
EVIDENCE OF ASSOCIATION IN THE TETRAHYDROFURAN-WATER SYSTEM

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INTRODUCTION. Lattice hydrates have been under investigation at the University of Oklahoma since 1945 (1, 5). The more familiar types of hydration due to hydrogen bonding and to co-ordination are fairly well understood and are encountered with substances showing complete water miscibility. By contrast, lattice hydrates, formed by liquids with so little affinity for water as to be insoluble, have not been thoroughly studied or explained. In general, they exist only in the solid state and melt or decompose to form two immiscible liquid layers since the compound composition lies well within the region of immiscibility.

H. A. Palmer, an ONR fellow, has shown that tetrahydrofuran forms a hydrate which contains a relatively large number of molecules of water and apparently is a member of the lattice hydrate group in spite of the fact that tetrahydrofuran is completely miscible with water (4).

Accordingly, it was of interest to examine the tetrahydrofuran-water system for evidence of association in the liquid state. Such evidence is sometimes found in data on vapor pressure, viscosity, surface tension and other physical properties of solutions.

Very little physical data exists; before its introduction as an industrial intermediate and solvent early in 1949, tetrahydrofuran was not commonly available.

Evidence of positive deviation from Raoult's Law was provided by the minimum boiling azeotrope containing 4.3% water and boiling at 63.4-63.8°C (2). The normal boiling point of tetrahydrofuran was 65.4°C. This did not rule out the possibility of association in the water-rich concentration range.

EXPERIMENTAL. Data on viscosity and surface tension were not available, and since precise results were not required, the measurements were assigned to laboratory students enrolled in a Physico-Chemical Measurement course at the University of Oklahoma. The tetrahydrofuran had a refractive index of 1.4057 at 20°C and was used as obtained from the Columbia Organic Chemical Company, without further purification. Densities of solutions were obtained by means of student-type Westphal density balances, and all calibrations were made on distilled water. The procedures were those described in a widely used laboratory manual (3).

Surface tensions were measured by the capillary rise method on solutions that were mixed by volume.

Viscosities were measured with Ostwald viscometers. In this case stock solutions were mixed by weight. Thermostatting was accomplished manually at 0, 20, 30, and 40°C using large beakers of water. The solution containing 25% by weight tetrahydrofuran was supercooled at 0°C, and in a few instances the hydrate crystallized. However, the supercooling tendency was sufficient to permit reproducible viscosity measurements through the metastable region.

TABLE I

Surface Tension (Dynes/Cm) at 25°C.

STUDENT	VOLUME	PERCENT		TETRAHYDROFURAN	
GROUP	0	25	50	75	100
A	71.97 dynes/cm	34.2 dynes/cm	30.4 dynes/cm	29.1 dynes/cm	26.9 dynes/cm
B	71.97 dynes/cm	35.3 dynes/cm	30.8 dynes/cm	28.4 dynes/cm	26.6 dynes/cm
C	71.97 dynes/cm	32.8 dynes/cm	29.6 dynes/cm	28.7 dynes/cm	26.3 dynes/cm
D	71.97 dynes/cm	34.5 dynes/cm	29.9 dynes/cm	29.0 dynes/cm	27.4 dynes/cm
E	71.97 dynes/cm	32.8 dynes/cm	27.5 dynes/cm	26.0 dynes/cm	25.0 dynes/cm
F	71.97 dynes/cm	33.6 dynes/cm	30.2 dynes/cm	33.3 dynes/cm	26.2 dynes/cm
Av.	71.97* dynes/cm	33.6 Dynes/cm	29.7 dynes/cm	29.0 dynes/cm	26.4 dynes/cm

*Lange, Handbook of Chemistry, Sixth Edition, (1946).

