$$\left(\frac{\partial H}{\partial A}\right)_T = h = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_{P.A} \text{ ergs/sq. cm.}$$

$$\left(\frac{\partial S}{\partial A}\right)_T = s = -\left(\frac{\partial \gamma}{\partial T}\right)_{P.A} \text{ ergs/deg./sq. cm.}$$

and

$$l = -T\left(\frac{\partial \gamma}{\partial T}\right)_{P.A} \text{ ergs/sq. cm.}$$

where A is the surface area. The values of h, s and l below and above the melting point do not differ significantly because of the same value of $(\partial\gamma/\partial T)$ in the two regions. However, for a comparison of their individual values, the melting point has been taken as the reference point, and the corresponding data are assembled in Table III. It appears that significant differences exist between the *m*- and *p*-chlorophenols and also between *m*- and 2,4-dichlorophenols in their enthalpy and latent heat values. Also, a similar difference is noticeable in the case of *o*-chloro- and *m*-chloronitrobenzene.

The Eötvös constants [slope of the plot of $\gamma(M/\mathrm{d})^{2/3}$ against temperature] for phenol and chlorophenols are given in the last column of Table III.

ACKNOWLEDGMENT

We are grateful to A.M. Dighe for checking all the least square calculations.

LITERATURE CITED

(1) Dodd, C., *Proc. Phy. Soc. (London)* **64B**, 761 (1951).
(2) Dodd, C., Hu Pak Mi, *Ibid.*, **62B**, 454 (1949).
(3) Greenwood, N.N., Martin, R.L., *Proc. Roy. Soc. (London)* **A215**, 46 (1952).
(4) Harkins, W.D., "The Physical Chemistry of Surface Films," p. 64, Reinhold, New York, 1952.
(5) Harkins, W.D., Alexander, A.E., in "Technique of Organic Chemistry," Weissberger, A., Ed., Vol. I, Pt. I, Chap. XIV, p. 757, Interscience, New York, 1959.
(6) Lipkin, M.R., *Ind. Eng. Chem. Anal. Ed.* **16**, 55 (1944).
(7) Moore, D.W., Burkardt, L.A., McEwan, W.S., *J. Chem. Phys.* **25**, 1235 (1956).

RECEIVED for review May 3, 1963. Resubmitted October 21, 1964. Accepted December 22, 1964. Communication No. 588 from National Chemical Laboratory, Poona-8, India.

Ternary Systems of Acetonitrile

ALFRED W. FRANCIS[1]
Socony Mobil Oil Co., Paulsboro, N. J.

This paper presents experimental graphs of 19 aqueous and 97 nonaqueous ternary systems of acetonitrile. Also included are 34 quaternary systems plotted as triangular graphs, with the extra component assigned as a diluent to one of the other three components. The purpose of the research was to observe effects of diluents on selectivity, gross solubility, and elimination of isopycnics, which are otherwise prevalent in acetonitrile systems. Carbon disulfide is the most effective cosolvent for these functions. The graphs exhibit a wide variety of features with isopycnics, twin density lines, iso-optics, an island curve, and two and three separate binodal curves, as well as the usual types.

ACETONITRILE has high selectivity for certain types of hydrocarbon. It has a convenient boiling point, 82°, and low melting point, −42°. Development as a commercial selective solvent was retarded by its excessive cost, now considerably reduced. It also presents two technical difficulties: It dissolves very low volumes of high molecular weight hydrocarbons in the lubricating oil range; and it has a low density, 0.7824, which is close to those of some of the hydrocarbons to be treated. Thus, there is a risk of isopycnics or systems of two layers of equal density.

Both of these difficulties can be overcome by the use of appropriate cosolvents. For example, dilution of the hydrocarbon mixture with carbon disulfide increases the density considerably, so that the acetonitrile-rich layer is definitely the upper one (*14*). Carbon disulfide has only a moderate mutual miscibility with acetonitrile; but its mixtures with lubricating oils and other hydrocarbons are appreciably more soluble in acetonitrile than without the diluent. Other cosolvents of either high or low density may be employed similarly. Carbon tetrachloride, though with higher density, is less effective than carbon disulfide for preventing isopycnics, because it is more evenly distributed. On the other hand, it may be satisfactory for the other purposes.

Critical solution temperatures (CST) have been listed for acetonitrile with about 37 hydrocarbons and with nearly 50 nonhydrocarbons (*4*, pp. *17–19*). Only a few ternary systems of acetonitrile have been published previously, not all with graphs. These are aqueous systems of ethylene (*2*), heptane (*16*), and trichloroethylene (*17*); and nonaqueous systems of benzene-heptane (*16*), ethane-ethylene (*1*), heptane-methylcyclohexane or 2-methyl-2-butene (*3*), and toluene-methylcyclohexane (*3*).

