Mutual Solubility in the Ternary System *n*-Propyl Alcohol–Water–Hexamethyldisiloxane

W. W. CHEW and VIRGIL ORR
Louisiana Polytechnic Institute, Ruston, La.

The solubility data for the ternary liquid system *n*-propyl alcohol-water-hexamethyldisiloxane were experimentally determined as the initial phase of a continuing fundamental inquiry into the phase characteristics of this system. Reviews on silicones (*2,3*), and solubility tables (*4*) contain practically no information on the mutual solubilities of these compounds with organic compounds or with water.

MATERIALS

The *n*-propyl alcohol (Eastman Organic Chemicals) and hexamethyldisiloxane (Dow Corning Corp.) used in these determinations were distilled in an efficient distillation column with the middle 80% retained. Distilled water was used as the third component. The refractive indices (n_D20° C.) were 1.3867 and 1.3777 for *n*-propyl alcohol and hexamethyldisiloxane, respectively.

PROCEDURE AND RESULTS

Solutions of known compositions of two of the miscible components were prepared by weighing the added amounts of each of the substances on an analytical balance. The third immiscible component, either water or silicone, was added with the use of a buret until a cloud point was obtained. The solutions were kept at 25° C. in a constant temperature bath except for short intervals required in adding the third component. At the equilibrium cloud point the amount of the third component was also determined by weighing and densities and refractive indices were determined by use of a 10-ml. pycnometer and an Abbe refractometer, respectively. The pycnometer was calibrated at 25° C. and the refractometer was used at a constant temperature of 25° C.

Figure 1 and Table I show the compositions of the miscibility

Table I. Composition, Density, and Refractive Index at the Binodal Curve for the System *n*-Propyl Alcohol–Water–Hexamethyldisiloxane at 25° C.

Mass Per Cents			Density, Gram/Ml. at 25° C.	Refractive Index n_D25° C.
Water	Hexamethyldisiloxane	*n*-Propyl alcohol		
0.36	91.55	8.09	0.7624	
0.36	91.50	8.14	0.7626	
0.37	91.48	8.15	0.7623	
1.06	88.65	10.29		1.3758
1.33	84.60	14.07	0.7656	
1.35	85.18	13.47	0.7666	
1.59	81.88	16.53		1.3760
1.61	85.41	12.98		1.3758
1.62	84.18	14.20	0.7664	
1.72	84.87	13.41		1.3763
2.06	76.74	21.20		1.3764
2.51	72.79	24.70		1.3770
2.87	77.49	19.64		1.3771
2.89	73.20	23.91		1.3766
3.11	72.31	24.58	0.7752	
3.40	69.35	27.25		1.3766
3.45	69.00	27.55		1.3780
4.06	66.03	29.91		1.3769
4.20	66.05	29.75		1.3784
4.73	62.83	32.44		1.3775
4.94	60.60	34.46	0.7840	
5.26	59.65	35.09	0.7848	
5.44	57.78	36.78		1.3784
5.59	56.84	37.57	0.7863	
5.67	59.40	34.92	0.7854	
5.88	57.50	36.62	0.7862	
6.58	55.07	38.35		1.3780
6.58	49.91	43.51		1.3780
6.90	49.55	43.55		1.3781
6.95	50.94	42.11		1.3786
7.28	50.70	42.02		1.3780
7.80	48.17	44.03		1.3789
8.79	45.07	46.14		1.3782
8.81	40.49	50.70	0.8013	
8.93	43.08	47.99	0.7964	
9.18	40.17	50.64	0.8009	
11.88	33.74	54.38		1.3781
12.98	28.79	58.23	0.8173	
13.58	28.03	58.39		1.3782
13.84	29.51	56.65	0.8174	
13.95	27.20	58.85		1.3780
14.25	26.66	59.09		1.3780
14.33	28.26	57.41		1.3778
14.96	26.89	58.15		1.3779
16.60	24.08	59.32		1.3773
17.23	23.33	59.44	0.8278	
18.57	21.52	59.91		1.3770
19.30	20.03	60.67	0.8343	
19.54	20.12	60.34	0.8340	
24.31	16.02	59.67	0.8496	
24.59	15.78	59.63	0.8473	
25.94	14.90	59.16	0.8500	
28.51	12.70	58.79	0.8576	
28.99	12.48	58.53	0.8611	
32.60	9.43	57.97		1.3731
34.22	9.01	56.77	0.8683	
34.83	8.78	56.39	0.8691	
36.87	7.58	55.55		1.3716
36.88	7.34	55.78	0.8733	
37.94	6.84	55.22		1.3718
42.67	5.01	52.32		1.3693
43.35	5.01	51.64		1.3698
44.88	4.57	50.55	0.8910	
47.63	3.67	48.70	0.8982	
48.46	3.51	48.03		1.3671
48.92	3.44	47.64	0.8998	
52.48	2.66	44.86	0.9126	
52.61	2.58	44.81		1.3652
56.27	1.89	41.84		1.3639
56.68	1.91	41.41	0.9175	
58.76	1.53	39.71	0.9262	
64.28	0.86	34.86		1.3598
69.35	1.07	29.58	0.9492	
78.18	0.21	21.61	0.9655	
78.25	0.21	21.54		1.3510
83.97	0.22	15.81		1.3469
87.53	0.53	11.94	0.9811	
99.75	0.25	0.00		1.3325