TABLE II

Viscosity of Tetrahydrofuran — Water Solutions (Millipoises)

	WEIGHT PERCENT TETRAHYDROFURAN											
STUDENT			0%				25%				50%	
GROUP	0°C	20°C	30°C	40°C	0°C	20°C	0°C	20°C	30°C	40°C	30°C	40°C
A					42.5	19.2	13.3	11.2	43.7	20.3	15.0	12.8
B					41.5	19.8	13.4	11.6	42.2	20.8	15.1	12.0
C					42.6	19.7			42.1	21.6		
D					41.2	19.0			41.8	20.8		
E										21.2		
F										20.4		
Average	17.94*	10.09*	8.004*	6.536	41.9	19.4	13.3	11.3	42.2	20.9	15.0	12.4

	WEIGHT PERCENT TETRAHYDROFURAN								
STUDENT GROUP	0°C	20°C	30°C	40°C	0°C	20°C	30°C	40°C	0°C
			75%				100%		
A		21.5	13.5	10.4	6.61	6.70	5.48	4.94	4.26
B		21.7	13.4	10.1		6.72	5.55	4.65	
C		22.1	12.7			6.32	5.34		
D		22.7	14.7			7.46	5.50		
E		22.9	12.9			6.41	5.58		
F			13.3						
Av.		22.2	13.4	10.2	6.61	6.52	5.49	4 80	4.26

*Lange, Handbook of Chemistry, Sixth Edition, (1946).

RESULTS. The values reported in Tables I and II are the result of a careful screening of students' reports and the rejection of doubtful values. The maximum deviation from the median was 5% for surface tension, and 2.5% for viscosity except at 30° and 40° where only a few students worked and selected values were chosen. For graphing in Figure 1 and 2 compositions were converted to mole percent.

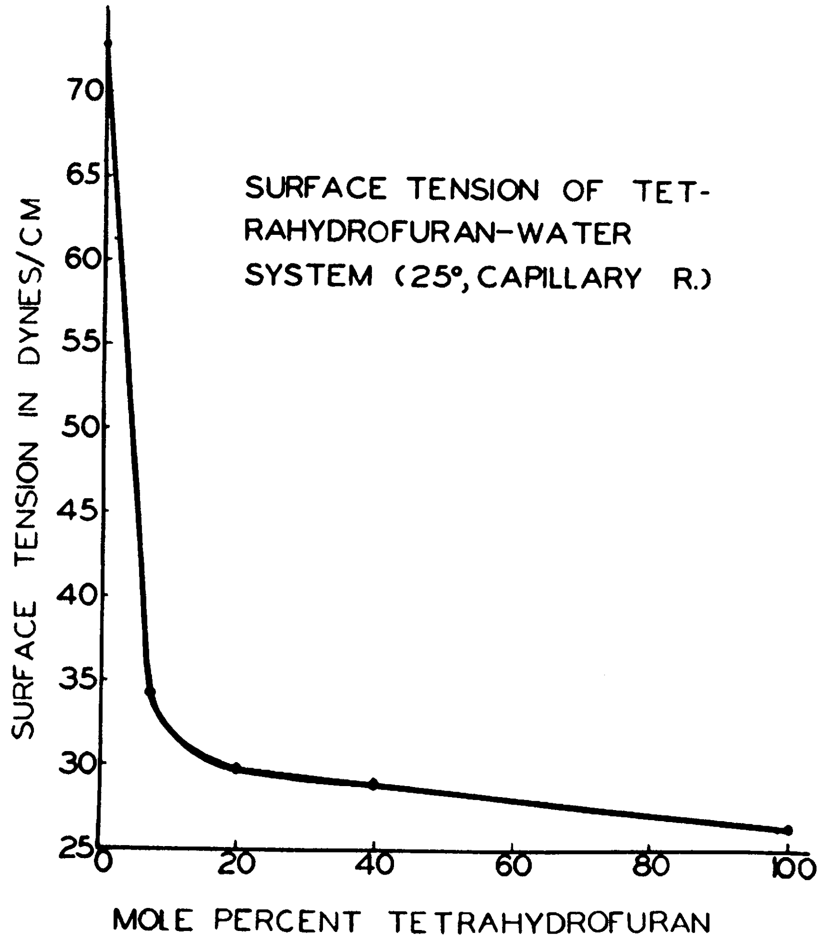

FIGURE 1

Conclusions. The marked viscosity maximum at about 15 mole percent tetrahydrofuran indicates a high degree of association. The fact that the temperature coefficient is greater for the maximum than for pure water may mean a higher degree of association than is found in pure water because the "energy of activation" for viscosity presumably depends, among other things, on the size of "hole" required for "rolling" aggregates. According to the absolute reaction rate theory, larger "holes" for bigger aggregates require larger energies of activation giving correspondingly greater temperature coefficients.

