Liquid Equilibrium Data for the System Propane, Propylene, and Ammonia Solvents

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Liquid-liquid equilibrium values have been determined between −30° and 33.6° C. for the binary, ternary, and quarternary systems of propane, propylene, ammonia, and water. Methods of measurement and apparatus are described. The tie line data satisfy a new correlation.

THE SEPARATION of olefins from hydrocarbon mixtures has been one of the most important problems in the refinery field. A large number of stages and, consequently, extensive equipment is required in the fractionation of the mixtures of propane and propylene because of the small difference between their vapor pressures. Liquid extraction is another important process and the utility and versatility of liquid ammonia as a solvent have been stressed (*5*). The increasing use of propylene has prompted the present study of the liquid properties of the mixtures of propane fraction and several solvents. Besides the mutual solubilities of hydrocarbons and liquid ammonia, and the ternary liquid equilibria for propane propylene–liquid ammonia systems at the temperatures of 0° and 20° C., some quaternary liquid equilibria for hydrocarbon–liquid ammonia–water systems at 20° C. were determined.

MATERIALS AND EXPERIMENTAL PROCEDURE

Standard reagent propane and propylene for use in gas chromatographic determination were furnished by Takachiho Chemical Industry Co., Ltd. They were reported to be more than 99.9 mole % and were further purified by repeated distillation; the initial fraction and the residue were discarded, and the middle fraction was retained for the succeeding distillation. The deaerated samples distilled into the measuring bottle under pressure were used for the determination. Liquid ammonia, purified from the commercial product by repeating the careful distillation more than three times, and distilled water were used.

Mutual solubilities of hydrocarbons and liquid ammonia were determined by the method described in a previous paper (*9*). Cloud points could be determined within 0.05° C. or better. Mutual solubilities at the temperatures far from the critical solution temperature were obtained by the analytical method of determining the compositions of the two liquid phases in equilibrium at a given temperature (±0.1° C.). A blank test showed that the presence of propylene had no effect on the determination of ammonia by absorbing with $2N$ sulfuric acid solution. The determination was repeated several times for each phase at a given temperature, and averaged. The average error was less than 0.1% with a maximum error of 0.4%.

The general procedure for determining ternary and quaternary liquid equilibria for hydrocarbons and ammonia solvents consisted of two steps—obtaining the equilibrium conjugate phases and analyzing them. The procedure for the four-component system of propane, propylene, ammonia, and water was as follows:

A mixed solvent of ammonia and water—namely, 95.18 or 90.17% ammonia by weight—was prepared in a large pressure bottle. A part of the mixed solvent was transferred into a measuring bottle, *E*, shown in Figure 1, by connecting the valve joints from the large pressure bottle. In the same way, propane and propylene were successively added to the mixed solvent in *E* in the liquid state from bottles containing each component. Thus, mixtures of about 50% hydrocarbons and about 50% solvent by weight were prepared in *E*.

To avoid contamination of system with air, care was taken to evacuate and replace the measuring bottle and the connecting part successively after ammonia, propane, and propylene had been introduced. Manipulation under pressure (about 16 atm.) made it difficult to obtain compositions of the over-all mixture in exact equiratio of mixed solvent and hydrocarbons.

Liquid compositions should be corrected slightly for the amounts of components existing as vapor. The amounts are determined from the volume of vapor phase, total vapor pressures, and vapor compositions. The volume and pressure were measured, and compositions of the vapor phase were estimated, assuming that water was absent in the vapor phase, that the mixture of propane and propylene obeyed Raoult's law, and that the mole ratio of ammonia to hydrocarbons in the vapor phase was equal to the ratio of vapor pressures of mixed solvents to those of hydrocarbons. Literature values of vapor pressures of hydrocarbons (*15*) and ammonia solvent (*8*) were used for the calculations.

