the molecule. The relative constancy of the function, $[\phi-1]/$ polar groups per molecule, at each concentration substantiates the role of solvation and indicates a possible problem in the use of colligative property measurements for the determination of the molecular weights of some polymers. These sugars and alcohols may be considered as polymers having a repeating hydrophilic (OH) group. The osmotic coefficient of a 2 molal solution of sorbital (having six such groups) is 3% greater than unity. Polymers of higher molecular weight which have a large number of lyophilic groups must, therefore, exhibit gross deviations from Raoult's Law.

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Ternary Systems of Liquid Ammonia

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This paper presents 60 new observed ternary or quaternary systems of liquid ammonia. Most of them involve two liquid phases in equilibrium under pressure. Graphs include several systems with isopycnics, iso-optics, twin density lines, or twin index lines; but none with solutropes, island curves, or those with two or three separate binodal curves. Systems with sulfur as a component show a deep purple color, the result of a reversible reaction, but only in the ammonia-rich phase. Other systems include urea, which is extremely soluble in ammonia. These solutions do not form adducts with straight chain paraffins. Liquids found miscible in all proportions with liquid ammonia at room temperature include water, benzonitrile, 2-butanone, butenes, Chlorex, diethanolamine, diethylene glycol, dioxane, ethanolamine, ethylene glycol, formamide, glycerol, isopropyl ether, nitrobenzene, pyridine, propylene, and aromatic hydrocarbons up to C_9.

LIQUID ammonia is a cheap, noncorrosive solvent operable for extractions at ordinary temperature and moderate pressures, and easily separable from hydrocarbon products. When pure, it is fairly selective for aromatic hydrocarbons and slightly so for some other hydrocarbon pairs.

Some misleading values for solubility in liquid ammonia appear in the early literature. Franklin and Kraus (*10*) list cuprous chloride as "sl. sol.," but indicate that toluene is only slightly soluble, ethylbenzene much less so, and higher aromatics not perceptibly soluble. Actually, cuprous chloride is insoluble, but all liquid aromatic hydrocarbons up to C_9 are miscible with liquid ammonia in all proportions (*3*). The discrepancy may be due to the presence of water (which also is miscible) in the ammonia used by the early workers. The water would decrease miscibility of hydrocarbons, and increase solubility of cuprous chloride. Their observations were at atmospheric pressure, and therefore at about −33° C. These and some unpublished observations of Franklin are reported by Bergstrom and coworkers (*1*). De Carli (*2*) likewise reported many solubilities of hydrocarbons in liquid ammonia, which are excessively low, probably because of the same low temperature.

Critical solution temperatures of liquid ammonia are listed in references *3*; *8*, pp. 221–2; *12*, *15*, and *20*. Extensive investigations of liquid ammonia as a selective solvent have been made by Ishida (*12–15*), and by Long (*17*). Fifteen of their ternary graphs (at various temperatures) are shown in Landolt-Börnstein (*16*), for hydrocarbon pairs. Also included as cosolvents are pyridine, thiophene, or methylamine. Four other systems of liquid ammonia are presented (*7*, graphs 8, 9, 34, 35).

EXPERIMENTAL

This paper presents observations on 60 additional ternary or quaternary systems (on 46 graphs) with ammonia as a component (Figure 1). Most of them show two or more liquid phases. As in the observations on liquid sulfur dioxide systems (*6*), a thick-walled glass tube was charged by weight with the nonvolatile components, and cooled in a cold bath. Ammonia was condensed into the tube, which was then sealed, warmed to room temperature, and weighed. When a hydrocarbon gas was a component also, it was charged in the same way, but with intermediate sealing and weighing. Additional ammonia as required was introduced similarly to titrate the mixture to a composition on a phase boundary. The resulting graphs are shown in concise form.

DISCUSSION

Pure liquid ammonia is not entirely satisfactory as a selective solvent for aromatics. Although it is completely miscible at ordinary temperatures with aromatic hydrocarbons boiling up to about 160°, it also dissolves moderate amounts of paraffins or cycloparaffins. Consequently, with pure ammonia as a solvent, an extract cannot be concentrated above about 85% benzene or toluene except at very low temperatures.

Dilution of the ammonia with water or an organic solvent such as ethylene glycol would diminish solubility of the

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hydrocarbon mixture; and so supposedly would increase the concentration of the extract (*20*). However, this dilution also increases the density of the ammonia phase to approximately that of the hydrocarbon mixture (*11*). It becomes difficult, therefore, to design an operable process free from the risk of phase inversion (*5*). Dilution also diminishes the moderate selectivity of liquid ammonia.