The general purpose of this investigation was to find novel methods of combining solvents for improved separation of hydrocarbon mixtures. Some systems studied are reflected in patents (*12–15*). Silver nitrate, which has a strong affinity for lower olefins, is almost as soluble in acetonitrile as it is in water; but acetonitrile contrasts with water in being miscible with the liquid olefins (graph 91). Various combinations of the two solvents permit considerable flexibility, provided the cost of the silver is tolerable.

This paper presents in graphic form (Figure 1) experimental observations on 150 new systems of acetonitrile, most of them ternary, and most of them with at least two

---

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

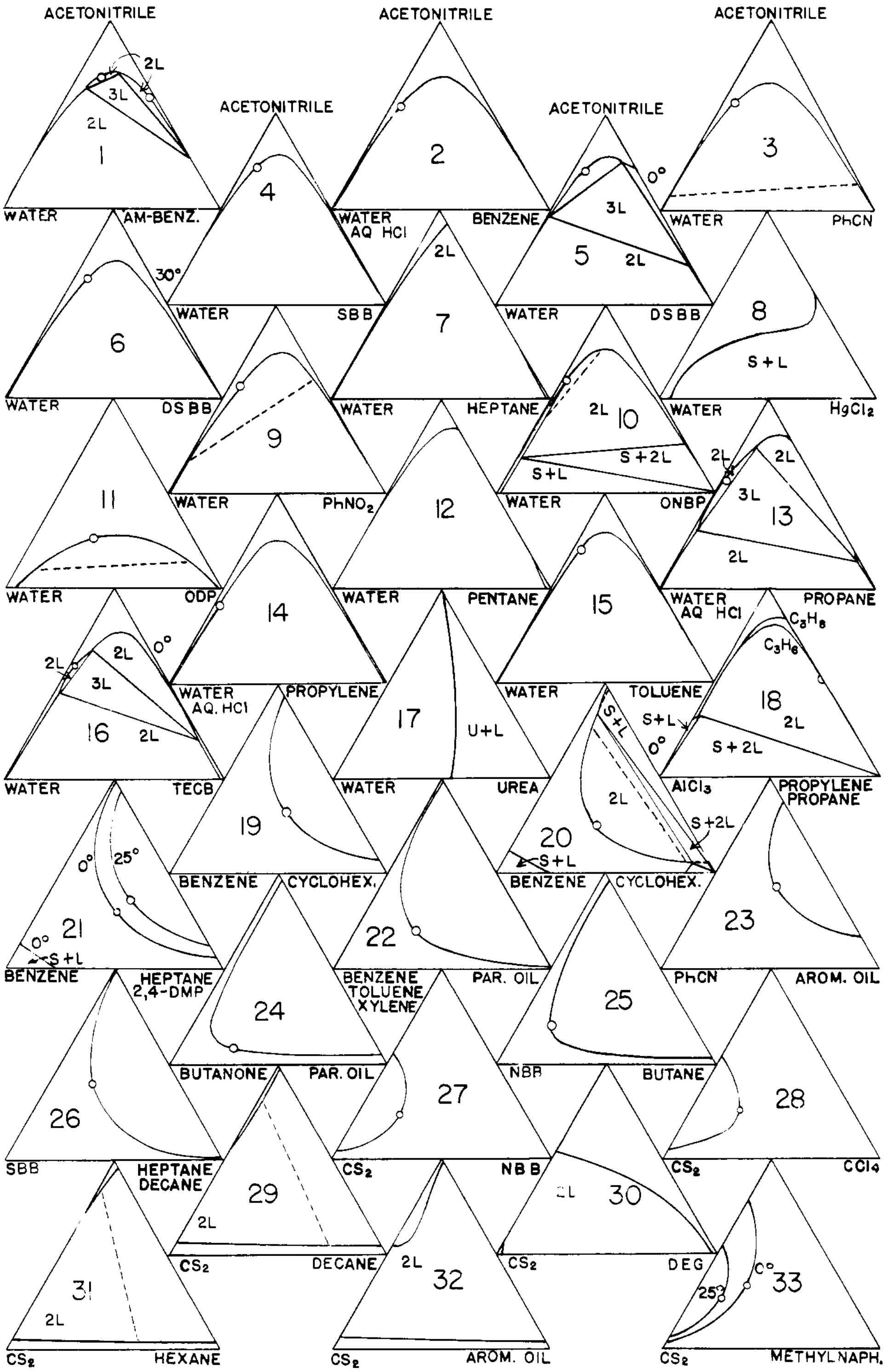

Figure 1. Systems of Acetonitrile

Top corner acetonitrile (pure except in the last 12 graphs) in each of 132 independent triangular graphs. All plots are in weight percentages, at atmospheric pressure, and at about 25°, except when another temperature is marked near the right hand side line (graphs 5, 6, 16, 20, 61, 66) or on a curve (graphs 21, 33, 34, 80, 87).