The compositions of the two liquid phases in equilibrium were determined by a slightly modified version of the mutual solubility determination at temperatures far from the critical solution temperature. An aliquot of homogeneous phase in measuring bottle *E*, in equilibrium at a given temperature, was effused carefully and slowly into the receiver *C*, which contained some granular potassium hydroxide; gas mixtures evaporated from the receiver were dried by slow passage through a column packed with granular potassium hydroxide, and then collected in a large graduated gas bottle together with purified dry nitrogen injected to the receiver at the end of the operation after all ammonia was absorbed by $2N$ sulfuric acid solution. The collected gas mixtures in the gas bottle were analyzed gas chromatographically using alumina as absorber. Figure 1 shows the schematic diagram for the assembly in the determination. The water content in each phase was obtained from the increase of the weight of the receiver containing potassium hydroxide (±0.0001 gram). The concentration of

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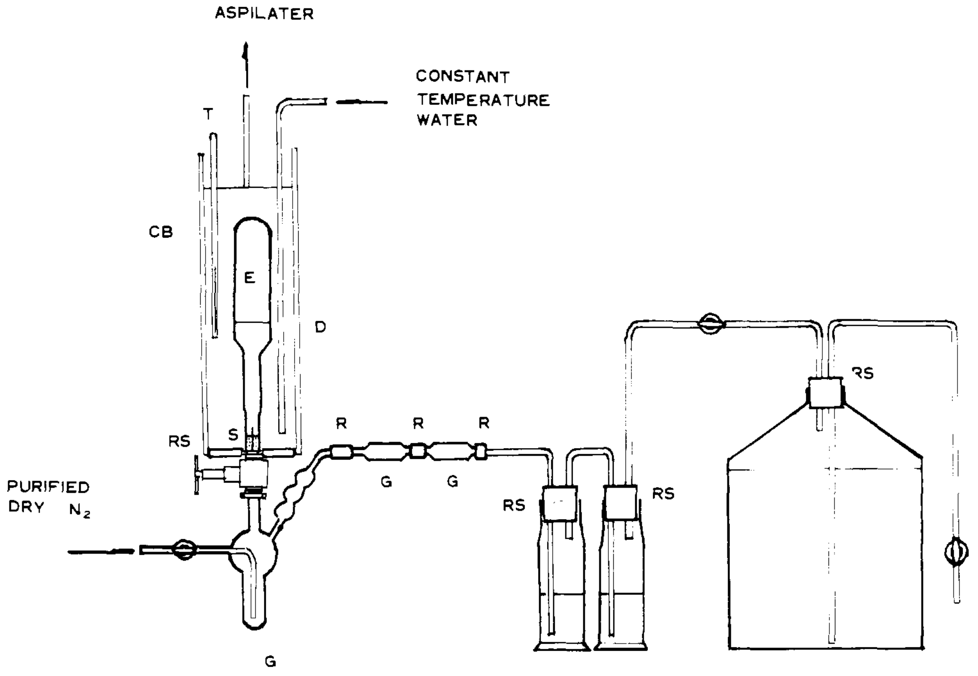

Figure 1. Schematic of experimental assembly

C, Receiver; D, Dewar cylinder for constant temperature bath; E, Graduated glass pressure bottle which contains equilibrated sample liquid mixture; G, Granular potassium hydroxide; R, Rubber tube; RS, Rubber stopper; T, Thermometer; V, Valve; S, Syringe needle

Table I. Mutual Solubility Data for Binary System of Hydrocarbons and Ammonia, Weight Fraction

Temperature, °C.	Hydrocarbon-Rich Phase,[a] Ammonia	Ammonia-Rich Phase, Ammonia	Cloud Points and Their Composition	
			Cloud Pt., °C.	Ammonia
		PROPANE-AMMONIA SYSTEM		
30.0	0.2856	0.7733	32.83	0.3873
20.0	0.1618	0.8637	33.21	0.4308
10.0	0.1003	0.9104	33.58	0.5025
0.0	0.0670	0.9354	33.61	0.5223
−10.0	0.0469	0.9519	33.52	0.6048
−20.0	0.0330	0.9643	33.6[a]	0.563[b]
−30.0	0.0248	0.9712		
		PROPYLENE-AMMONIA SYSTEM		
−10.0	0.2795	0.7076	−9.00	0.3300
−12.0	0.2210	0.7605	−8.14	0.4221
−15.0	0.1673	0.8100	−8.11	0.5081
−20.0	0.1264	0.8507	−8.15	0.5204
−25.0	0.1011	0.8763	−8.14	0.5367
−30.0	0.0846	0.8939	−9.00	0.6560
			−9.16	0.6653
			−12.16	0.7644
			−8.1[a]	0.5050[b]

[a] Critical solution temperature. [b] Critical composition.

ammonia was found by titrating the excess sulufuric acid of 2*N* acid solution which absorbed all ammonia in the liquid phase with 0.5*N* sodium hydroxide solution, using methyl red as the indicator. The ratio of propane and propylene was calculated from that of the areas on the gas chromatograph, correcting by an appropriate factor determined by known compositions of the hydrocarbon mixtures. Thus, saturation compositions and tie-line data were determined at the same time. The analysis of equilibrium conjugate phases for ternary systems was carried out in a similar manner.