For these reasons, it is preferable in the primary extraction to use pure liquid ammonia, which has a specific gravity at 15° C. of 0.62 (*11*), well below those of most hydrocarbon mixtures involved. The purification of the aromatic hydrocarbons can be completed by extractive evaporation, described in another paper (*5, 9*). Graphs 10, 11, 34, and 40 to 44 are pertinent to that process.

The graphs are explained in the figure caption. Graphs 7, 29 to 33, and 46 have purple marked in an area indicating homogeneous solution of sulfur in liquid ammonia (solubility 25.65% at 16.4°, 32.34% at 0°, 38.1% at -20.5°) (*19*).

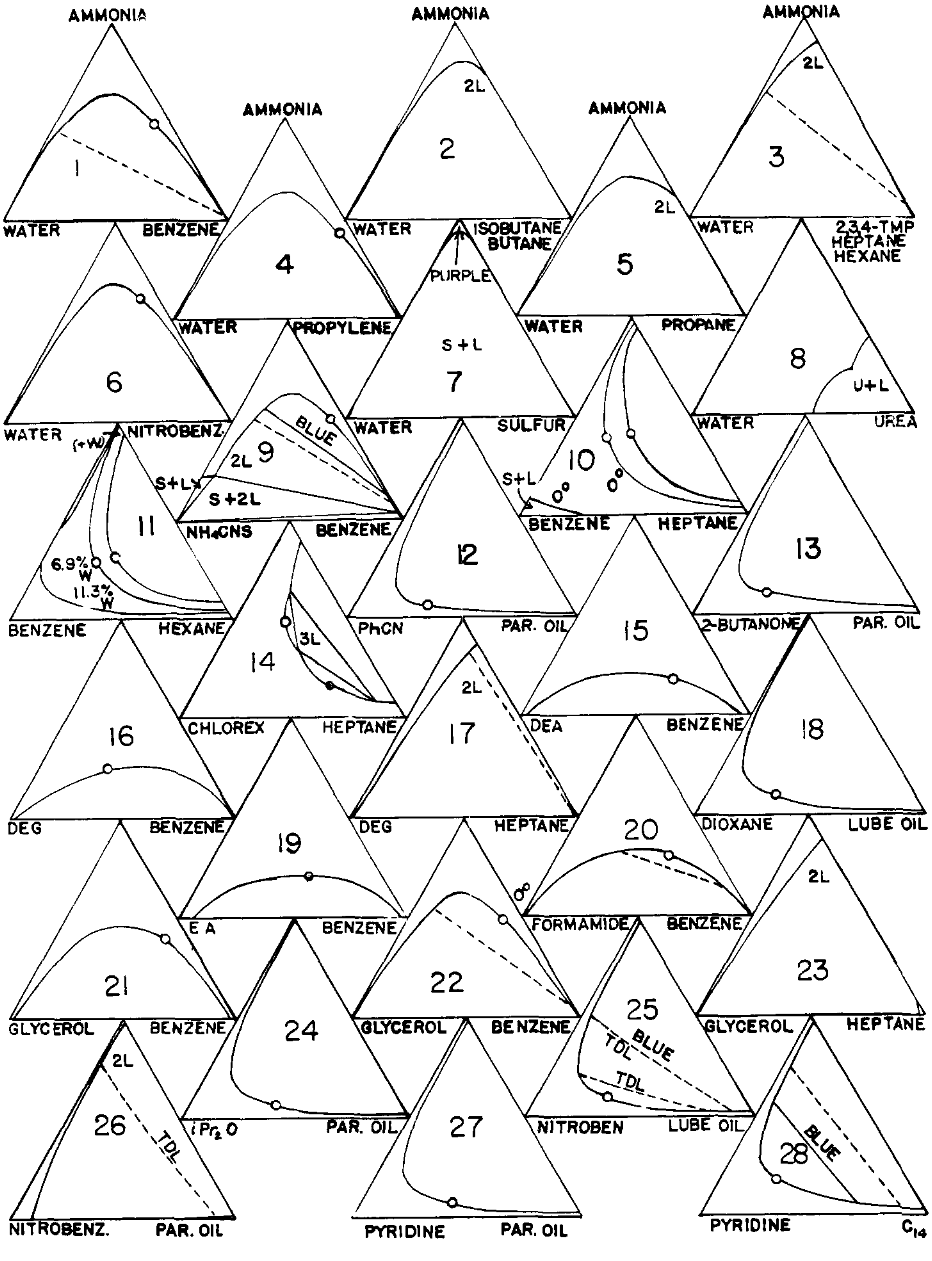

Figure 1. Systems of Liquid Ammonia

Sixty new systems are presented on 46 independent triangular graphs, all under pressure, and at 25° except in graphs 10, 22, 32, 34, 39. All plots are in weight percentage. The top corner of each graph indicates ammonia, pure except in graph 11 and in the last six graphs.

