$\bar{V}_1$ = partial specific volume of solvent (water), cm.^{3}/gram
W = molecular weight of water
Z = ionic charge
S = Debye-Hückel limiting slope for an ionic mixture
S_1 = Debye-Hückel limiting slope for a 1-1 electrolyte
$\left.\begin{matrix}\alpha\\ \gamma\end{matrix}\right\}$ = coefficients in expression of partial specific volume of water *vs.* wt. % salt (Equation 19)
Δ = change in a quantity, e.g., ΔG = change in the Gibbs free energy
ΔC_p = change in heat capacity between that at an arbitrary concentration and that in the standard state
κa = expression involving concentration in the Debye-Hückel equation, here set equal to $1.5\ (I)^{1/2}$
Π = osmotic pressure, atm.
ρ = density of water, gram/cm^3.

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Ternary Systems of Glycols

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This paper presents experimental graphs for 33 new ternary or quaternary systems of ethylene glycol, 13 for diethylene glycol, 16 for triethylene glycol, and four involving higher glycols. Some show unusual types; and certain requirements for three separate binodal curves are discussed. A novel concept of "shadow graphs" is applied to triangular graphs showing three components completely miscible and a fourth practically immiscible with the other three.

ETHYLENE GLYCOL is not usually suitable as a single solvent for separation of hydrocarbons because of its low miscibilities with all hydrocarbons, even the most aromatic. However, its complete miscibility with water and with many alcohols and some other organic compounds makes it unique in some solubility relations. It is a convenient and higher boiling substitute for water as a diluent for certain solvents. For some of these—e.g., sulfur dioxide—it is better, because it mixes while water does not mix (*3, 10*).

About 135 critical solution temperatures (CST) (some with > or < signs) have been compiled (*1*, pp. 87-9; *8*, pp. 225-61). Published ternary systems involving ethylene glycol include 26 aqueous and about 61 nonaqueous systems (*3*, graphs 29 to 33, 62, 64, 66; *4*, graphs 55 to 62; *8*, pp. 155-6, 205; *9*, pp. 941, 1078-83, 1117).

Diethylene glycol dissolves somewhat larger volumes of hydrocarbons, and at elevated temperatures is considered very selective as to type. It is a favorite solvent (Udex process) because of convenient adjustment of solubility with temperature and water concentration (*12, 13*, and numerous technical papers). CST with 39 hydrocarbons and 14 nonhydrocarbons are listed (*1*, pp. 70-1) for diethylene glycol; and about 16 ternary systems are published (*3*, graphs 2, 27, 28; *4*, graphs 30, 38, 49, 50, 51, 124; *8*, pp. 148, 203).

Triethylene glycol is one of the most selective water miscible solvents for hydrocarbons. CST have been observed for 34 hydrocarbons (*1*, pp. 174-5); and about 16 ternary systems have been published (*4*, graphs 96, 97; *8*, pp. 192, 220). Several systems of propylene glycol and 2,3-butene glycol also have been published (*3*, graph 2; *8*, pp. 137, 183, 217; *9*, pp. 1006-7, 1089).

This paper presents observations on 33 new ternary (or quaternary) systems of ethylene glycol, 13 of diethylene glycol, 16 of triethylene glycol, and four systems of other glycols (Figure 1). All are plotted in concise form as in previous papers (*3, 4, 7*) to save space.

