ethyl sulfate	55
	(*14*)	Acetic acid	69
Cuprous chloride	(*12*)	Methanol	40–45
Dinitrochlorobenzene	(*12*)	Methanol	49, 50
	(*13*)	Hydrocarbons	66, 67, 68
Ferric chloride	(*8*)	Sulfur dioxide	34
Freon 12 (CCl_2F_2)	(*13*)	*o*-Nitrobiphenyl	60
	(*15*)	Furfural	5
Freon 114 $(CClF_2)_2$	(*8*)	Sulfur dioxide	43
	(*15*)	Furfural	6, 7, 23
Freon 316 ($C_4Cl_2F_6$)	(*15*)	Furfural	8, 9
Haloheptane (C_7ClF_{15})	(*9*)	Acetonitrile	72
Hydrogen chloride	(*8*)	Sulfur dioxide	8
	(*9*)	Acetonitrile	2, 13, 14, 59, 73, 74, 102, 116, 117
	(*12*)	Methanol	6–9, 40–45, 60–62
	(*13*)	Nitromethane	29
	(*14*)	Sulfur trioxide	27, 28
	(*15*)	Alcohols	57, 61
Lithium chloride	(*12*)	Methanol	43, 64, 65
Mercuric chloride	(*9*)	Acetonitrile	8, 60, 127, 128
	(*10*)	Glycol	3, 6, 20
	(*12*)	Methanol	9
Sodium chloride	(*8*)	Sulfur dioxide	15
	(*15*)	Isopropyl alcohol	40
Stannous chloride	(*9*)	Acetonitrile	116, 117
Trichloroacetic acid	(*12*)	Methanol	107
Triethylchlorobenzene	(*9*)	Acetonitrile	16
Zinc chloride	(*8*)	Sulfur dioxide	19

By contrast with mercury solutions, concentrated silver nitrate solutions, even 71% in water, are unsatisfactory for determination of gaseous olefins, though dissolving large volumes, because the absorption is reversible. Even after 6 months' residence in this solvent, propylene is evolved almost completely when swept with several volumes of air.

At room temperature the solubility of mercuric chloride in water is only 7%; but it is increased greatly, up to 60% (of the solution) with certain chlorides. Aqueous hydrochloric acid and sodium chloride are most efficient for this purpose (*27*). The solubility is increased to about the same extent with acetone, and nearly as much with methanol (*27*) and other organic solvents even under anhydrous conditions.

Systems of mercuric chloride with water-miscible liquids are shown for mutual comparison in graph 37. Those of methanol, ethyl alcohol, and hydrogen chloride are plotted from published data (*27*, pp. 622, 628, 629) (confirmed in this investigation). For hydrogen chloride a curve (not observed and not shown) is postulated across the other curves to the point spotted on the left side line, about 64% HCl, for solubility of liquid hydrogen chloride in water. No midget binodal curve similar to those in graph 24, 26, or 28 is shown or expected, since mercuric chloride is probably insoluble in hydrogen chloride. It is practically insoluble in *tert*-butyl alcohol.

The curve for mercuric chloride with acetonitrile has been presented previously (*9*, graph 8). Its reverse curvature and those for methanol, acetone, dimethylformamide, and *tert*-butyl alcohol are noted. There is no indication of a reverse curvature (lower solubility of mercuric chloride in anhydrous solvent than in the same solvent slightly diluted with water) for ethyl alcohol, ethylene glycol, or formamide, nor in the curve for glycerol (*27*, p. 630, not shown), which would be slightly above the curve for ethylene glycol.

The straighter portions of the acetone and hydrogen chloride curves, extrapolated to the right side line (anhydrous composition), shown with dashed lines, give points corresponding to equimolar composition for the binary system. This may be fortuitous. "Solutions" on graph 37 means single liquid phases. Compositions below or to the right of any curve indicate equilibrium with anhydrous crystalline mercuric chloride. Tie lines would all radiate from the mercuric chloride corner.