Possibly the surface tension curve should be considered as two contiguous curves. In the region from pure water to the break, the mixtures are comprised of water and hydrated aggregates. Beyond the break, the mixtures are comprised of hydrated aggregates and tetrahydrofuran.

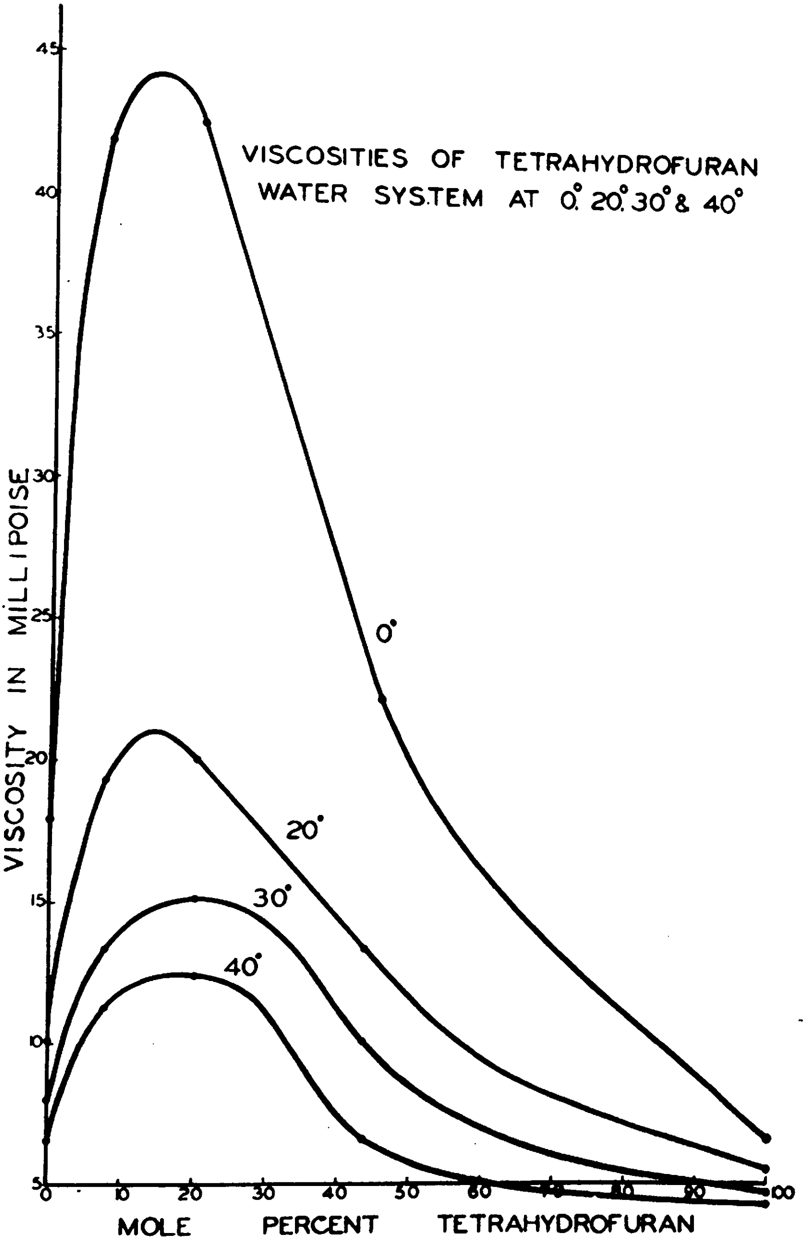
VISCOSITIES OF TETRAHYDROFURAN WATER SYSTEM AT 0° 20° 30° & 40°
VISCOSITY IN MILLIPOISE
45
40
35
30
25
20
15
10
5
0°
20°
30°
40°
0
10
20
30
40
50
60
70
80
90
100
MOLE PERCENT TETRAHYDROFURAN

FIGURE 2.

This same mechanism or a related one may be operating in other systems showing a similar viscosity and surface tension behavior, as for example, water solutions of methanol and ethanol.

LITERATURE CITED

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