Other components are indicated by name or formula or abbreviation *under* the appropriate corner. Graphs are arranged alphabetically (by name) for each group of graphs, aqueous systems (graphs 1–17) (ternary except with aqueous hydrochloric acid, graphs 2, 13); nonaqueous systems (graphs 18 to 99) (ternary except with lubricating or gas oils); quaternary systems with pure acetonitrile as a component (graphs 100 to 120); and those in which acetonitrile is modified by a diluent (graphs 121 to 132). The percentage of diluent in the last group is indicated inside the triangle, near top.

Two or three substances named in the same small triangle indicate alternative components—i.e., different systems, unless there is a plus sign showing a mixture (graphs 100 to 120 only).

(Continued)

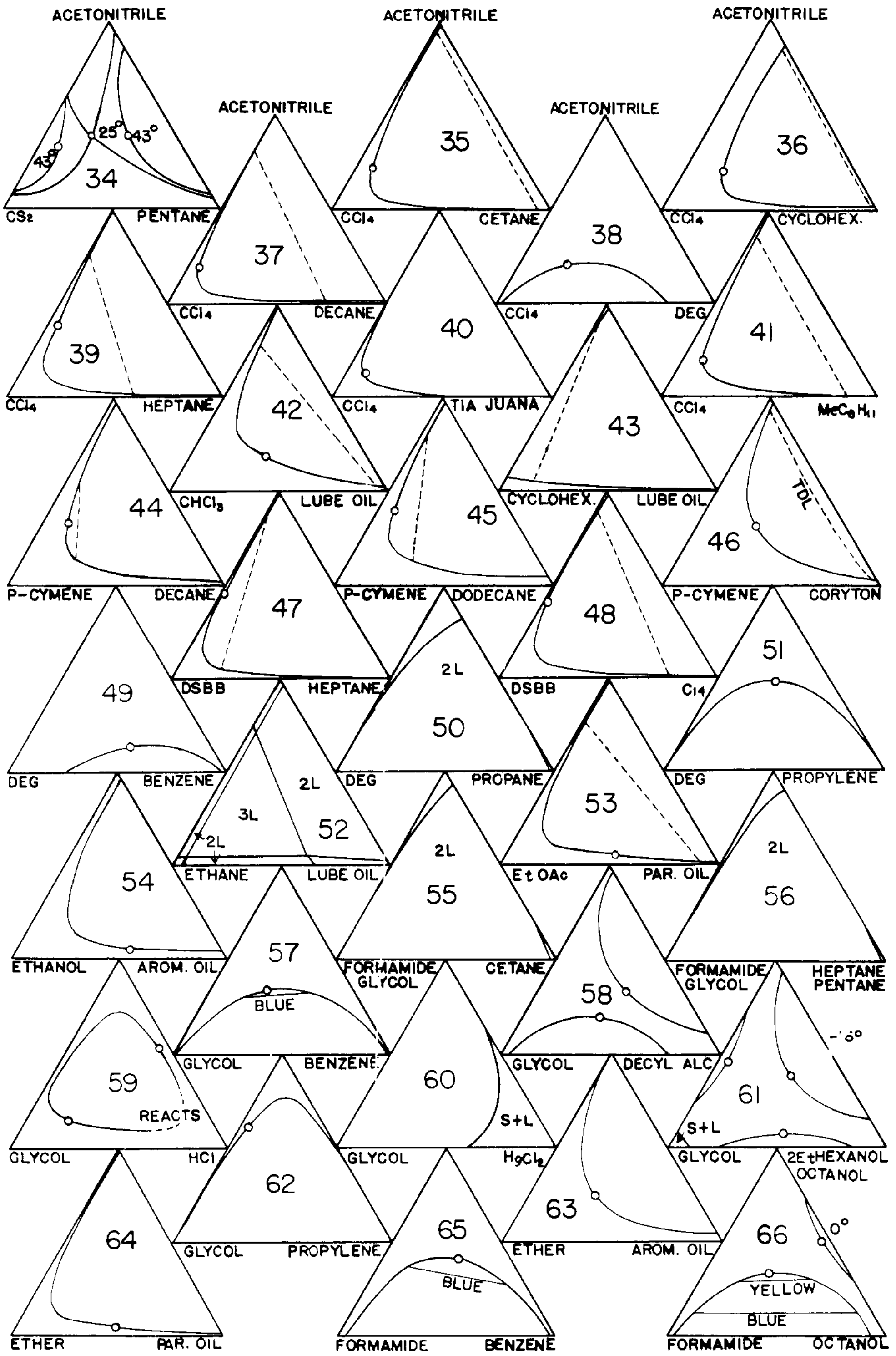

Figure 1. (*Continued*)

$AcNH_2$	Acetamide	121
ALC	Alcohol	58
AM-BENZ	*tert*-Amylbenzene	1
AQ HCl	Aqueous (or conc.) HCl	2, 13
AROM	Aromatic	23, 32, 54, 63, 83, 84 (Table I)
CORYTON	A gas oil	46 (Table II)
C_7ClF_{15}	Perfluorochloroheptane (Halo)	72
$C_{11}F_{20}$	Perfluoromethylnaphthalene	101
C_{14}	*n*-Tetrodecane	71, 80, 85, 115
CYCLOHEX.	Cyclohexane	19, 20, 36, 43, 77
DEG	Diethylene glycol	30, 38, 49, 50, 51, 124
2,4-DMP	2,4-Dimethylpentane	21

(*Continued*)

