Ternary Systems of Nitro Compounds

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New experimental graphs are reported for 34 ternary and two quaternary systems of nitrobenzene, 31 ternary systems of nitromethane, 13 of other nitrohydrocarbons, and six systems of nitro nonhydrocarbons. They include four examples of graphs with two separate binodal curves, five with isopycnics, four with iso-optics, 13 systems with compositions showing two liquid phases and a solid, and two with three liquid phases; but apparently only one example of a solutrope. No new systems with island curves are reported. Nitrobenzene is one of a few liquids capable of diluting sulfuric acid without appreciable evolution of heat and without drastic changes in solubility of additional components. It is not satisfactory for mixtures with aluminum chloride in molar excess, or with oleum.

IN THE EARLY DAYS of solvent extraction of lubricating oils, nitrobenzene was one of the most widely used solvents. It is highly selective for aromatic hydrocarbons in preference to nonaromatic hydrocarbons in the lubricating oil range. Nitrobenzene was chosen by comprehensive observations of critical solution temperatures (CST) with two or more typical oil stocks (*1*), using many solvents. Its selectivity for types of oils is shown in graphs 76, 78, and 79 of Reference (*10*). Nitrobenzene is used less extensively now because of certain deficiencies. One is excessive miscibility at plant temperatures with all but highly paraffinic oils. Its high boiling point, 210° C., introduces a difficulty in recovery, especially with the lower boiling oils.

CST's of nitrobenzene with 46 individual hydrocarbons and 21 nonhydrocarbons (including some with > or < signs) have been compiled (*2*, pp. 129–130; *13* p. 213). About 40 ternary systems have been listed (*13*, p. 174). These include six systems with two separate binodal curves (*5*), a phenomenon which was very unusual at the time, but is now common.

Thanks largely to Mulliken and Wakeman (*19*), about 180 CST's have been observed for nitromethane (*2*, pp. 134–137), more than for any substance except aniline, water, and furfural. However, only about 25 ternary systems which include nitromethane are published (compiled in *13*, pp. 174, 214). These include two systems with three separate binodal curves each (*12*), the first published in that category. Nitromethane is very selective, and is reasonably safe as a laboratory reagent, but probably would be considered less suitable as a large scale industrial solvent because of its explosive characteristics (*18*).

As do other nitrohydrocarbons, nitroethane and *o*-nitrobiphenyl (ONBP) have a tendency to show separate binodal curves. Nitroethane shows three of them in each of two different systems (*12*), and Vreeland and Dunlop (*20*) remarked on the formation of three liquid phases in a system in which two of the components are miscible. ONBP shows two separate curves with methanol and a nonaromatic hydrocarbon (*10*, graphs 84, 85). Eight other of its ternary systems have been presented (*7*, graphs 10, 84); (*8*, graphs 43, 56); (*10*, graphs 82, 83, 86, 87). It is highly selective for aromatic hydrocarbons, probably more so than nitrobenzene; but not enough so to justify the awkward operation required by its high melting and boiling points—37° and 320° C. A cosolvent such as methanol (*10*), is needed to re-extract the solvent from the oil.

This paper presents 36 new systems of nitrobenzene, 31 of nitromethane, 10 of *o*-nitrobiphenyl, two of nitroethane, one of *o*-nitrotoluene (six systems are in two categories), and seven other systems of nitro compounds.

EXPERIMENTAL

As in the paper on systems of acetonitrile (*7*), glycols (*8*), and methanol (*10*), known mixtures of two miscible components were titrated with the third until the appearance of another liquid phase at the selected temperature; or two not miscible components were titrated to a single phase, using in each case reagents of the highest grade available. Nine systems involving liquefied gases, (graphs 23 to 28, 60) required the titration in a sealed tube as in References (*6*, *9*). Investigation of the three systems in graphs 16 and 29 required use of a visual autocalve (*11*).