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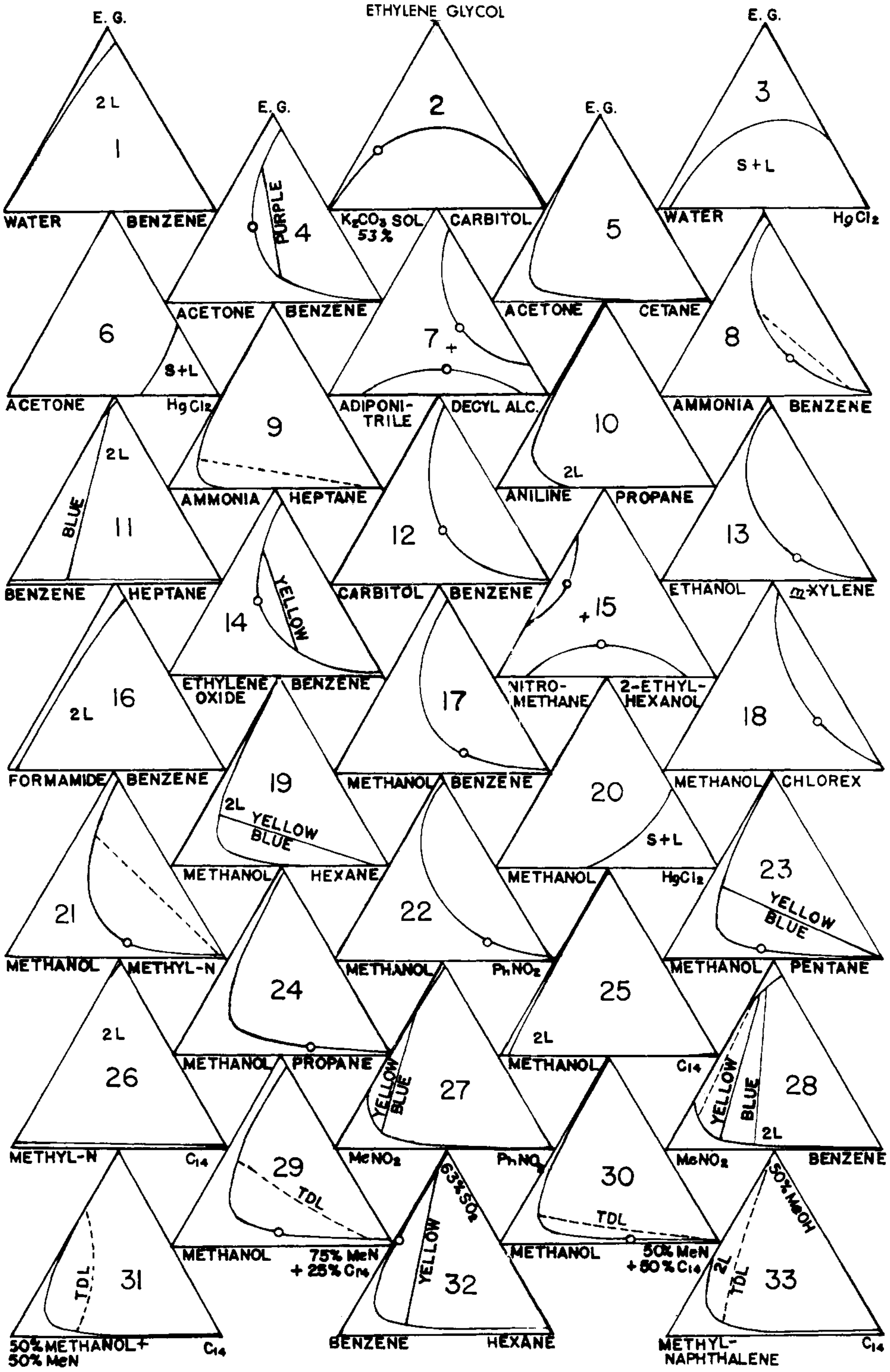

Figure 1. Systems of Glycols

Systems are presented on 70 independent triangular graphs. The top corner in the first 64 graphs is a glycol (pure except in graphs 32, 33, 46, 61) namely, ethylene glycol, graphs 1 to 33; diethylene glycol, graphs 34 to 46; and triethylene glycol, graphs 47 to 61, as indicated by headings. See text for discussion of graphs 65 to 70.

Circles on binodal curves are plait points. The temperature is 25° C. except where indicated otherwise in graphs 41, 59, and 65 to 68. Plots are in weight % in all graphs.

Straight dashed lines on graphs 8, 9, 21, 28, 35, 43, indicate isopycnics or tie lines connecting compositions in equilibrium having equal densities (2). Curved dashed lines, graphs 29, 30, 31, 33, and 54 are twin density lines, the loci of compositions in equilibrium having equal densities, but not uniform along the line because the system is quaternary.

Tie lines marked with a color (blue, purple, or yellow) graphs 4, 11, 14, 19, 23, 27, 28, 50 are iso-optics, connecting compositions with equal refractive indices, and exhibiting a structural color on shaking an emulsion anywhere along the line (*2, 4, 8,* pp. 46–9). The lines in graphs 32 and 46 are not rigorously straight, and are really twin index lines because the systems are quaternary.

Other components are indicated by names, formulas, or abbreviations *under* the appropriate corner. Two names under the same corner, (graphs 29, 30, 31, 60) with a plus sign indicate a mixture (% shown) forming a quaternary system.