In these, the amount of diluent is shown on the curves or inside the top corner. Other components are indicated by names, formulas, or abbreviations *under* the appropriate corner.

A small circle on a phase boundary curve is a plait point. A straight dashed line, graphs 1, 3, 9, 17, 20, 22, 28, 35, indicates an isopycnic or tie line connecting compositions of equal density in equilibrium (*4, 8*, pp. 46–9). Dashed lines which are slightly curved (graphs 25, 26, 45, 46) are twin density lines (marked TDL)(*4*). These are loci of compositions with two layers of equal density, which are not uniform all along the curve because the systems are quaternary.

A straight line with blue marked on it, graphs 9 and 28, indicates an iso-optic or tie line connecting compositions with equal refractive indices (*4, 8*, pp. 46–9). If the line is curved, graph 43, 44, it is a twin index line, which shows loci of compositions having equal refractive indices.

This is a very deep purple resulting from a chemical reaction (cf. *18*, pp. 249–50). On releasing the ammonia, the color reverts quickly to a yellow powder or coating (sulfur). In the aqueous system, graph 7, only a small amount of water is required to precipitate most of the sulfur, which is colored almost black by the intense color of the solution. Benzene or toluene, which are also miscible with ammonia, likewise precipitate solid sulfur, but less abruptly, graph 29. With aromatic oils, propane, methylnaphthalene, or heptane which are not miscible with ammonia, graphs 30, 31, 33, two liquid phases appear, one of them colorless if isolated from the deep purple one. Propylene and the butenes, graph 32, though miscible with ammonia, can be salted out at 0° by a small amount of sulfur dissolved in the ammonia. In graphs such as 46, the purple blends gradually with a colorless phase, giving a peculiar green at certain concentrations. This would permit colorimetric estimates of concentration.

Since urea has a solubility of about 60% in liquid ammonia, several combinations were tried, graphs 35 to 38. Those with dodecane and cetane (graph 36), showed no evidence of adduct formation. Such a crystalline precipitate was expected because it appears readily with concentrated urea solutions in water, methanol, and acetic acid. However, in the presence of such solvents, ammonia is less inhibitive. Compositions on the curve below the break in graph 8 (cf. *21*) form adducts with *n*-octane.

Eight of the graphs contain triangular areas indicating equilibrium of a solid with two liquid phases; and there are two, (graphs 14 and 39), with three liquid phases. But no examples among ammonia systems were found with island curves, solutropes, or systems with two or three separate binodal curves. These types are not unusual with other systems (*6*, *7*). Ishida (*13*) studied a solutropic system of ammonia-thiophene-heptane.

Graphs 39 to 46 are quaternary. They show phase boundaries and not binodal curves since equilibrium concentrations are not necessarily on the curves (cf. *8*, Chap. 8). The curve near the top of graph 39 shows only the amount of water extracted from the alkali solutions, originally 56% water. There is no appreciable amount of alkali in the ammonia-rich phase.