DISCUSSION

Graphs 6, 10, and 11 have two separate binodal curves. They were all tabulated (*5*), but no graphs were presented. On cooling the systems, these curves meet at their plait points (graph 10) indicated by plus signs in graphs 6 and 11 (at lower temperatures). The curves in the Chlorex systems are extremely sensitive to temperature. Graph 16 also shows two separate binodal curves resembling those occurring frequently in carbon dioxide systems (*11*). Graph 29 shows a band, presumably resulting from the merger of two separate binodal curves. It resembles graphs 7 and 8 of sulfur dioxide systems (*6*). Graph 7 shows the high solubility of aluminum chloride, about 70% (*3*, *15*, *17*) as with some other oxygen containing solvents such as ether, ethyl acetate, acetone, and sulfur dioxide (*6*). Solutions of aluminum chloride in excess in nitrobenzene become explosive when heated (*3*).

Graphs 25 and 56 have areas indicating three liquid phases. The peculiar relations are due in part to the fourth component, water, and glycol, respectively. Graphs 7, 15, 22, 28, 49, 57, 60, 61, 62, 66, 69, 73, and 74 have areas with three phases, one of which is a solid. No island curves were noted among the systems of nitro compounds.

As indicated in graph 26, sulfuric acid reacts with the olefin, so that the curve is approximate. It could not be observed at all, except for the moderating effect of nitrobenzene. This is one of a few organic compounds which mixes completely with high concentrations of sulfuric acid, with negligible heat evolution, and so acts as a true diluent. In contrast with water and alcohols, it only modifies the sulfating activity of the acid, permitting its use as a selective physical solvent for olefins (*16*). On the other hand, nitrobenzene is not useful in controlling the activity of oleum, as are sulfur dioxide (*6*), and alkyl sulfates, because it is itself sulfonated by oleum. This will be discussed in a later paper.

The system of graph 74 lacks a real plait point, which is submerged below the equilibrium with picric acid. The dashed metastable lines shown are schematic. Graph 72 exemplifies the analysis of butane isomers by linear interpolation of critical solution temperatures with *o*-nitrotoluene (*4*, *14*).

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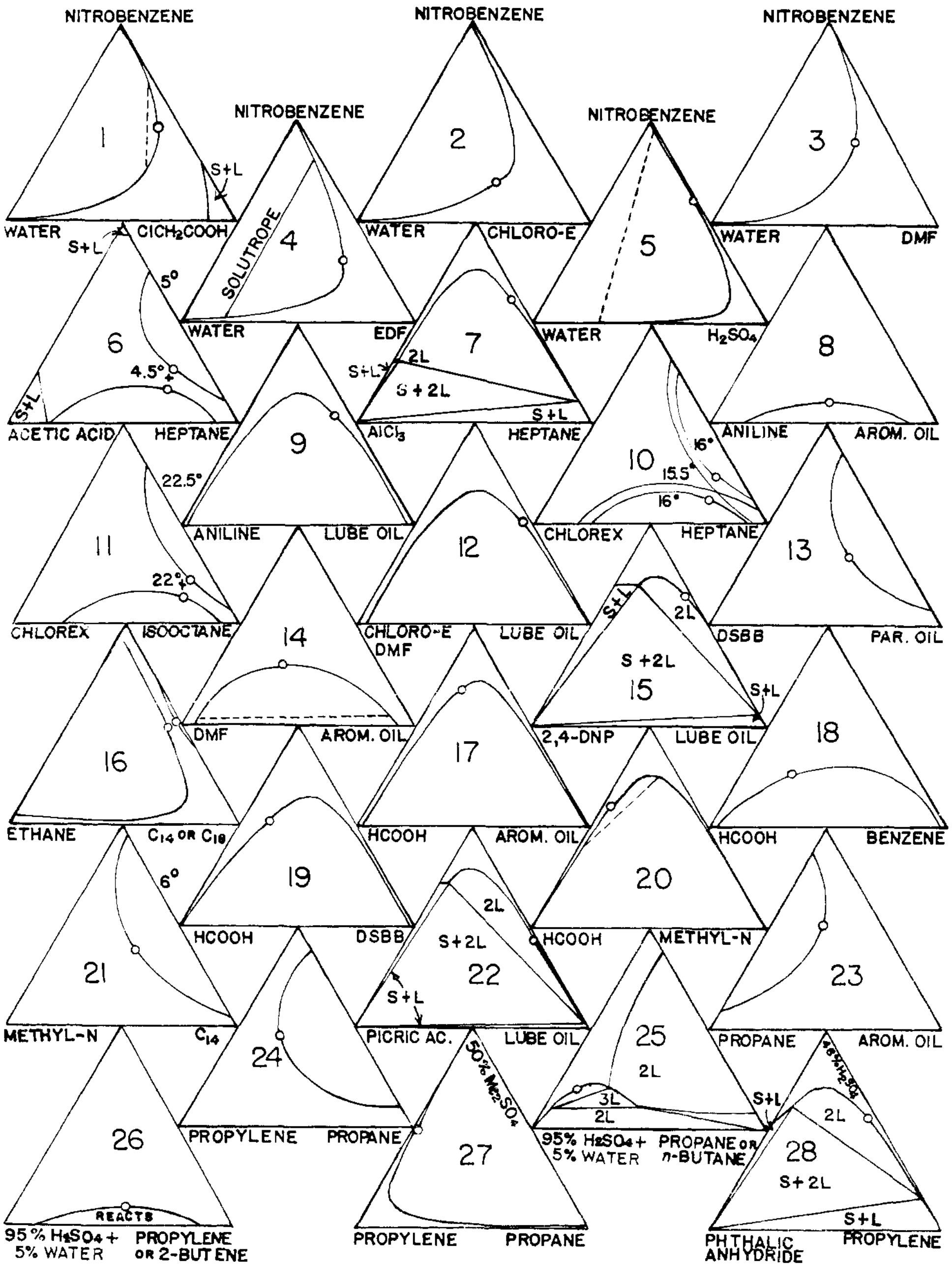

