

---

## EVIDENCE OF ASSOCIATION IN THE DIMETHYL FORMAMIDE-WATER SYSTEM

FORREST BLANKENSHIP and BERT CLAMPITT,  
University of Oklahoma, Norman

Dimethyl formamide, ( $\text{CH}_2$ ),  $\text{NCHO}$ , became industrially available in large quantities in the early part of 1950. Very little physical data for the dimethyl formamide-water system existed; the present study was undertaken to supply part of the missing information.

Further interest accrued from the possibility that dimethyl formamide might be expected to form one or more hydrates, and that the resulting association in the liquid state could be compared or contrasted with that recently reported to the Academy for the tetrahydrofuran-water system (6).

No mention of a hydrate of dimethyl formamide could be found in the literature. As shown below, a dihydrate is found, but this hydrate is not related to the hydrocarbon-type hydrate exhibited by tetrahydrofuran. The dimethyl formamide (DMF) was supplied by the E. I. du Pont de Nemours & Co., and was used without further purification.

### EXPERIMENTAL

**FREEZING POINTS.** Freezing point data were obtained through the use of an alcohol and dry-ice bath which permitted a minimum temperature of  $-72^\circ\text{C}$ . The thermometer was calibrated at  $0^\circ\text{C}$ . only.

Difficulty with supercooling was encountered, and seeding was necessary in some cases. A marked increase in viscosity at low temperature was noted. Also, at temperatures  $5^\circ$  or  $10^\circ$  above the freezing point of solutions containing

TABLE I  
Freezing Point in Degrees Centigrade

MOLE % DMF	TRIAL 1	TRIAL 2	TRIAL 3	TRIAL 4	TRIAL 5	AVERAGE
0	0	1	0	0	0	0
1.3	-2	-1	-2	-1	-2	-1.5
2.7	-3	-3.5	-3	-2.5	-3	-3
5.8	-5.75	-5.0	-6.0	-6.0	-6.0	-5.75
9.5	-11.25	-10.25	-10.50	-12.0	-11.0	-11.0
14.2	-19.5	-18.5	-19.5	-20.0	-20	-19.50
19.8	-32.5	-34.0	-33.5	-32	-33	-33.0
27.5	-49.0	-50	-51.25	-60.0	-50	-50.5
36.5	-51.25	-49	-50	-49	-51	-50.5
49.8	-57.5	-57.0	-56.5	-57	-57	-57.0
60.7	-68	-66	-66	-65	-65	-65
69.0	below -72					
86.0	below -72					
100.0	-63	-63	-63	-63	-63	-63

TABLE II

Density ( $g/cm^3$ ) at 25°

MOLE % DMF	TRIAL 1	TRIAL 2	TRIAL 3	TRIAL 4	TRIAL 5	AVERAGE
0	.9971 <sup>1</sup>					.9971
5	.9960	.9958	.9963	.9956	.9961	.9960
10	.9956	.9955	.9964	.9954		.9957
20	.9948	.9938	.9928	.9941		.9939
30	.9969	.9947	.9940	.9897	.9903	.9931
40	.9900	.9879	.9895	.9844	.9869	.9881
50	.9796	.9802	.9762	.9751	.9752	.9773
60	.9747	.9712	.9679	.9727	.9727	.9718
80	.9616	.9584	.9545	.9602	.9592	.9588
100	.9487	.9452	.9442	.9469	.9463	.9463

TABLE III

Surface Tension (Dynes/cm) at 25°

MOLE % DMF	TRIAL 1	TRIAL 2	TRIAL 3	TRIAL 4	TRIAL 5	AVERAGE
0	72 <sup>1</sup>					72.00
5	58.50	58.70	58.10	57.80	59.15	58.45
10	53.00	52.80	54.20	53.30	53.15	53.29
20	46.50	48.00	47.50	46.25	48.00	47.25
30	45.50	47.00	46.50	47.20		46.55
40	44.00	44.25	43.20	44.60		44.01
50	42.00	43.80	41.10	41.90		42.20
60	39.50	39.00	40.80	40.00	40.50	39.96
80	36.25	38.00	36.90	37.00		37.05
100	34.20	36.00	35.40	35.40	35.00	35.20

