

# Surface Tension of *p*-Difluorobenzene, Hexafluorobenzene, and Some *p*-Difluorobenzene-*p*-Xylene Solutions

RICHARD S. MYERS, BRIAN A. BERENBACH, and H. LAWRENCE CLEVER  
Department of Chemistry, Emory University, Atlanta, Ga. 30322

The surface tension of *p*-difluorobenzene and hexafluorobenzene was measured between 25° and 45° C. by the maximum bubble pressure method. The surface tension and density of eight *p*-difluorobenzene-*p*-xylene mixtures were measured at 30° C. Both the excess volume and excess surface tension of the solutions show a change in sign near 0.8 mole fraction *p*-difluorobenzene.

THE MAXIMUM bubble pressure method was used to measure the surface tension of *p*-difluorobenzene and hexafluorobenzene at 5° intervals from 25° to 45° C. and of eight *p*-difluorobenzene-*p*-xylene solutions at 30° C. Densities of the *p*-difluorobenzene and the *p*-difluorobenzene-*p*-xylene solutions were measured.

## EXPERIMENTAL

**Materials.** *p*-Difluorobenzene, Columbia Organic Chemical Co., Inc., distilled immediately before use through a 26-inch stainless steel helice-packed column (b.p. 88.8° C.).

Hexafluorobenzene, Imperial Smelting Corp., Avonmouth, U. K., purified by directional freezing and furnished by R. Battino, Wright State University (5), 99.993 mole % by GLC.

*p*-Xylene, Eastman White label, shaken with concentrated H<sub>2</sub>SO<sub>4</sub>, water-washed until neutral, dried and distilled over sodium (b.p. 138.4° C.).

**Apparatus.** Surface tensions were measured by the maximum bubble pressure method on apparatus built and described by Quayle (11). This method involves the measurement of the pressure differential developed within the system as bubbles of dry air presaturated with vapor are drawn alternately through two tubes, with different radii, immersed to the same depth in a liquid. The pressure differential is developed by a mercury aspirator and measured on a xylene-filled manometer. The larger tube has a diameter of 0.1624 cm., the smaller tube is not measured, but the bubbler is calibrated with purified samples of benzene, *n*-heptane, and *n*-octane of known surface tension. The bubbler air was dried and presaturated with sample vapor to prevent evaporation and cooling of the sample surface during the measurement. Surface tensions are normally reproducible to 0.03 dyne per cm.

Densities were measured in 15-ml. density bottles with a true-bore capillary neck of 1.000 ± 0.007-mm. diameter. Solutions were prepared in special weighing and mixing bottles (1), and the composition was corrected for material in the vapor phase assuming Raoult's law. The temperature was controlled to ±0.01° C. by a Bayley Instrument Co. thermoregulator, Model 123, for the surface tension and density measurements. Temperatures were read on a 0.1° graduated thermometer which had been calibrated against a National Bureau of Standards calibrated thermometer.

## RESULTS AND DISCUSSION

The surface tensions of *p*-difluorobenzene and hexafluorobenzene are given in Table I. Densities required to convert the maximum bubble pressure measurement to surface tension were measured for *p*-difluorobenzene and taken from the literature (3) for hexafluorobenzene. The least squares equations

$$\sigma = 29.17 - 0.106 t$$

$$d = 1.18925 - 0.001338 t$$

reproduce the *p*-difluorobenzene surface tension,  $\sigma$ , to ±0.02 dyne per cm. and the density,  $d$ , to ±0.0003 gram per cc. over the 25° to 45° C. temperature range. Earlier values (4) of surface tension and density at 20° C. are also reproduced within experimental error by these equations. The equation

$$\sigma = 24.62 - 0.113 t$$

reproduces the hexafluorobenzene surface tension to ±0.04 dyne per cm. A surface tension value of 21.4 dynes per cm. at 25° C. is reported in the industrial literature (13).

The changes in free energy,  $\sigma$ , entropy,  $S = -(\delta\sigma/\delta T)$ , enthalpy,  $H = \sigma - T(\delta\sigma/\delta T)$ , and latent heat,  $l = -T(\delta\sigma/\delta T)$ , of forming 1 sq. cm. of new surface (7) were calculated from the above equations for *p*-difluorobenzene and hexafluorobenzene. The thermodynamic values at 30° C. are compared with those for benzene in Table II.

The surface tension and density of the eight *p*-difluorobenzene-*p*-xylene solutions at 30° C. are given in Table III. The excess surface tension and excess volume were calculated from the data and are shown as a function of composition in Figure 1. The curves of Figure 1 were calculated from the fitted excess properties equation (10)

$$\text{Excess property} = X_1 X_2 \sum A_n (1 - 2X_2)^n$$

where  $X_1$  is the *p*-xylene mole fraction,  $X_2$  is the *p*-difluorobenzene mole fraction, and  $n$  and  $A_n$  are the fitting parameters (Table IV). The equation reproduces the solution surface tension with an average deviation of ±0.03 dyne per cm.

Table I. Surface Tension of *p*-Difluorobenzene and Hexafluorobenzene

Temp., ° C.	<i>p</i> -Difluorobenzene		Hexafluorobenzene Surface Tension, Dynes/Cm.
	Surface tension, dynes/cm.	Density, g./cc.	
25	26.50	1.1557	21.80
30	25.98	1.1491	21.16
35	25.45	1.1430	20.69
40	24.90	1.1350	20.13
45	24.41	1.1293	19.48

Table II. Thermodynamic Changes on Forming New Surface, 30° C.