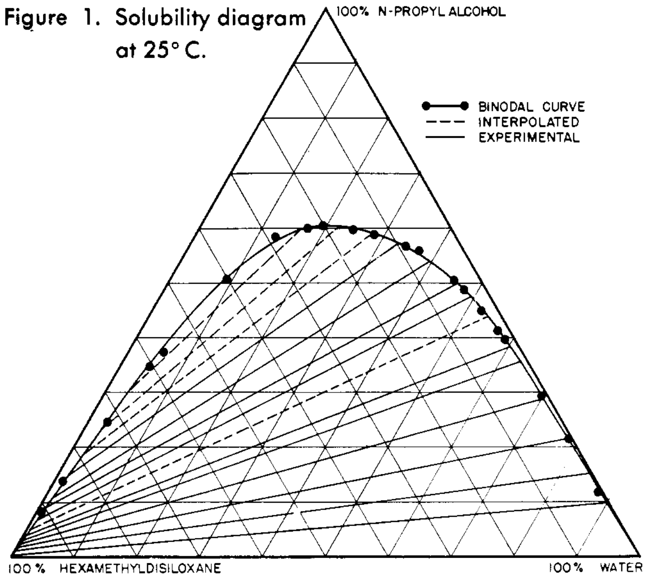

Figure 1. Solubility diagram at 25° C.

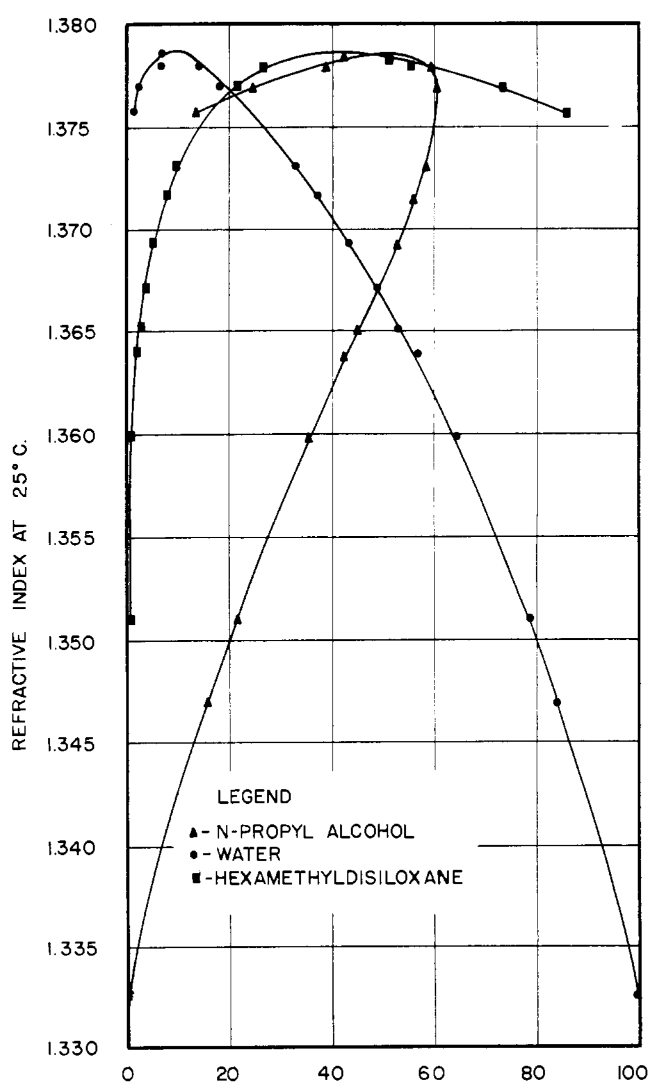

Figure 2. Refractive index variation along the binodal curve at 25° C.