Figure 1. Ternary system of nitrobenzene (graphs 1 to 28)

Eighty-three systems are presented on 74 independent graphs on three figures. As indicated by headings, the top corner on each graph of Figure 1 is nitrobenzene, that in Figure 2 is nitromethane, and that in graphs 57 to 65 of Figure 3 is o-nitrobiphenyl. These are pure except in graphs 27, 28, 56, in which the cosolvent is indicated inside the top corner; and in graph 63 in which it is 33% *m*-dinitrobenzene; and in graph 64 in which it is 65% 2,4-dinitrochlorobenzene. Top corners in graphs 66 to 74 are named individually and arranged alphabetically. Other components are indicated by names, formulas, or abbreviations under the appropriate corner. Two or more names in the same location—graphs 12, 16, 25, 26, 33, 40, 41, 57, 69—indicate alternative components giving graphs so similar that the precision of drawing would not distinguish between them. Thus there are presented 83 actual systems. The arrangement is alphabetical in each group according to left hand component except that aqueous systems are first (and in graph 65, added later).

Circles on binodal curves are plait points.

Straight dashed lines on graphs 1, 5, 14, 20, and 37 indicate isopycnics or tie lines connecting compositions having equal densities. Tie lines marked with colors—graphs 44, 56, 70, and 71—are iso-optics, connecting compositions having equal refractive indices. Compositions on these lines show the structural color named, and those near them, some other color. A solutrope is marked in graph 4. Other tie lines are omitted to avoid confusion, since they can be approximated readily from the positions of the plait points.

All isotherms are at 25° C. except those indicated otherwise by temperatures above the right side line—graphs 6, 11, 21, 31, 52, 55, 58, 63, 64, 67, and 68,—or with a curve—graphs 10 and 43.