Systems of mercuric chloride, water, and nonmiscible solvents are presented in graphs 38, 39, 41, 42, and 43. Each has an area indicating crystals and two liquid phases. Data for the ethyl acetate system (graph 39) are given in part by Seidell (*27*, p. 629), but do not include the isopycnic. This system and that of 2,2′-oxydipropionitrile (graph 43) indicate considerable enhancement in solubility of mercuric chloride by the presence of increased amounts of water in the solvent; but the methyl formate system (graph 42) shows the opposite effects.

The system of graph 40 was disappointing in that, like other chlorides, mercuric chloride inhibits absorption of olefins by mercuric acetate. Solutions of mercuric chloride in methoxyethanol (graphs 44 and 45) show moderate selectivity for triptane over *n*-heptane. When liquid propylene was added to a heavy suspension of mercurous chloride (insoluble) in water, a considerable portion of the propylene layer seemed to be absorbed by the white suspension. However, this was a false impression. Just as large a volume of liquid propane seemed to be absorbed when treated similarly. Apparently the liquefied gases collect in the spaces between the suspended particles without dissolving, and completely unselectively. Graphs 76 and 77 exploit the high solubility of lithium chloride in pyridine to diminish its excessive miscibility with lubricating oil, thus making its selectivity operable (*20*).

ORGANIC CHLORINE COMPOUNDS

Two systems (graphs 52 and 64) have both a band and a bite type of binodal curve. They are due to the proximity of the isotherm to the critical temperatures of the carbon dioxide (*16*) and of the ethane. Other graphs (46 to 75) in this category are normal, allowing for solid phases, isopycnics, and iso-optics. Locations of 121 published graphs are listed in Table I. "Another Component" lists the more pertinent one. In most cases the third component is a hydrocarbon.

LITERATURE CITED

(1) Campbell, D. E., Laurene, A. H., Clark, H. M., *J. Am. Chem. Soc.* **74**, 6193 (1952).
(2) Chatt, J., *Chem. Revs.* **48**, 32 (1951).
(3) Curme, G. C., U. S. Patent **1,315,541** (Sept. 9, 1919).
(4) Ellis, C., "Chemistry of Petroleum Derivatives," pp. 142, 582, Chemical Catalog Co., New York, 1934.
(5) Francis, A. W., *Ind. Eng. Chem.* **42**, 342 (1950).
(6) *Ibid.*, **45**, 2789 (1953).
(7) Francis, A. W., *J. Am. Chem. Soc.* **73**, 3709 (1951).
(8) Francis, A. W., J. Chem. Eng. Data **10**, 45 (1965).
(9) *Ibid.*, p. 145.
(10) *Ibid.*, p. 260.
(11) *Ibid.*, p. 327.
(12) *Ibid.*, **11**, 96 (1966).
(13) *Ibid.*, p. 234.
(14) *Ibid.*, p. 557.
(15) *Ibid.*, **12**, 262 (1967).
(16) Francis, A. W., *J. Phys. Chem.* **58**, 1099 (1954).
(17) *Ibid.*, **62**, 579 (1958).
(18) Francis, A. W., "Liquid-Liquid Equilibriums," Wiley, New York, 1963.
(19) Francis, A. W., in "Solubilities of Inorganic and Organic Compounds," A. Seidell and W. F. Linke, Eds., Supplement to 3rd ed., Van Nostrand, Princeton, N. J., 1952.
(20) Francis, A. W., U. S. Patent **2,133,691** (Oct. 18, 1938).
(21) *Ibid.*, **2,368,653** (Feb. 6, 1945).
(22) *Ibid.*, **2,735,878** (Feb. 21, 1956).
(23) Francis, A. W., James, W. H., *Ibid.*, **2,389,250** (Nov. 20, 1945).
(24) Francis, A. W., Lukasiewicz, S. J., *Ind. Eng. Chem., Anal. Ed.* **17**, 703 (1945).
(25) Francis, A. W., Reid, E. R., U. S. Patent **2,445,520** (July 20, 1948).
(26) Keller, R. N., *Chem. Revs.* **28**, 245 (1941).
(27) Seidell, A., "Solubilities of Inorganic and Metal Organic Compounds," Vol. **I**, pp. 622-38, Van Nostrand, Princeton, N. J., 1940.

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