(Continued)

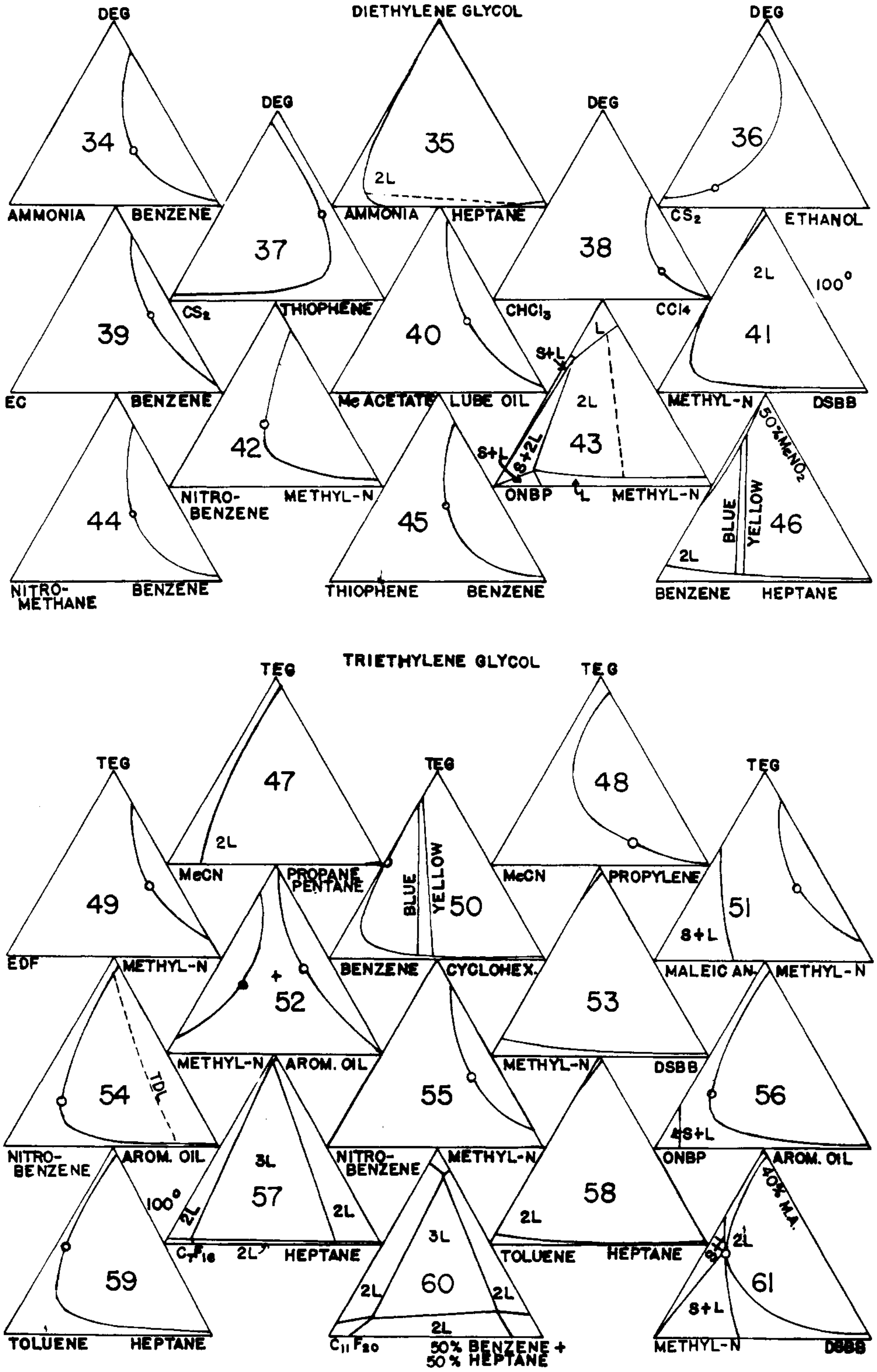

Figure 1. (*Continued*)

Such components are selected so as to minimize fuzziness (*8*, Chap. 8). Diluent in the glycol and its percentage is indicated by a note just inside the top corner, graphs 32, 33, 46, 61.