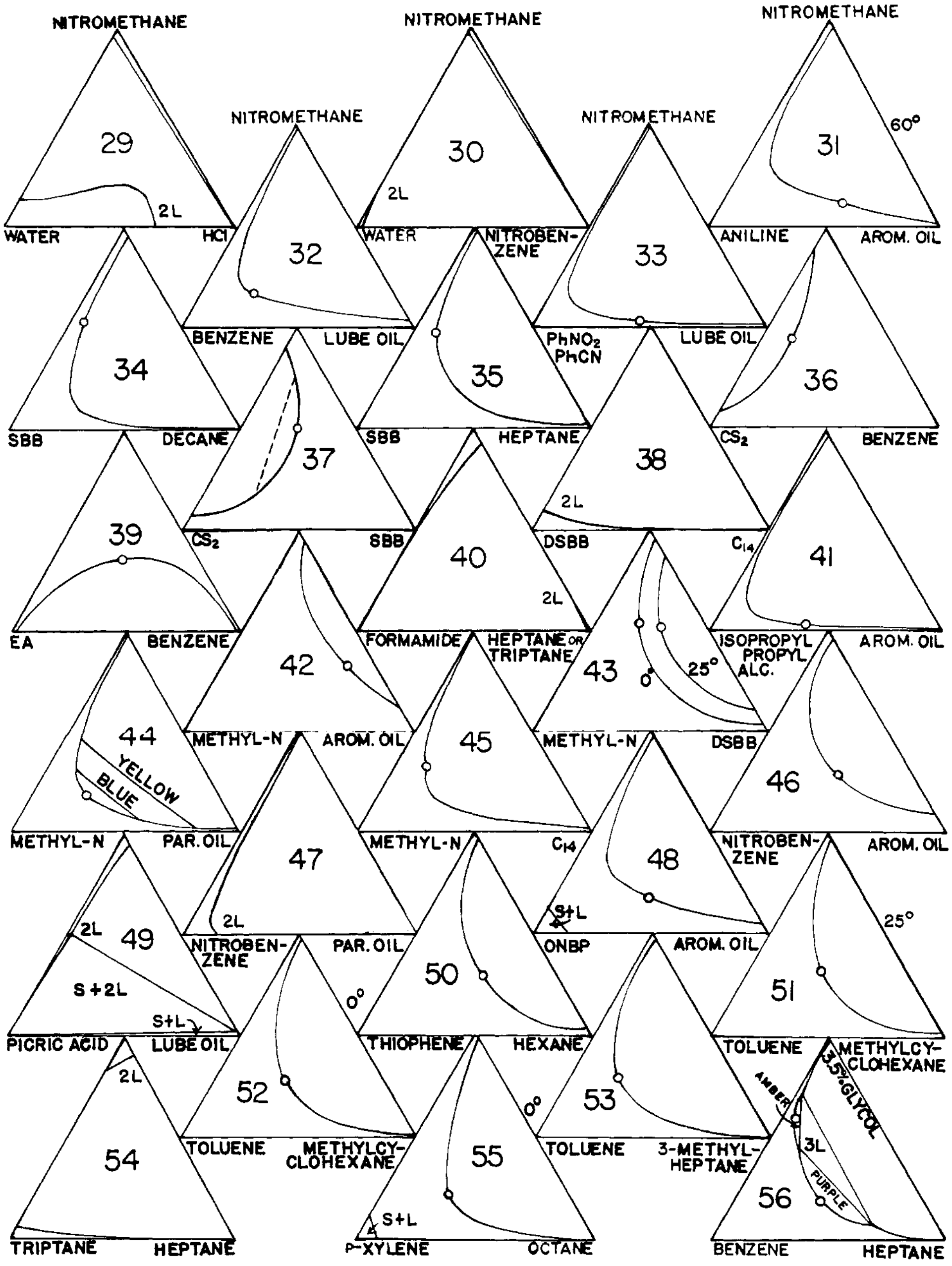

Figure 2. Ternary systems of nitromethane (graphs 29 to 56)

Abbreviation	Name	Graphs
AC	Acid	22
ALC	Alcohol	41
AROM. OIL	Aromatic lubricating oil (see 6, or 7, Table I)	8, 14, 17, 23, 31, 41, 42, 46
tert-BuCl	*tert*-Butyl chloride	66
C_{14}	*n*-Tetradecane	16, 21, 38, 45, 62, 63, 67, 71
C'_{18}	*n*-Octadecane	16
CETANE	*n*-Hexadecone	64
CHLOREX	2,2'-Dichloroethyl ether	10, 11, 58
CHLORO-E	2-Chloroethanol	2, 12
DMF	Dimethylformamide	3, 12, 14
DNCB	2,4-Dinitrochlorobenzene	66, 67, 68
2,4-DNP	2,4-Dinitrophenol	15
DSBB	*m*-Di-sec-butylbenzene	13, 19, 38, 43, 59, 63, 64
EA	Ethanolamine	39
EDF	Ethylene diformate	4
Freon 12	Dichlorodifluoromethane, CCl_2F_2	60