In the determination of water for ternary and quaternary systems, the error was less than 5% for the solvent-rich phase. In the case of the hydrocarbon-rich phase, however, hydrocarbons and ammonia evaporated as soon as saturated mixtures were effused into the receiver, so the error was relatively large because of the sparing solubilities. No claim of accuracy is attempted here; the data serve only to show the order of magnitude.

RESULTS AND DISCUSSION

Mutual Solubilities of Hydrocarbons and Liquid Ammonia. The experimental results for the binary systems propane-ammonia and propylene-ammonia are given in Table I.

Critical compositions were estimated according to Cox and Herington (*3*). The critical solution temperature for propane and liquid ammonia mixtures in the present investigation, 33.6° C., agreed with the published data (*6*), while that for propylene, −8.1° C., is lower than Francis' value of 11° C. (*6*).

The straight-line relationships between saturation compositions and temperatures are satisfied by Equation 4.1 in the previous paper (*11*) rather than by the equations described by Cox and Herington (*3*).

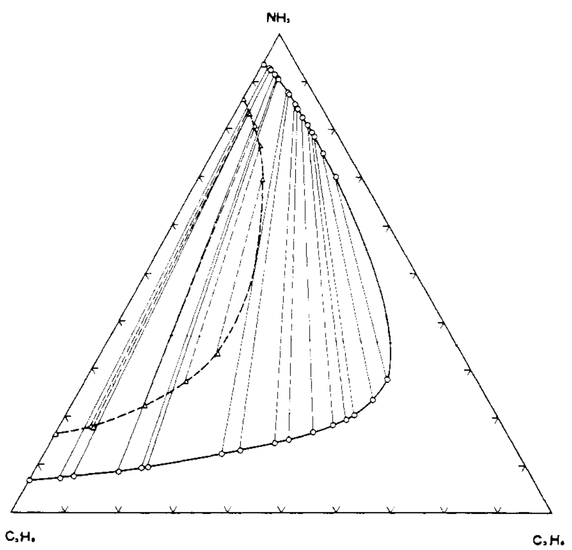

Figure 2. Propane-propylene-ammonia system
○ At 0° C. △ At 20° C.

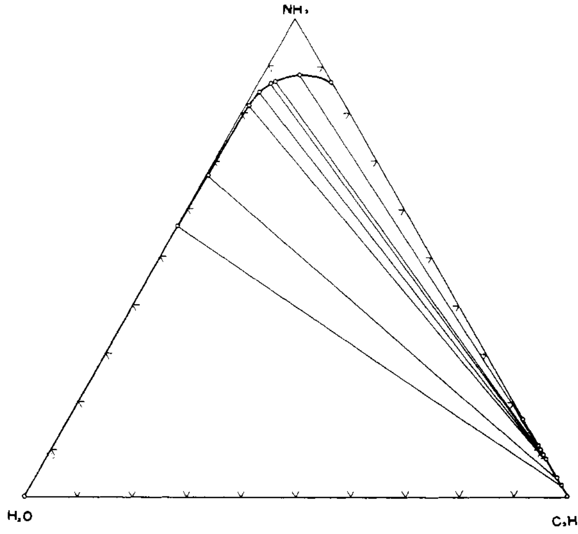

Figure 3. Propane-ammonia-water system at 20° C.

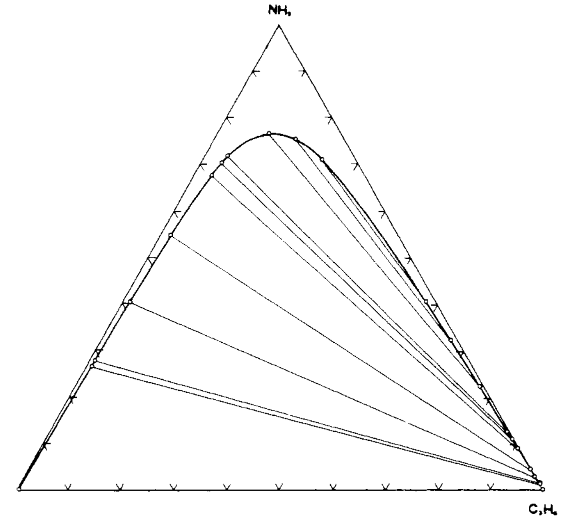

Figure 4. Propylene-ammonia-water system at 20° C.