AROM OIL	An aromatic lubricating oil	52, 54, 56 (2, 3, Table I)
C_{14} '	*n*-Tetradecane	25, 26, 29, 30, 31, 33
C_7F_{16}	Perfluoro-*n*-heptane	57
$C_{11}F_{20}$	Perfluoromethylnaphthalene	60
CARBITOL	Diethylene glycol monoethyl ether	2, 12
CETANE	*n*-Hexadecane	5
CHLOREX	2,2′-Dichloroethyl ether	18
CYCLOHEX	Cyclohexane	50
DECYL ALC.	*n*-Decyl alcohol	7
DEG	Diethylene glycol	34, 36–38
DSBB	Di-sec-butylbenzene	41, 53, 61, 63

(*Continued*)

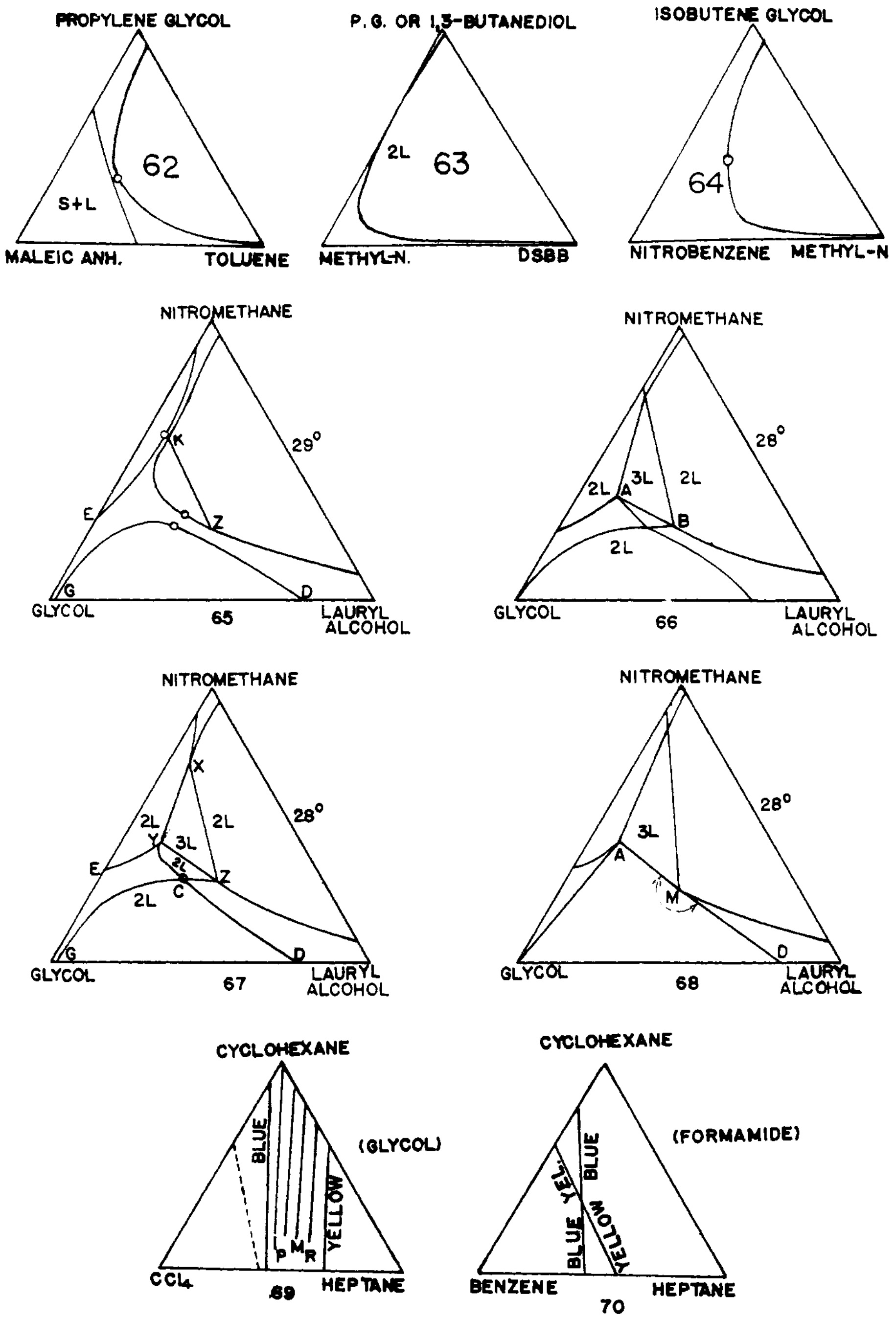

Figure 1. (*Continued*)

EC	Ethylene carbonate	39
EDF	Ethylene diformate	49
E.G.	Ethylene glycol	1, 3, 4, 5
ETHANOL	Ethyl alcohol	13, 36
GLYCOL	Ethylene glycol	65 to 69
K_2CO_3 SOL	Potassium carbonate solution	2
LUBE OIL	Lubricating oil	40(2, 3 Table I)
MALEIC AN(H)	Maleic anhydride	51, 62
MA		61
Me ACETATE	Methyl acetate	40
MeN	1-Methylnaphthalene	30, 31
MeOH	Methanol	33
METHYL-N	1-Methylnaphthalene	21, 26, 41, 42, 43, 49, 51, 52, 53, 55, 61, 63, 64
ONBP	o-Nitrobiphenyl	43, 56
P.G.	Propylene glycol	63
TEG	Triethylene glycol	47–51

In certain areas, L is a liquid phase, and S is a crystalline phase. 2L (two liquid phases) is usually omitted as obvious when there is a plait point.