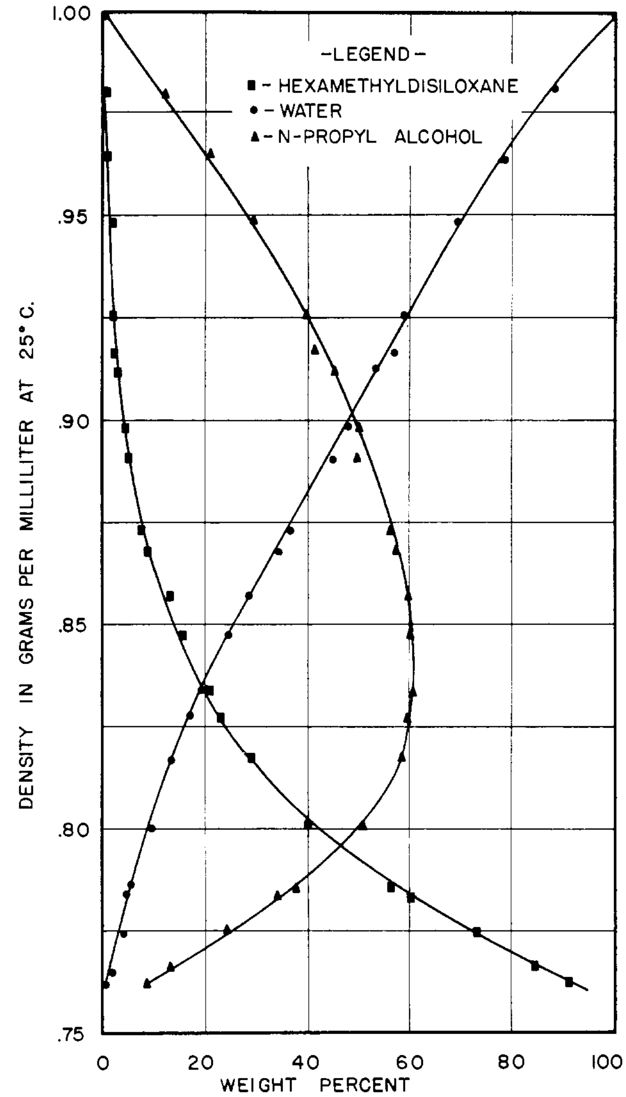

Figure 3. Density variation along the binodal curve at 25° C.

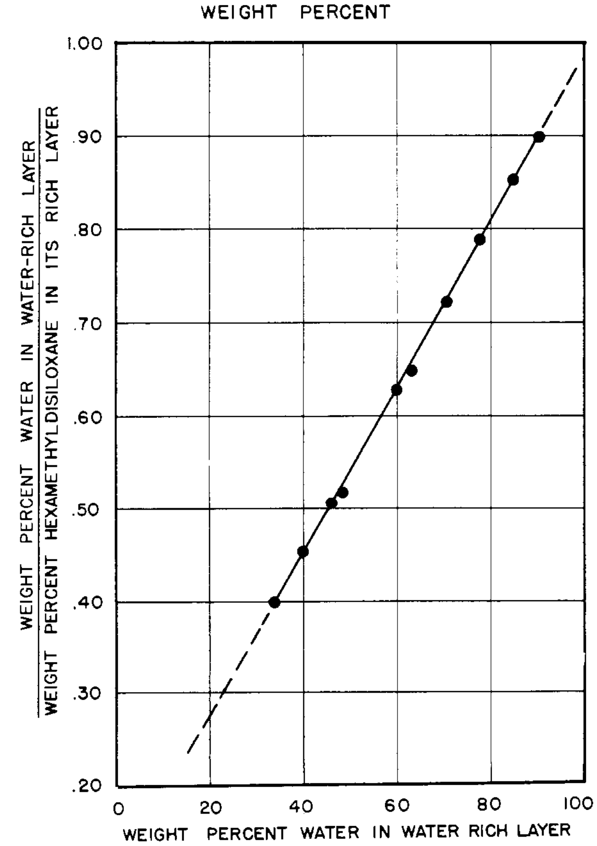

Figure 4. Bachman plot of tie line data

Table II. Tie-Line Data at 25° C.

n-Propyl Alcohol, Per Cent			
In hexamethyldisiloxane layer	In water layer	In hexamethyldisiloxane layer	In water layer
0.1	10.0	6.8	47.6
1.2	15.3	9.0	49.7
1.9	22.0	10.8	53.8
2.4	28.8	14.5	57.4
3.0	35.6	18.6[a]	59.3[a]
3.9	38.2	23.5[a]	60.3[a]
4.9[a]	43.7[a]	30.4[a]	59.2[a]

[a]Values determined from Bachman plot of tie-line data by extrapolation and interpolation.

boundary or binodal curve. Figure 2 presents the variation of refractive index of mixtures of the same components as a function of the same binodal curve compositions and Figure 3 is a similar plot of density.