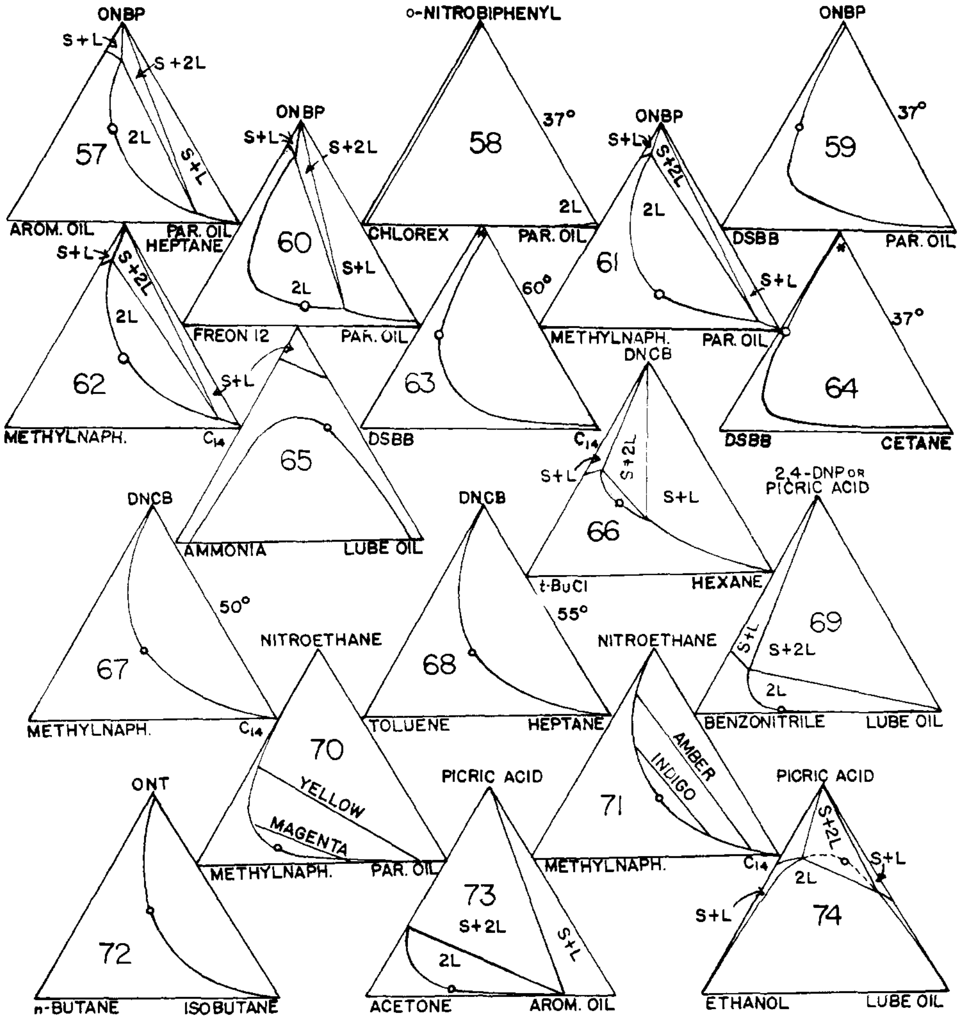

Figure 3. Ternary systems of o-nitrobiphenyl (graphs 57 to 65) and other nitro compounds (graphs 66 to 74)

Abbreviation	Name	Graphs
GLYCOL	Ethylene glycol	56
HCl	Anhydrous Hydrogen chloride	29
ISOOCTANE	2,2,4-Trimethylpentane	11
LUBE OIL	a Typical clean lubricating oil (see 6 or 7, Table I)	9, 12, 15, 22, 32, 33, 49, 65, 69, 74
METHYL-N or METHYLNAPH.	1-Methylnaphthalene	20, 21, 42, 43, 44, 45, 61, 62, 67, 70, 71
ONBP	o-Nitrobiphenyl	48, 57, 59, 60, 61
PAR. OIL	Paraffinic lubricating oil (see 6 or 7, Table I)	13, 44, 47, 57, 58, 59, 60, 61, 70
SBB	sec-Butylbenzene	34, 35, 37
TRIPTANE	Trimethylbutane	40, 54

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