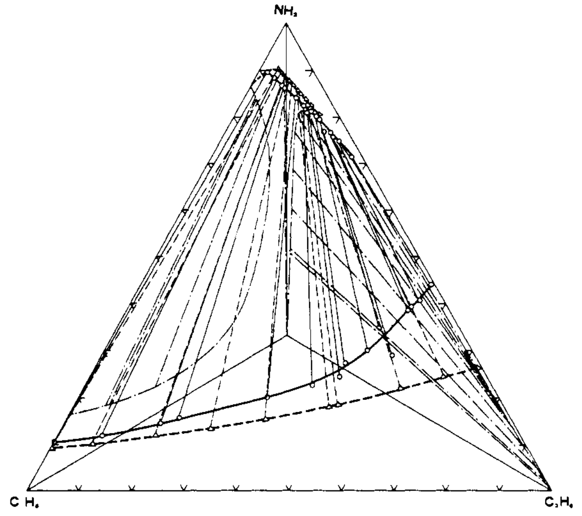

Figure 5. Projected diagram of ammonia-propane-propylene plane for propane-propylene-ammonia-water system at 20° C., wt. fraction
○ 5 wt. % water △ 10 wt. % water

Ternary Systems. The results for the system propane-propylene-ammonia are given in Table II and are plotted in Figure 2.

Equilibria at temperatures near 20° C. for this system are similar to those for the propane–propylene–sulfur dioxide system at −78° C. (*4*), which shows the smaller solvency of ammonia for hydrocarbons compared with sulfur dioxide. In spite of possible experimental error, which may be due to the determination of ammonia and the estimation of propane and propylene ratio of the gas chromatography chart, the obtained tie lines passed through the points representing initial total mixtures, and material balances were checked satisfactorily. Equilibrium distribution curves of propylene and selectivity diagrams of ammonia solvents for propylene at 20° C. compared with mixed solvent are shown in Figure 6. Tie lines are correlated well by straight lines in the way proposed by Ishida (*10, 12*) although plots by Hand (*7*) or Othmer (*14*) give two straight lines with changing slopes. Plots for this system by the method described in reference (*10*) are quite similar to the plots for the quaternary system shown in Figure 7.

The results for systems propane-ammonia-water and propylene-ammonia-water at 20.0° C. are given in Tables III and IV, respectively. These data are plotted in Figures 3 and 4.

The solubilities of propane and propylene in water are estimated by interpolating the data of Kobayashi (*13*) and McKetta *et al.* (*1*), respectively. In both systems, water is selective for the separation of ammonia and hydrocarbon.

Quaternary System. This system at 20° C., is made up of two kinds of ternary systems—that is, propane-propylene-ammonia, shown in Figure 2, propylene-ammonia-water, shown in Figure 4, propane-ammonia-water, shown in Figure 3, and propane-propylene-water, not shown in this paper. The former two are made up of one partially miscible binary system, and the later two, on the other hand, are of two partitially miscible binary systems. Phase equilibria consisted of propane, propylene, and mixed solvents of ammonia and water whose compositions at higher water concentrations will be little different from the ternary of propane-propylene-water although solubilities in both layers may increase mutually somewhat. Determinations were confined to the range of low water concentrations; two kinds of definite composition of mixed solvent—namely, 95% NH_3-5% H_2O and 90% NH_3-10% H_2O by weight—were used for the determination in order to study the effect of water on the selectivity and solvency of ammonia solvents.

Experimental data are given in Table V and plotted on Figure 5. The quaternary system requires a three-dimen-

Table II. Ternary Liquid Equilibrium Data for Propane-Propylene-Ammonia System at 0° and 20° C., Weight Fraction