TABLE IV

Viscosity (Millipoise) at 25°

MOLE % DMF	TRIAL 1	TRIAL 2	TRIAL 3	TRIAL 4	TRIAL 5	AVERAGE
0	9.1 <sup>1</sup>					9.10
5	13.06	14.59	13.19	15.14	14.92	14.18
10	16.84	18.15	17.09	18.39	18.05	17.70
20	21.82	23.20	22.99	24.00	23.70	23.12
30	25.20	25.30	25.20	25.30		25.25
40	27.55	22.70	27.40	22.60		25.06
50	21.60	19.10	18.90	19.20		19.73
60	16.91	15.42	15.05	15.82	15.90	15.77
80	10.51	10.59	11.03	9.89	10.70	10.65
100	9.03	8.78	8.45	8.54	8.56	8.69

<sup>1</sup>Lange, Handbook of Chemistry, Sixth Edition (1946).

appreciable amounts of dimethyl formamide, a large amount of gas (presumably air) was evolved.

**DENSITIES, VISCOSITIES, AND SURFACE TENSIONS.** These measurements were assigned to a laboratory class of 20 students in physico-chemical measurements. Stock solutions were mixed by weight to give selected mol per cents and supplied to the students for measurements with individual apparatus. The data were compiled from a critical screening of the independent measurements reported by the students.

Densities were determined by means of pycnometers, viscosities by Ostwald viscometers, and surface tensions by capillary rise. The procedures are described in a widely used laboratory manual (2).

### RESULTS

The measurements are summarized in Tables I, II, III, and IV. The maximum deviation occurring in the data used to obtain the averaged values is 2% for freezing point, 0.5% for density, 8% for viscosity, and 3% for surface tension.

### DISCUSSION

The freezing point curve (Fig. 1) shows evidence of a compound containing 33% dimethyl formamide and changes of slope occur at approximately this same composition on the other curves (Figs. 2, 3, and 4).

Although the hydrate melts at  $-50^{\circ}\text{C}$ ., there is apparently sufficient persistence of hydrate structure, or association related to hydrate formation, to cause appreciable deviation from ideal behavior at  $25^{\circ}\text{C}$ .

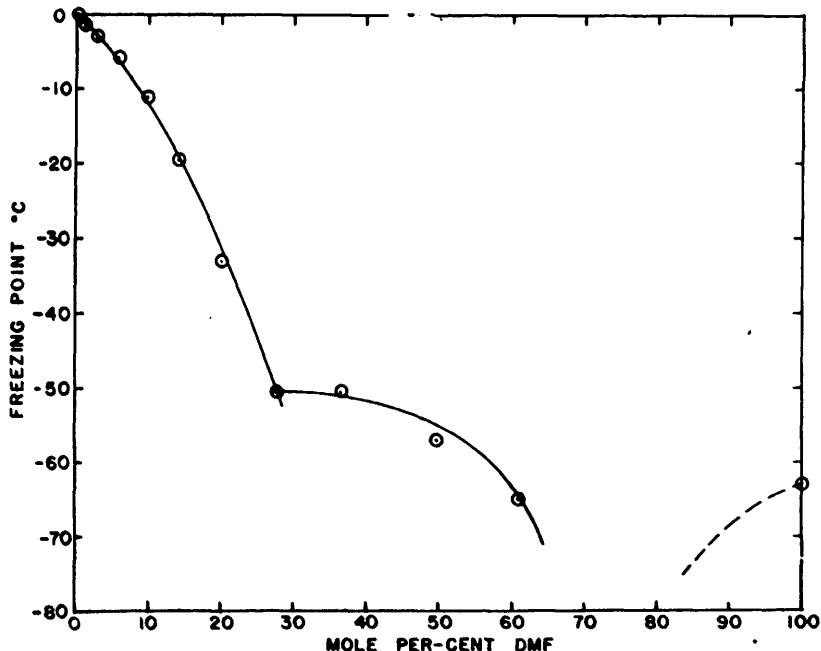


FIGURE 1. Freezing Point in DMF-H<sub>2</sub>O System

In a preliminary estimation of partial molal volumes based on the density data presented in Fig. 2, Mr. Kenneth Lewis obtained the following results (4):