EXPERIMENTAL

As in the paper on acetonitrile systems (*4*), known mixtures of two miscible components were titrated with the third until the appearance of another liquid phase at the temperature indicated; or two not miscible components were titrated to a single phase, using the best grades of chemicals available. Seven systems involving liquefied gases, graphs 8, 9, 10, 14, 34, 35, 47, and 48 required the titration in a sealed tube, as with the paper on sulfur dioxide systems (*3*), using a separate seal with each tentative observation.

DISCUSSION

Presentation of the graphs is explained in the legend. One graph, 43, is complicated by the presence of a solid phase with boundaries intersecting the binodal curve; and two other graphs, 57 and 60, by the presence of three liquid phases, indicated by an internal triangle. They illustrate an expedient (*11*) for simultaneous double extraction with two mutually immiscible solvents, one of which, triethylene glycol, selects the aromatic hydrocarbon over the nonaromatic, and the other solvent, the fluorocarbon, selects the nonaromatic hydrocarbon. Graphs 7, 15, and 52 each show two separate binodal curves. The plus sign indicates the position of the col (at a lower temperature) where the two curves meet at their plait points.

Most published systems with three separate binodal curves have as one component either carbon dioxide [21 systems (*6*,)] or ethylene glycol [five systems (*4*, graph 61; *7*)]. One such system published by the present author (*7*), involving nitromethane and lauryl alcohol, was confirmed closely by Markuzin and Nikanorova (*14*). They emphasized as had the present author (*7, 8*, pp. 72–6, and in many places) that such separate binodal curves, on merging during cooling to form a three-phase area, must obey Schreinemakers' rule (*15*). At each corner of the internal triangle indicating three phases, the extensions of both binary equilibrium curves must enter that area, or else cross each other at that point and enter different two-phase areas.

Markuzin and Nikanorova (*14*) confirmed graph 65, including the slight concavity near *K*, which is necessary to observe the rule. But in copying graph 67, which obeys the rule, they allowed it to appear as in graph 66, which would violate the rule at *A*, as do graphs in schematic illustrations in several physical chemical textbooks. A similar difficulty was encountered in Markuzin and Nikanorova's graph, shown as graph 68, which disobeys the rule at *M*. The angle *AMD* is greater than 180°, which is contrary to another phase diagram principle (arc shown).

Zhuravlev and Mel'nikova (*16*) presented an aqueous system with succinonitrile and *n*-butyl alcohol, also having three separate binodal curves over a considerable range of temperature, 16° to 55°. This is apparently the first aqueous system of this class.

The last two graphs, 69 and 70, have been called "shadow graphs." The three components shown on each triangle are miscible in all proportions so that there are no binodal curves or other phase boundaries or tie lines. The overshadowing component, ethylene glycol or formamide, is virtually immiscible with all mixtures of the other three components, giving a separate layer. The dashed, apparently straight line on graph 69 is similar to a twin density line in being the locus of ternary compositions of the other three components having the same density as glycol. In compositions to its left, glycol is the upper layer, and in those to its right, glycol is the lower layer, regardless of the amount of glycol present.

In the same manner, the other lines are similar to twin index lines in being loci of compositions with the same refractive index as glycol for various wave lengths. The colors named are exhibited in emulsions of the quaternary system on shaking (*5*), light blue and yellow for the extremes. The letters, *I*, *P*, *M*, and *R* stand for indigo, purple, magenta, and red, which are intermediate in the opalescent spectrum. Again, the positions and colors are independent of the amount of glycol.

In the formamide shadow graph, 70, there is no twin density line; but the twin index lines cross apparently at a point, which shows a clear and colorless emulsion, corresponding to zero dispersion. This is similar to an achromatic pair of lenses. The crossing was unexpected because of a natural but erroneous inclination to relate lines to tie lines, which cannot cross. The lines, however, are not tie lines, and crossing is not forbidden. Since the systems are quaternary, these loci are probably not rigorously straight; but it is difficult to establish their curvature because the observation of the colors is fleeting.

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