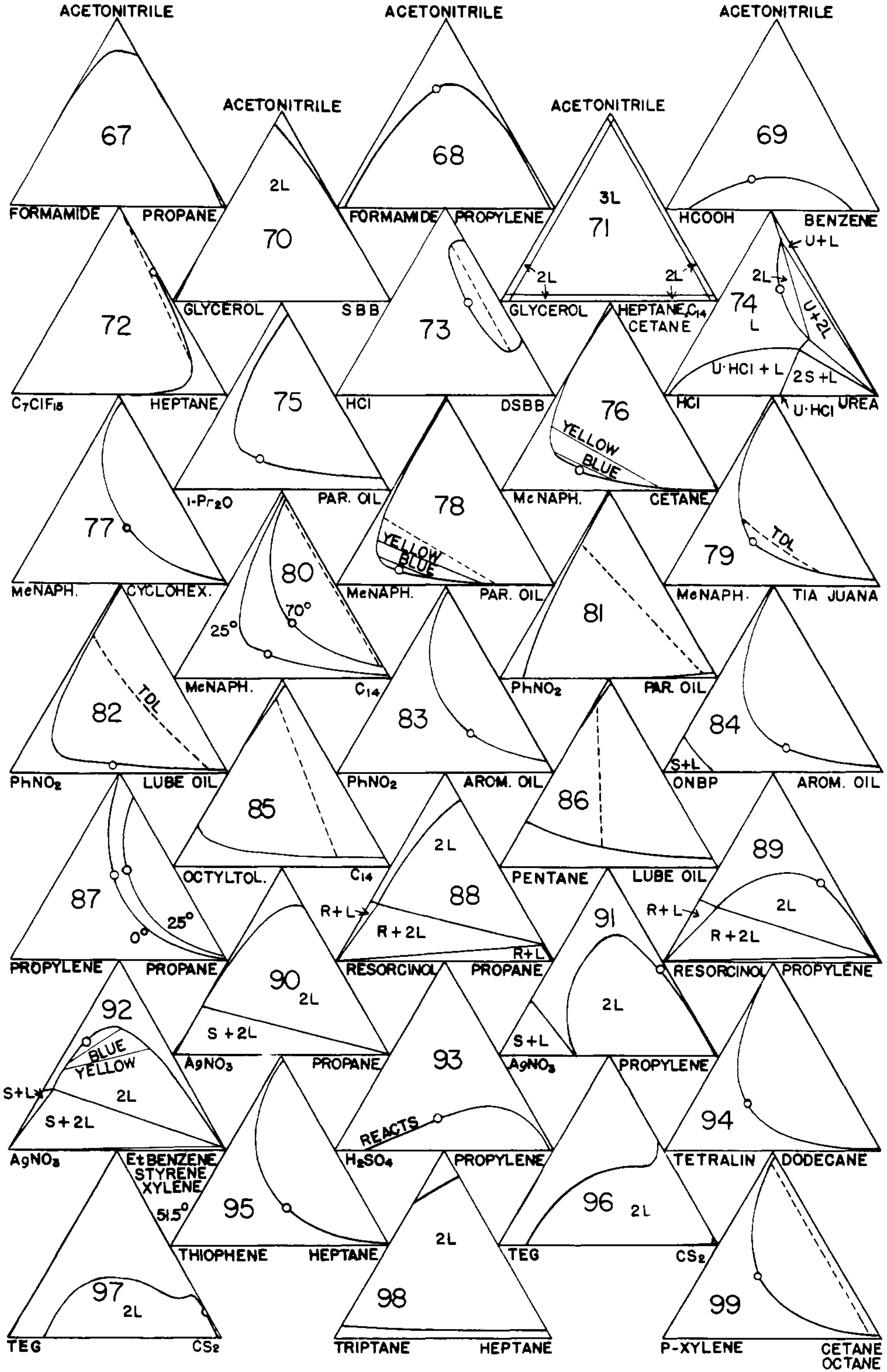

Figure 1. *(Continued)*

DSBB	Di-sec-butylbenzene	5, 6, 47, 48, 73
EtBENZENE	Ethylbenzene	92
2-EtHEXANOL	2-Ethylhexanol	61
FORM.	Formamide	125
GLYCOL	Ethylene glycol	55 to 62
HCl	Hydrogen chloride	59, 73, 74
iPr2O	Isopropyl ether	75
LUBE OIL	Lubricating oil (a clean charge stock for studies of solvent extraction)	42, 43, 52, 82, 86 (Table I)
MeC_6H_{11}	Methylcyclohexane	41
Me-NAPH.	1-Methylnaphthalene	33, 76–80, 110–4, 122
NBB	*n*-Butylbenzene	25, 27, 103
OCTYLTOL.	*n*-Octyltoluene	85, 115

(Continued)