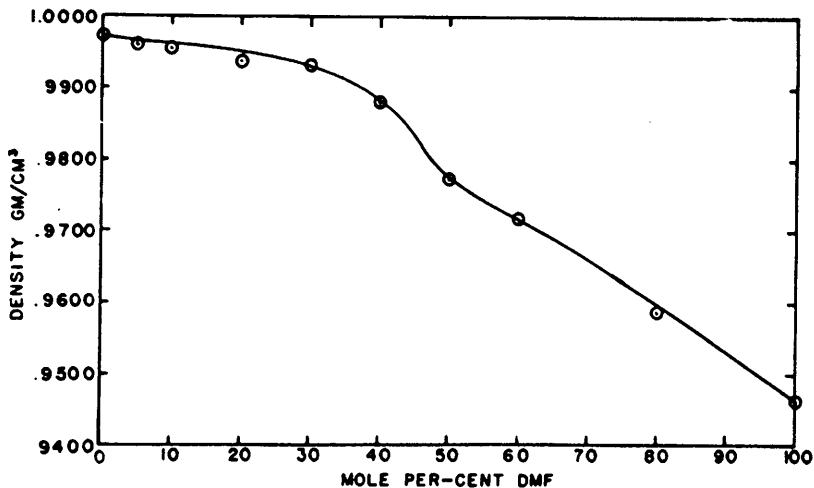


FIGURE 2. Density of DMF-H<sub>2</sub>O System at 25°C.

The partial molal volume of water remains constant at about 18.07 ml. on the water-rich side of the break in the density curve, and remains constant at about 15.92 ml. on the other side. The dimethyl formamide has an essentially constant partial molal volume of 73.71 ml. and 77.2 ml. in these same regions,

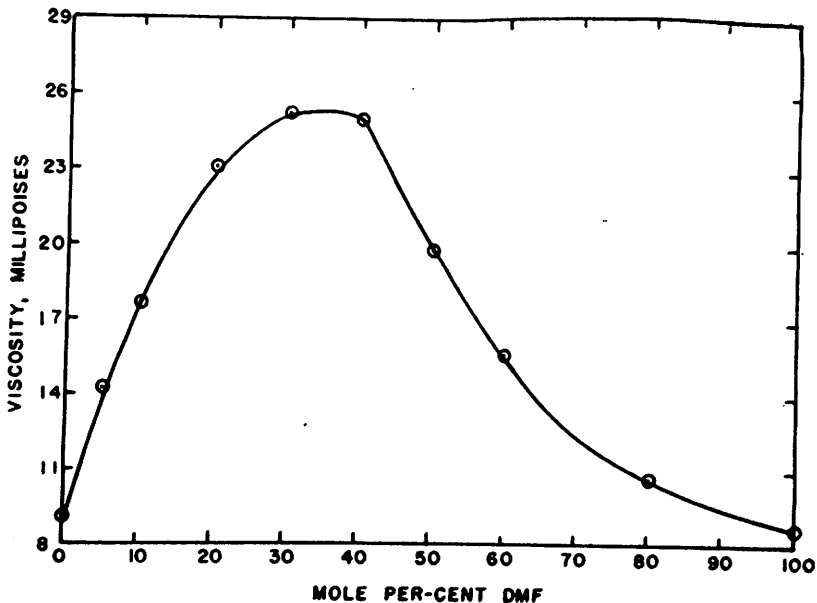


FIGURE 3. Viscosity of DMF-H<sub>2</sub>O System at 25°C.