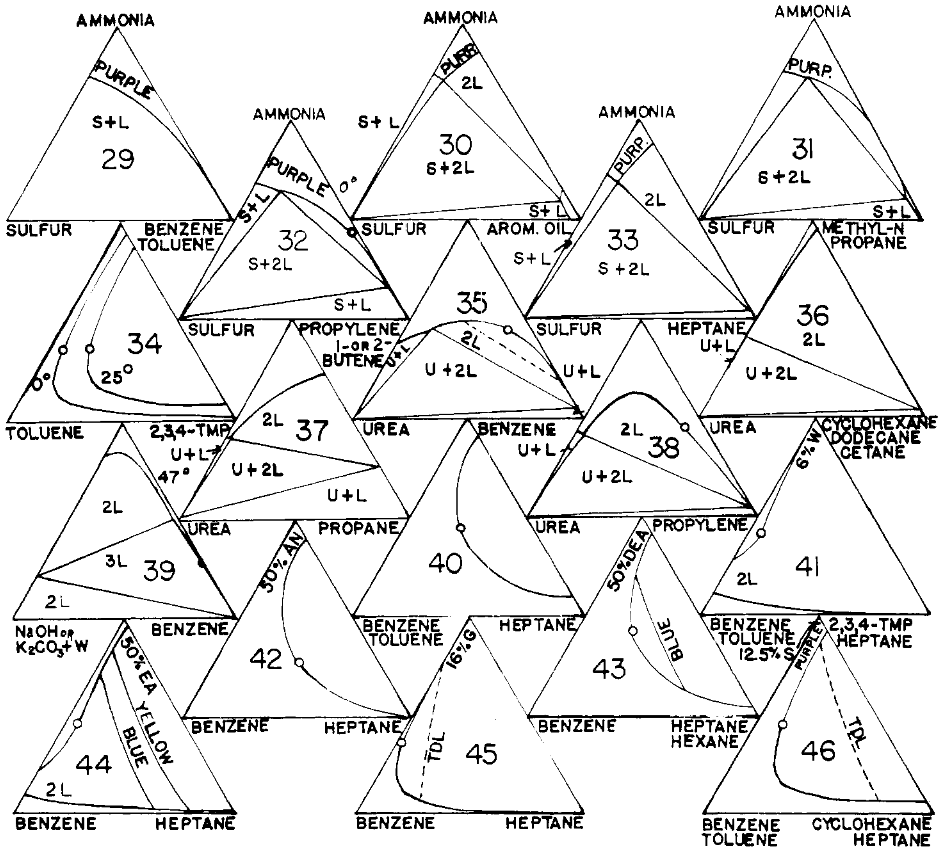

Figure 1. *(Continued)*

AN	Aniline	42
AROM. OIL	An aromatic lube oil	30 (6, Table I)
C_{14}	*n*-Tetradecane	28
CHLOREX	2,2′-Dichloroethyl ether	14
DEA	Diethanolamine	15, 43
DEG	Diethylene glycol	16, 17
EA	Ethanolamine	19, 44
G	Ethylene glycol	45
iPr_2O	Isopropyl ether	24
L	Liquid phase	7–10, 29–33, 35–38
2L	Two liquid phases (omitted as obvious when there is a plait point)	2, 3, 5, 17, 23, 26, 30, 31, 32, 33, 36, 37, 39, 41, 44
LUBE OIL	Lubricating oil	18, 25, (6, Table I)
METHYL-N	1-Methylnaphthalene	31
NITROBEN(Z)	Nitrobenzene	6, 25, 26
PAR. OIL	A paraffinic lube oil	12, 13, 24, 26, 27, (6, Table I)
PURP	Purple (sulfammonium in solution)	30, 31, 33
S	Solid phase	7, 9, 10, 29–33
2,3,4-TMP	2,3,4-Trimethylpentane	3, 34, 41
U	Solid urea	8, 35–38
W	Water	11, 39, 41

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Refractive Index and Density of Acetone-Water Solutions

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Data for the density and refractive index of mixtures of acetone and water are presented. Deviations from ideality for such data are clearly shown if data are correlated with ideal volume per cent composition. If there is no deviation from ideality, density and refractive index may be exactly calculated from the ideal volume per cent composition. With deviation from ideality, a plot of refractive index *vs.* density in which the actual points are connected with the ideal points is very revealing. The slope of these tie lines may be related to the slopes corresponding to various specific refraction equations. In the case of the acetone-water blends, the simple Gladstone and Dale relation accurately represents the change of refractive index in relation to the change of density owing to the contraction on mixing. The possible effect of hydrogen bonding on the relation between refractive index and density for binary aqueous mixtures is pointed out. The presence of hydrogen bonding, or absence of it, may determine which specific refraction function best represents the data for a particular aqueous binary mixture.

THE study of data for binary mixtures of liquids, and of simple solutions of solids in liquids, is important for developing a better understanding of the liquid state (*5, 6, 20, 22, 23*). The properties of binary mixtures of liquids, particularly aqueous solutions, cannot be predicted with certainty from the properties of the pure materials but must be quantitatively evaluated from experimental data (*5, 6, 20, 22, 23*). This paper contributes data on binary mixtures of acetone and water and discusses briefly the application of refraction functions to the generalization of such data.

Data on binary mixtures of acetone and water were obtained some time ago for analytical use. These data have been checked recently in a second laboratory. These two sets of data are presented in Tables I and II. The composition data are recorded both as ideal volume % and weight %.

Mole per cent composition is used in many discussions of binary mixtures (*19, 21, 22, 28*), but consideration from the volume % point of view still has some advantages. The space separating molecules is, of course, closely related to volume % composition.

Table III compares three sets of data at 50.26 ideal volume % water. The agreement among the three sets of data is satisfactory. Table IV compares the experimental density and refractive index data for the acetone and water used in this work with literature data. As the agreement is good, one may conclude that the materials used were of adequate purity.

Ideal volume % is the volume % calculated from the weight % assuming no volume change on mixing. By definition, density must plot linearly against ideal volume % if there is no volume change on mixing (*13, 19, 24, 25*), therefore the deviation from linearity when density is plotted against ideal volume % is a direct measure of deviation from

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[1] Deceased.