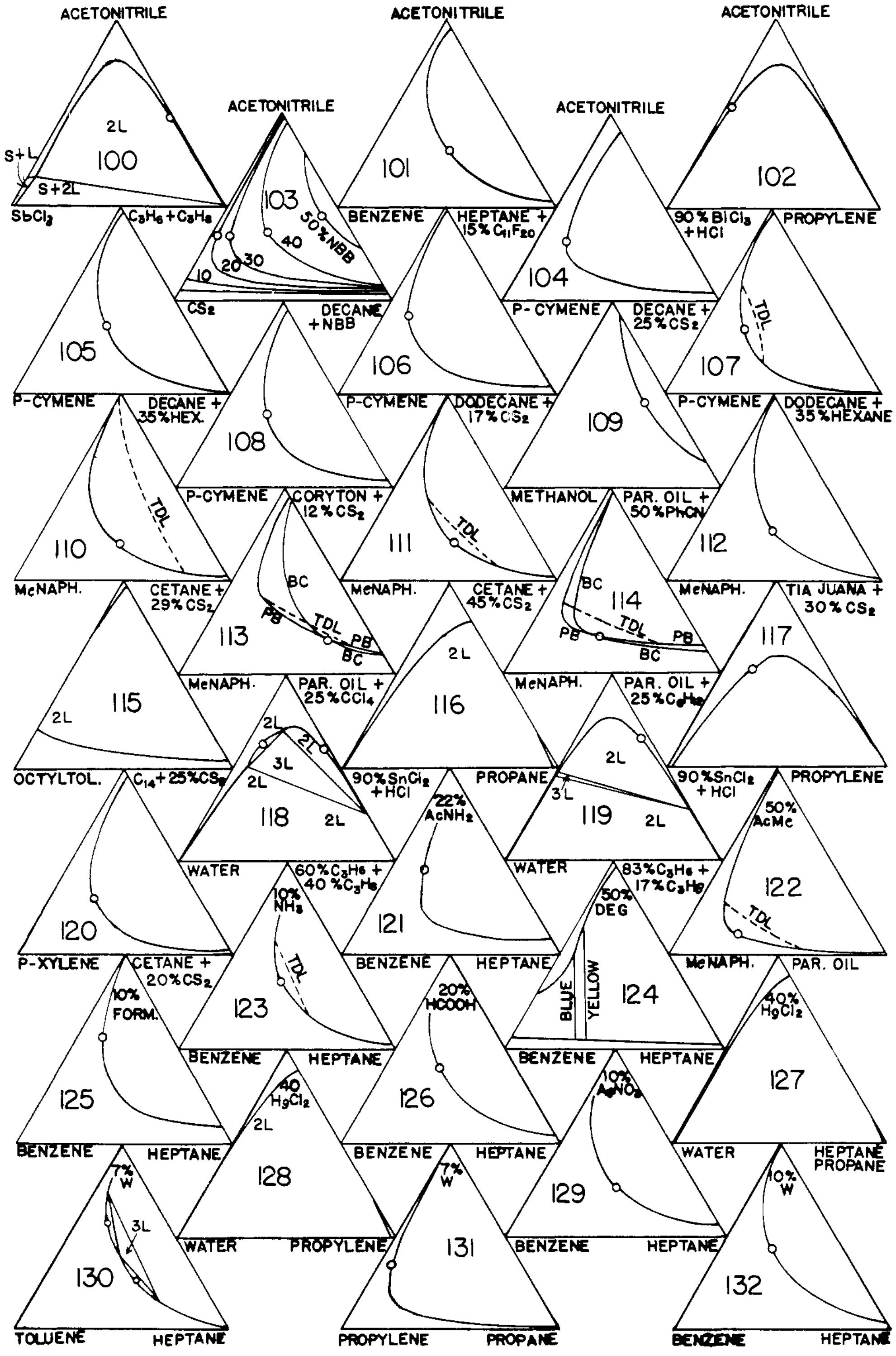

Figure 1. (*Continued*)

ODP	Oxydipropionitrile	11
ONBP	o-Nitrobiphenyl	10
PAR.	Paraffinic	Eleven graphs (Table I)
SBB	sec-Butylbenzene	4, 26, 70
TECB	Triethylchlorobenzene	16
TEG	Triethylene glycol	97
TIA JUANA	A gas oil	40, 79, 112 (Table II)
W	Water	130–2

A circle on a binodal curve indicates a plait point. In certain areas, the phases are indicated by L for a liquid phase or S for a solid phase, sometimes also by R for solid resorcinol or U for solid urea. A dashed line shows an isopycnic tie line if straight, or a twin density line (TDL) if curved. In graphs 113, 114 are shown PB for phase boundary, and BC for binodal curve. A color on a tie line, blue or yellow, indicates an iso-optic.

Table I. Properties of Lube Oils Tested

Property	Aromatic	Lube Oil	Paraffinic Oil
API gravity	22.1	23.8	27.3
Specific gravity	0.918	0.910	0.89
Refractive index	1.5231	1.5076	1.4923
Aniline point	45	72	80
Pour point, ° F.		20	15
Flash, (open cup), ° F.		395	350
Fire, ° F.		455	400
Viscosity, centistokes at 100° F.	51.65	28.65	24
Viscosity, centistokes at 210° F.	6.23	4.51	4.3
Viscosity gravity constant	0.83	0.871	0.875
Color, lovibond	28	18	14

Table II. Properties of Gas Oils Tested

Property	Tia Juana	Coryton
API gravity	23.5	46.2
Specific gravity	0.9123	0.795
Refractive index	1.5060	1.44
Aniline point, ° C.	35	61.5
Pour point	−45	−59
Color, lovibond	8	21.

liquid phases. Because of their large number, the graphs are shown in very concise form, as with earlier presentations of systems of liquid carbon dioxide (*7*), hydrogen cyanide (*9*), and liquid sulfur dioxide (*6*). Further condensation results from occasional use of a single graph for two or three systems so similar that the precision of observation would not distinguish between them. Future work will provide graphs for similar groups of unpublished systems of glycols, methanol, nitrohydrocarbons, liquid ammonia, and other primary solvents. Each of these solvents exhibits some unusual features with respect to extraction or miscibility relations.

EXPERIMENTAL

All of the observations, except those involving ethane, propane, or propylene, were made in a glass stoppered 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 to incipient clouding or to complete mixing. The tube was shaken vigorously and settled before each observation. Then, the third component was added to reverse this effect until the tube was filled or all required data were obtained. When a liquefied gas was a component, the observations were made in a sealed glass tube as in the sulfur dioxide investigation (*6*). The temperature was controlled by immersion in a bath of water or ice water. About six to 10 points were established for each phase boundary curve.

DISCUSSION

In each graph of this paper, acetonitrile is the component at the top corner; water or another highly polar substance is at the lower left corner; and the least polar component is usually at the right. Some of the systems also include additional components, as indicated, which are associated with the primary three. These are really quaternary or higher systems, and strictly make the binodal curves fuzzy (*5, 10*, Chap. 8). This is the reason for separate phase boundaries (PB) and binodal curves (BC), (graphs 113 and 114), which are not coincident (*10*, p. 107) and also for the curved twin density lines in 10 of the graphs. A twin density line (TDL) is the locus of compositions having two liquid phases of equal density in equilibrium. The components are assigned and plotted so as to minimize fuzziness (*5, 10*).