Total Mixture			Hydrocarbon-Rich Phase			Ammonia-Rich Phase		
Ammonia	Propylene	Propane	Ammonia	Propylene	Propane	Ammonia	Propylene	Propane
				0° C.				
			0.067		0.933	0.935		0.065
0.767	0.019	0.204	0.070	0.054	0.876	0.930	0.012	0.058
0.607	0.039	0.354	0.076	0.078	0.846	0.926	0.016	0.058
0.585	0.083	0.332	0.087	0.153	0.760	0.915	0.031	0.054
0.629	0.094	0.277	0.093	0.194	0.713	0.911	0.038	0.051
0.514	0.123	0.363	0.094	0.205	0.701	0.908	0.041	0.051
0.509	0.196	0.295	0.122	0.329	0.549	0.882	0.071	0.047
0.499	0.270	0.231	0.130	0.359	0.511	0.874	0.078	0.048
0.457	0.274	0.269	0.143	0.417	0.440	0.853	0.100	0.047
0.384	0.327	0.289	0.152	0.438	0.410	0.843	0.109	0.047
0.467	0.316	0.217	0.169	0.475	0.356	0.825	0.128	0.047
0.484	0.331	0.185	0.183	0.504	0.313	0.807	0.146	0.047
0.456	0.364	0.180	0.197	0.521	0.282	0.793	0.161	0.046
0.439	0.385	0.176	0.204	0.532	0.264	0.782	0.171	0.047
0.476	0.388	0.136	0.239	0.550	0.211	0.749	0.204	0.047
0.483	0.410	0.107	0.280	0.557	0.163	0.699	0.252	0.049
		Plait Point*	0.560	0.375	0.065			
				20° C.				
			0.162		0.838	0.864		0.136
0.537	0.037	0.426	0.177	0.058	0.765	0.835	0.020	0.145
0.622	0.039	0.339	0.179	0.062	0.759	0.834	0.022	0.144
0.649	0.076	0.275	0.222	0.136	0.642	0.808	0.050	0.142
0.579	0.122	0.299	0.274	0.188	0.538	0.764	0.081	0.155
0.516	0.168	0.316	0.331	0.213	0.456	0.694	0.118	0.188
		Plait Point*	0.559	0.177	0.264			

* Plait point was estimated according to (*16*).

Table III. Ternary Liquid Equilibrium Data for Propane-Ammonia-Water System at 20° C., Weight Fraction

Total Mixture			Hydrocarbon-Rich Phase			Water-Rich Phase		
Propane	Ammonia	Water	Propane	Ammonia	Water	Propane	Ammonia	Water
			0.999[a]		0.0001[a]	0.00059[a]		0.999[a]
0.367	0.362	0.271	0.977	0.023	0.0004	0.002	0.563	0.435
0.401	0.408	0.191	0.962	0.038	0.0007	0.003	0.671	0.326
0.388	0.508	0.104	0.922	0.076	0.0016	0.009	0.818	0.174
0.418	0.501	0.081	0.915	0.084	0.0017	0.012	0.843	0.145
0.414	0.520	0.066	0.905	0.093	0.0015	0.024	0.863	0.113
0.473	0.475	0.052	0.904	0.095	0.0014	0.029	0.868	0.103
0.448	0.525	0.027	0.896	0.103	0.0008	0.068	0.880	0.051
			0.838	0.162		0.136	0.864	

[a] Interpolated valve from the data of McKetta *et al.* (*1*).

Table IV. Ternary Liquid Equilibrium Data for Propylene-Ammonia-Water System at 20° C., Weight Fraction

Total Mixture			Hydrocarbon-Rich Phase			Water-Rich Phase		
Propylene	Ammonia	Water	Propylene	Ammonia	Water	Propylene	Ammonia	Water
			0.99969[a]		0.0003[a]	0.002286		0.997714[a]
0.355	0.177	0.468	0.989	0.011	0.0006	0.008	0.263	0.729
0.262	0.210	0.528	0.987	0.012	0.0006	0.008	0.279	0.713
0.430	0.240	0.330	0.976	0.023	0.0009	0.012	0.403	0.585
0.348	0.372	0.280	0.953	0.045	0.0016	0.020	0.547	0.433
0.249	0.531	0.220	0.906	0.091	0.0029	0.034	0.674	0.292
0.428	0.431	0.141	0.886	0.110	0.0035	0.039	0.701	0.260
0.380	0.475	0.145	0.868	0.128	0.0041	0.044	0.717	0.239
0.551	0.401	0.048	0.768	0.224	0.0078	0.097	0.764	0.138
0.436	0.515	0.049	0.664	0.323	0.0123	0.158	0.751	0.091
0.429	0.531	0.040	0.572	0.410	0.0175	0.228	0.709	0.063
		Plait Point[a]	0.427	0.543	0.030			

[a] Interpolated value from the data of McKetta *et al.* (*1*). [b] The plait point was estimated according to (*16*).

sional model for complete representation of compositions. It is less confusing to use a regular tetrahedron with each of the triangular faces representing one ternary combination. The geometric construction on ordinary plane triangular coordinates will be permitted by orthogonal projections upon one of the boundary surfaces. The projected diagrams made on the water-propane-propylene plane are shown in Figure 5 as an example. In this figure, three ternaries are plotted by fine chain lines, equilibria in the case of mixed solvent of 95% ammonia and 5% water by full lines, and those of 90% ammonia and 10% water by broken lines.