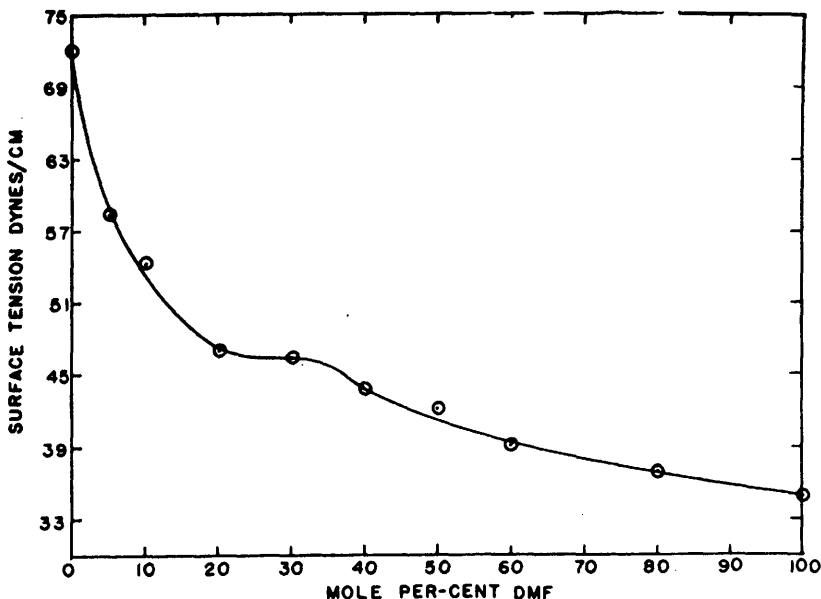


FIGURE 4. Surface Tension of DMF-H<sub>2</sub>O System at 25°C.

respectively. At concentrations of dimethyl formamide near but above the compound composition, there appears to be a maximum in the partial molal volume of dimethyl formamide, and a minimum for water.

Such maximum-minimum behavior is inverse to that found for the tetrahydrofuran-water system (1).

In view of the maximum in the viscosity curve (Fig. 3), and the change in slope in the surface tension curve, (Fig. 4), which are apparently related to the formation of a dihydrate of dimethyl formamide, it is interesting to note that formamide forms a monohydrate (3), and further that the formamide-water system has no maximum in its viscosity curve, no inflection point in the density curve (5). In other words, not all types of hydrates give rise to evidence of association in aqueous solutions at room temperature (7).

Acknowledgment is gratefully extended to the Office of Naval Research for support of a project which gave rise to this paper as a side issue, and for partial support of the work involved in preparing this paper.

#### BIBLIOGRAPHY

1. BLANKENSHIP, F. F., and E. L. LIPPERT, JR. 1950. An effect of association in the tetrahydrofuran-water system, partial molal volumes at 25°C. Paper in preparation. University of Oklahoma, Norman, Oklahoma.
2. DANIELS, F., J. H. MATHEWS, J. W. WILLIAMS, ET AL. 1949. Experimental physical chemistry, 4th edition. New York: McGraw-Hill Book Co., Inc.
3. ENGLISH, S. and W. E. S. TURNER. 1915. The freezing-point diagrams of formamide with water and the aliphatic acids, and their bearing on the interpretation of viscosity measurements. *J. Chem. Soc. (London)* 107: 779-783.

4. LEWIS, KENNETH. 1950. Private communication. Phillips University, Enid, Oklahoma.
  5. MERRY, E. W. and W. E. S. TURNER. 1914. The viscosities of some binary liquid mixtures containing formamide. *J. Chem. Soc. (London)* 105: 748-759.
  6. MONTGOMERY, D., B. O. HESTON, and F. F. BLANKENSHIP. 1949. Evidence of association in the tetrahydrofuran-water system. *Proc. Oklahoma Acad. Sci.* 30: 140-144.
  7. PICKERING, S. U. 1893. Some compounds of alkylamines and ammonia with water. *J. Chem. Soc. (London)* 63: 141.
-