In 27 other graphs, the TDL is straight (six of them not rigorously so because of oil mixtures as components) because there are only three components. These are tie lines and are called isopycnics. Similarly, other special tie lines have equality of refractive index for the two phases in equilibrium and are called iso-optics (*5, 10*). These compositions exhibit colored emulsions on shaking and are marked with a color—blue or yellow. Other colors appear in adjacent tie lines.

Since several of the graphs are complicated by phase boundaries of various kinds, other tie lines besides those mentioned are omitted to avoid confusion. From the positions of the plait points, the orientations of the tie lines can be approximated with fair precision. The frequent use of 2L, 3L, S+L, S+2L, 2S+L, in areas should clarify relations often suggested by tie lines.

One graph, 61, shows two ternary systems, each with three separate binodal curves. Previously published systems of this type have all included as one component either carbon dioxide (*7*) or a nitroparaffin (*8*). For systems at atmospheric pressure, the proximity of the three binary CST is a requirement, as illustrated by the following CST: ethylene glycol with acetonitrile −13.5°, *n*-octyl alcohol −13°, 2-ethylhexanol about −13°; acetonitrile with *n*-octyl alcohol +8.5°, with 2-ethylhexanol +10°. The system of graph 58, with two binodal curves, does not have three of them at any one temperature, because at the temperature where the third one appears on cooling, −13.5°, the other two curves have merged to a band. Graph 34 shows such a merger at 25°. The acetonitrile-rich layer is the upper one in the curve shown at the left, and the lower one in the curve at the right. Below 25° there would be a band, with an isopycnic across it near the middle.

Graph 8 shows a peculiar S curve for equilibrium of crystalline mercuric chloride with aqueous acetonitrile. The same phenomenon appears in systems of mercuric chloride with aqueous methanol, acetone, 2-butanone, methyl acetate, or dimethylformamide, but not with aqueous ethyl acetate, ethyl alcohol, ethylene glycol, or formamide (*11*). The graph also resembles that of the all-liquid system, triethylene glycol–acetonitrile–carbon disulfide (graph 96), which might be due to merging of two separate binodal curves. However, separate curves could not be detected near the CST of acetonitrile and carbon disulfide, graph 97. The similarity of graphs 8 and 96 suggests that mercuric chloride behaves like a liquid in certain aspects of phase equilibrium far below its melting point, 276°. Other crystalline inorganic solids which are highly soluble in certain organic solvents exhibit analogous phenomena, especially if they have chemical affinity for olefins, as in the case of silver nitrate, graph 91, and cuprous chloride (*10*, p. 101).

Two graphs, 59 and 93, are marked "reacts" in compositions with high concentrations of hydrogen chloride and sulfuric acid, respectively. This obviously prevents accurate observations of phase boundaries in these systems. Even in other portions of these graphs, the physical equilibriums must be considered approximate.

Although all of the graphs are based on observations, and are as accurate as the data permit, many of the systems were not investigated as thoroughly as would be expected if one or only a few systems were to be studied. When a system was found unsuitable for practical use, the less significant portions of its graph were approximated with the help of published solubilities (*18*) and CST (*4*).

LITERATURE CITED

(1) Elgin, J.C., U.S. Patent **2,736,756** (Feb. 28, 1956).
(2) Elgin, J.C.; Weinstock, J.J., J. Chem. Eng. Data **4**, 3 (1959).
(3) Fenske, M.R., McCormick, R.H., Lawroski, H., Geier, R.G., **1**, 335 (1955).
(4) Francis, A.W., *Advan. Chem. Ser.* **31**, (1961).
(5) Francis, A.W., *Ind. Eng. Chem.* **45**, 2789 (1953).
(6) Francis, A.W., J. Chem. Eng. Data **10**, 45 (1965).
(7) Francis, A.W., *J. Phys. Chem.* **58**, 1099 (1954).
(8) *Ibid.*, **60** 20 (1956).
(9) *Ibid.*, **63** 753 (1959).
(10) Francis, A.W., "Liquid-Liquid Equilibriums," Wiley, New York, 1963.
(11) Francis, A.W., Socony Mobil Oil Co., Paulsboro, N.J., unpublished data.
(12) Francis, A.W., U.S. Patent **2,402,954** (July 2, 1946).
(13) Francis, A.W., U.S. Patent **2,673,225** (March 23, 1959).
(14) Francis, A.W., U.S. Patent **3,092,571** (June 4, 1963).
(15) Francis, A.W., Johnson, G.C., U.S. Patent **2,663,670** (Dec. 22, 1953).
(16) Hartwig, G.M., Hood, G.C., Maycock, R.L., *J. Phys. Chem.* **59**, 52 (1955).
(17) Pratt, H.R.C., *Ind. Chemist* **23**, 658 (1947).
(18) Seidell, A., "Solubilities," Vol. **I** (1940); Vol. **II** (1941); Supplementary Volume (1952), Van Nostrand, Princeton, N.J.