In the solvent-rich phase resulting from over-all mixtures of an equiratio of hydrocarbons and mixed solvent having a definite composition, the concentrations of water are in the range between those for the terminal ternaries and are

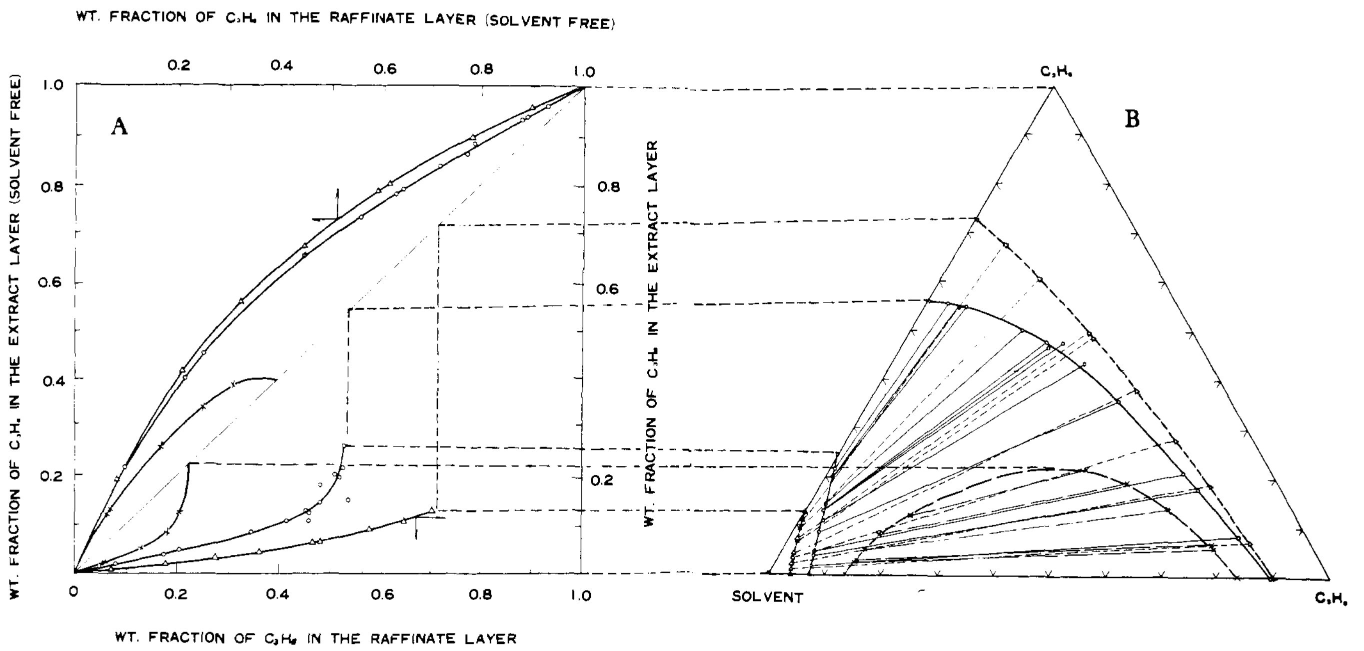

Figure 6. System propane-propylene-mixed solvent at 20° C.

A; Equilibrium distribution curves and selectivity diagrams
B; Liquid equilibria
Δ 10 wt. % water solvent
O 5 wt. % water solvent
X Pure ammonia solvent

Table V. Liquid Equilibrium Data for the Extraction of the Mixture of Propane and Propylene with the Use of Mixed Solvent of Ammonia and Water, Weight Fraction, at 20° C.