The data for the Bachman (*1*) plot (Figure 4) were obtained by preparing equilibrium liquid phase mixtures of the ternary system, allowing them to separate, and analyzing each layer separately by its density. The amount of each component present in the total mixture was predetermined by weighing and was used as a check on the tie-line data. From a knowledge of the density of each layer the weight per cents were determined using the data in Figure 3.

The isothermal phase diagram (Figure 1) was plotted using the weight per cents of the components determined as described above. Tie lines (Table II) were determined from experimental data and from interpolation and extrapolation of the Bachman plot.

ACKNOWLEDGMENT

The services of Donald Riggs, Myron Lindsey, Kenneth Davis, Leo Bondurant, Wayne Stevenson, Kenneth English, and Kay Fletcher, undergraduate students, in the experimental phases of this investigation are gratefully acknowledged.

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RECEIVED for review August 4, 1958. Accepted November 21, 1958.

Solubility Measurements on the Systems Ammonium, Sodium, and Potassium Perchlorate and Ammonium, Sodium, and Potassium Chloride

PHILIP R. MARSHALL and HERSCHEL HUNT
Department of Chemistry, Purdue University, Lafayette, Ind.

The solubilities of ammonium chloride, potassium chloride, sodium chloride, ammonium perchlorate, potassium perchlorate, and sodium perchlorate at -33°, 0°, 25°, and 50° C. in liquid ammonia have been determined as well as the solubilities of the salt pairs and the ternary mixtures necessary to prepare the quaternary phase diagrams for the two chemical processes:

$$NaClO_4 + NH_4Cl \rightleftharpoons NH_4ClO_4 + NaCl \quad (1)$$

$$\text{and } KClO_4 + NH_4Cl \rightleftharpoons NH_4ClO_4 + KCl \quad (2)$$

These equilibrium diagrams show the possibility of carrying out the above processes in liquid ammonia.

The research of Grubb, Chittum, and Hunt (*1*), Hunt (*2*), Hunt and Boncyk (*3*), Hunt and Larsen (*4*), Johnson and Krumboltz (*5*), Linhard (*6*), Linhard and Stephan (*7*), Patscheke (*8*), Patscheke and Tanne (*9*), Plank and Hunt (*10*), and Ritchey and Hunt (*11*) indicates that Reactions 1 and 2 may be carried out in liquid ammonia at temperatures ranging from -33° to 50° C. Because sodium chloride and potassium chloride are relatively insoluble, these reactions should go nearly to completion. By controlling the concentrations the type of ammonium perchlorate crystal can be regulated and ammonium perchlorate can be prepared with physical properties suitable for use as an oxidizing agent in solid propellants.

EXPERIMENTAL PROCEDURE

Two types of apparatus were used for measuring the solubilities of the salts in liquid ammonia (Figures 1 and 2). The apparatus shown in Figure 1 could also be used for measuring the vapor pressures of the solutions.

Process A. This apparatus was evacuated and heated to drive out moisture. A weighed amount of salt was placed in the bulb with a glass-covered iron stirrer. The proper amount of salt was previously determined in a trial run. The apparatus was again pumped out to remove air and moisture. Dry ammonia in excess was then condensed on the salt and in the bulb labeled ammonia. If the vapor pressure of the solution is low, no ammonia is condensed in the latter. The apparatus was cooled with dry ice and carbon tetrachloride for the condensation process. With sufficient ammonia in both bulbs, valve 1 was closed and the system evacuated to remove hydrogen.

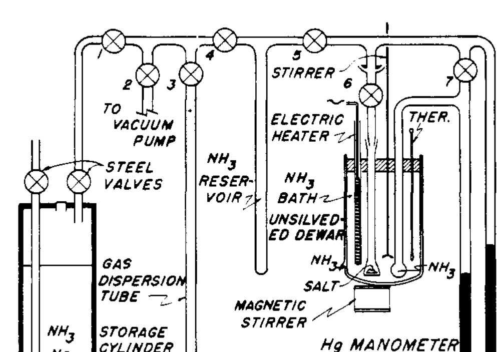

Figure 1. Solubility and vapor pressure apparatus