Received for review May 11, 1964. Accepted October 27, 1964. Presented before the Division of Physical Chemistry, 148th Meeting, ACS, Chicago, Ill., September 1964. The Central Research Division of Socony Mobil Oil Co., in which this research was conducted, is now located in Princeton, N.J.

Vapor Pressures of Some α-Amino Acids

HARRY J. SVEC and DALE D. CLYDE
Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa

The vapor pressures of several amino acids have been determined by the Knudsen cell effusion method. The thermodynamic quantities for the heat of sublimation, the entropy of sublimation, and the free energy of sublimation at the mean experimental temperature, 455° K., are calculated. The sensitivity of a mass spectrometer is calculated for an amino acid from its vapor pressure, its ionization cross-section, and the intensity of the (P-COOH)$^+$ ion currents relative to the total ion intensity.

A METHOD for the quantitative analysis of amino acid mixtures has been developed by Svec and Junk (*2*), based on empirically determined instrument sensitivities for these compounds. Since the vapor pressure of the individual acids is one of the factors upon which such sensitivities depend, a program was undertaken to measure the vapor pressures of a representative group of these compounds and then to compute relative sensitivities. Because these vapor pressures are low, the effusion technique was employed in which the loss of weight of a vessel of known physical dimensions which fulfill theoretical parameters was obtained by means of a quartz fiber microbalance. A cylindrical aluminum vessel was used whose inside dimensions were 0.375-inch in diameter, 0.562-inch deep. The cover was tantalum, 0.002-inch thick, pierced by a 0.013-inch circular hole. Research grade compounds were obtained from Calbiochem, Mann Research Laboratories, and Nutritional Biochemicals Corp.

The vapor pressures of 13 α-amino acids at various absolute temperatures are listed in Table I.

These vapor pressures as a function of temperature are given by

$$\log P_{\text{torr}} = -A/T + B$$

where A and B are constants whose least squares values are listed in Table II. The uncertainties cited in the table were also obtained by the least squares treatment in which a weighing factor proportional to $1/\sigma_P^2$ was applied to the data.

The enthalpy, free energy, and entropy of sublimation have been calculated from these data and are presented in Table III. These quantities for glycine are in good agreement with those published by Takagi, Chihara and Seki (*3*). No such data are found in the literature for other amino acids.

The relative mass spectrometer sensitivities for these α-amino acids were calculated from these vapor pressure data, the relative ionization cross sections computed by the method of Otvos and Stevenson (*1*), and the fraction of the

Table I. Vapor Pressure of Some α-Amino Acids[a]

Temp., ° K.	Press., (Torr) × 10^3
Glycine	
453	0.0587
457	0.0859
466	0.159
471	0.243
l-Alanine	
453	0.0759
460	0.122
465	0.203
469	0.258
l-α-Amino-*n*-butyric Acid	
449	0.0972
452	0.1290
455	0.163
462	0.360
dl-Norvaline	
439	0.0404
446	0.0664
452	0.1010
461	0.1930
dl-Norleucine	
435	0.0190
449	0.0576
461	0.129
469	0.184
Isoleucine	
442	0.0763
448	0.106
453	0.172
456	0.209
461	0.262
Cycloleucine	
443	0.0666
450	0.112
456	0.166
462	0.269
468	0.351
α-Amino-isobutyric Acid	
439	0.078
441	0.108
452	0.218
462	0.451
l-Valine	
438	0.0395
444	0.0682
448	0.103
452	0.150
456	0.233
l-Leucine	
446	0.0440
452	0.0844
454	0.0936
464	0.216
l-Methionine	
463	0.0384
472	0.0622
478	0.105
485	0.163
l-Phenylalanine	
451	0.0252
457	0.0463
463	0.0758
469	0.119
l-Proline	
442	0.0675
448	0.107
451	0.171
457	0.210
465	0.307
467	0.299

[a] Temperatures reported varied by ± 0.25° K.