Run No.	Total Mixture				Hydrocarbon-Rich Phase				Ammonia-Rich Phase			
	Water	Ammonia	Propylene	Propane	Water	Ammonia	Propylene	Propane	Water	Ammonia	Propylene	Propane
PROPANE–PROPYLENE–95% AMMONIA–5% WATER												
	0.025	0.475		0.500	0.0008	0.102		0.897	0.051	0.880		0.069
5	0.028	0.528	0.048	0.396	0.0008	0.118	0.084	0.797	0.051	0.866	0.018	0.065
4	0.023	0.456	0.119	0.402	0.0011	0.145	0.184	0.670	0.053	0.852	0.038	0.057
6	0.030	0.567	0.114	0.289	0.0009	0.157	0.212	0.630	0.051	0.846	0.046	0.057
3	0.024	0.463	0.241	0.272	0.0012	0.201	0.359	0.439	0.055	0.821	0.080	0.044
7	0.023	0.440	0.310	0.227	0.0017	0.223	0.435	0.340	0.058	0.803	0.101	0.038
2	0.020	0.392	0.378	0.210	0.0023	0.242	0.479	0.277	0.065	0.803	0.102	0.030
1	0.025	0.501	0.317	0.157	0.0030	0.270	0.470	0.257	0.052	0.793	0.121	0.034
10	0.024	0.470	0.369	0.137	0.0050	0.300	0.499	0.196	0.055	0.781	0.137	0.027
8	0.028	0.536	0.345	0.091	0.0069	0.346	0.499	0.148	0.050	0.751	0.171	0.028
9	0.023	0.422	0.440	0.115	0.0046	0.288	0.553	0.154	0.066	0.770	0.144	0.020
13	0.024	0.471	0.447	0.058	0.0109	0.379	0.536	0.074	0.057	0.745	0.184	0.014
11	0.025	0.483	0.440	0.052	0.0114	0.392	0.531	0 066	0.055	0.740	0.191	0.014
12	0.024	0.466	0.476	0.034	0.0143	0.399	0.546	0.041	0.059	0.726	0.206	0.009
	0.025	0.475	0.500		0.0192	0.434	0.547		0.058	0.693	0.249	
PROPANE–PROPYLENE–90% AMMONIA–10% WATER												
	0.050	0.450		0.050	0.0014	0.094		0.905	0.104	0.867		0.029
21	0.048	0.426	0.044	0.482	0.0016	0.102	0.074	0.823	0.109	0.858	0.006	0.027
19	0.051	0.463	0.107	0.379	0.0017	0.121	0.186	0.691	0.106	0.850	0.018	0.026
20	0.051	0.459	0.166	0.324	0.0019	0.136	0.282	0.580	0.106	0.842	0.029	0.023
18	0.058	0.516	0.199	0.227	0.0023	0.157	0.378	0.462	0.105	0.834	0.041	0.020
17	0.058	0.519	0.259	0.164	0.0029	0.183	0.485	0.329	0.106	0.819	0.059	0.016
15	0.056	0.505	0.279	0.160	0.0030	0.187	0.500	0.310	0.106	0.817	0.061	0.016
16	0.060	0.532	0.324	0.084	0.0045	0.222	0.603	0.171	0.104	0.802	0.084	0.010
14	0.057	0.514	0.389	0.041	0.0065	0.244	0.673	0.076	0.105	0.788	0.102	0.005
	0.050	0.450	0.500		0.0094	0.262	0.729		0.115	0.765	0.120	

proportional to the composition of hydrocarbon mixtures in that phase. Thus, a quaternary solubility contour of this system over the range of higher than 5% concentrations of water can be imagined as made up of straight lines connecting the two related saturated ternaries as for systems of water–benzene–ethyl isovalerate–ethyl alcohol, water–benzene–toluene–ethyl alcohol, and water–benzene–toluene–acetic acid (2). Furthermore, the concentrations of water in the solvent-rich phase are larger than those in the mixed solvent, while those in the hydrocarbon-rich phase are less than the order of several percentages, although they increase with the increase of the concentration of propylene. In general, most of the water in the mixed solvent is transferred to the ammonia-rich phase, and one end of the tie lines for this quaternary system will be located near the base plane of the ammonia-hydrocarbons ternary in the case of total mixtures of higher concentrations of water.

Solubilities of hydrocarbons and solvents increase mutually according to the increasing amount of propylene. As to water and ammonia distribution in the two conjugate phases, the concentration of water is higher in the solvent-rich phase and that of ammonia is lower in the hydrocarbon-

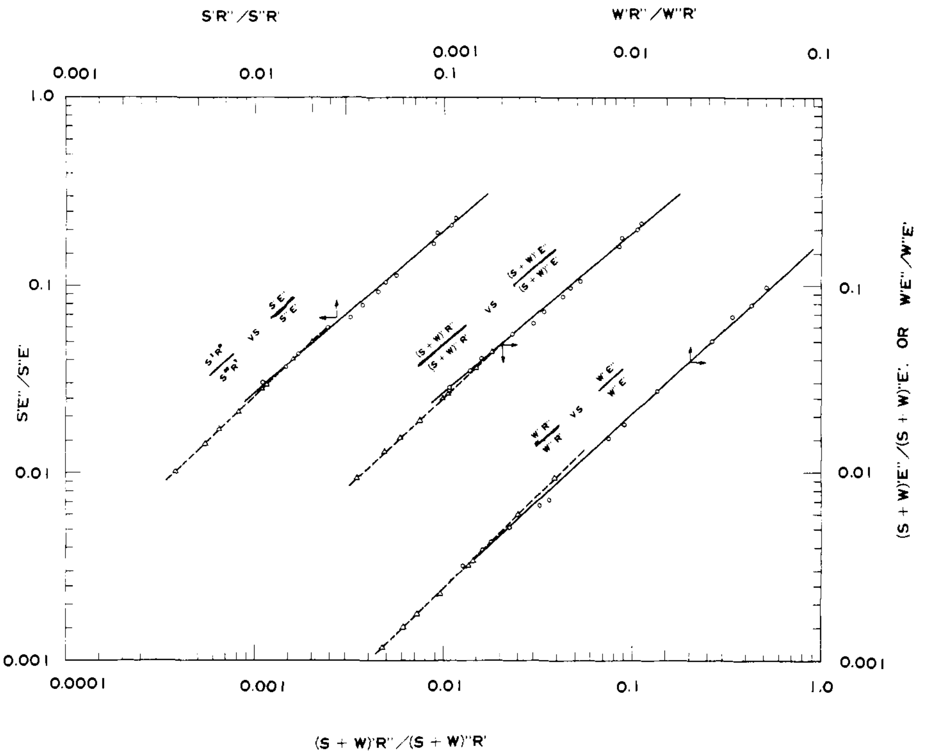

Figure 7. Tie line data correlation for propane (*R*)-propylene(*E*)-ammonia(S)-water(*W*) at 20° C.

○ 95% NH_3–5% H_2O solvent △ 90% NH_3–10% H_2O solvent

rich phase, compared with that of total mixtures prepared in equiratio of hydrocarbons and ammonia.

Addition of water to the ammonia solvent gave an effect on the ternary equilibria of propane-propylene-ammonia. This effect on equilibrium, distribution, and selectivity diagram is shown in Figure 6 using the parameter of water contents in mixed solvents.

Equilibrium distribution ratios for propylene, plotted in the lower right hand in Figure 6*A* decrease with the increase of the concentration of water in mixed solvents, while selectivities of solvents for propylene extraction increase in the experimental range of the concentrations of water, although the difference between 95% ammonia and 90% ammonia is small.

The authors have found that plots obtained by correlating the method of the tie-line data for ternary systems proposed in the previous paper (*10*) give straight lines for the quaternary equilibrium data resulting from the total mixtures composed of an equirato of hydrocarbons and mixed solvents in which the concentration of water is definite. When the respective fractions of water, ammonia, propylene, and propane are represented by W, S, E, and R, and one prime and two primes denote the hydrocarbon-rich phase and solvent-rich phase, respectively, straight lines are obtained by plotting $[(S'E'')/(S''E')]$ against $[(S'R'')/(S''R')]$, $[(W'E'')/(W''E')]$ against $[(W'R'')/(W''R')]$, and $\{[(S' + W')E'']/[(S'' + W'')E']\}$ against $\{[(S' + W')R'']/[(S'' + W'')R']\}$ on double logarithmic coordinates (Figure 7). Similar results are obtained among the equilibrium values calculated on an ammonia- or water-free basis (not shown in figure).

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NOMENCLATURE

E = weight fraction of propylene
R = weight fraction of propane
S = weight fraction of ammonia
W = weight fraction of water

Superscripts

' = raffinate phase (hydrocarbon-rich phase)
'' = extract phase (solvent-rich phase)

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