Compound	Gibbs Free			
	Energy, Ergs/ Sq. Cm.	Entropy, Ergs/Deg. Sq. Cm.	Enthalpy, Ergs/ Sq. Cm.	Latent Enthalpy, Ergs/ Sq. Cm.
Benzene	27.48	0.134	68.1	40.6
<i>p</i> -Difluoro- benzene	25.98	0.106	58.1	32.1
Hexafluoro- benzene	21.16	0.113	55.5	34.2

Table III. Surface Tension, Density, and Excess Surface Tension and Volume of *p*-Difluorobenzene-*p*-Xylene Solutions, 30° C.

<i>p</i> -Difluorobenzene Mole Fraction	Surface Tension Dynes/Cm.	Excess Surface Tension	Density, G./Cc.	Excess Volume, Cc./Mole
0.0000	27.29	0.00	0.8522	0.00
0.0988	27.10	-0.06	0.8756	0.06
0.1994	26.78	-0.25	0.9004	0.11
0.3368	26.62	-0.23	0.9367	0.12
0.5346	26.43	-0.21	0.9925	0.17
0.5936	26.45	-0.06	1.0105	0.14
0.7481	26.40	+0.09	1.0600	0.09
0.7992	26.29	0.05	1.0777	0.02
0.9001	26.14	0.03	1.1133	-0.045
1.0000	25.98	0.00	1.1491	0.00

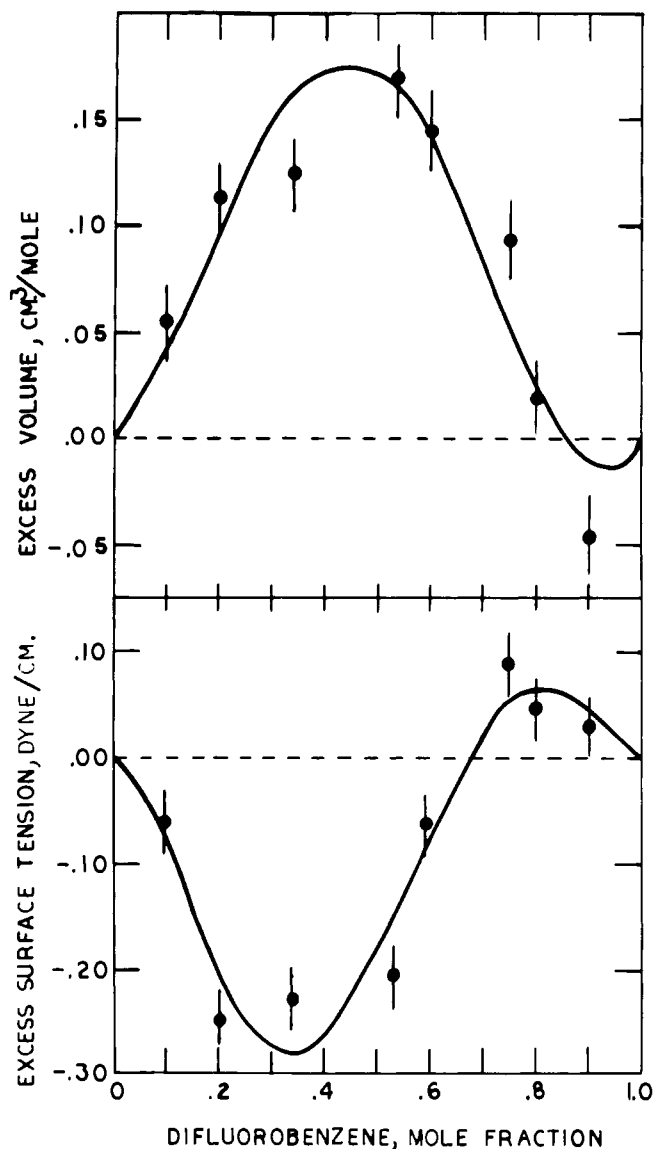


Figure 1. *p*-Difluorobenzene-*p*-xylene solutions  
Upper. Excess volume ( $\pm 0.03$  cc./mole.)  
Lower. Excess surface tension ( $\pm 0.03$  dyne/cm.) vs. mole fraction  
Individual and composite isotherms, 30° C.

Table IV. Parameters for Excess Properties Equation

Excess Property	<i>n</i>	<i>A<sub>n</sub></i>
Surface tension	1	-0.737
	2	-2.084
	3	0.816
	4	1.907
Volume	1	0.684
	2	0.358
	3	-0.813

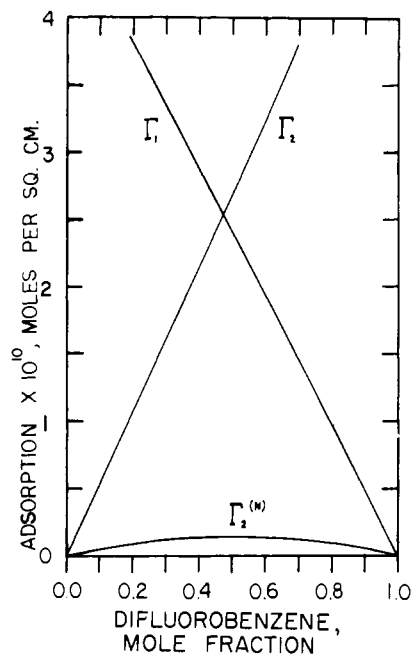


Figure 2. *p*-Difluorobenzene-*p*-xylene solutions

As expected, the *p*-difluorobenzene decreased the solution surface tension, although the other *p*-difluorobenzenes increase (2) the surface tension in *p*-xylene solutions. The change in sign of the excess surface tension was unexpected. Obviously, the ideal equations of Guggenheim (6) and Hildebrand and Scott (8), which are essentially one-parameter equations, do not apply to a solution for which the excess surface tension changes sign.

The excess surface tension equation was used to calculate the Gibbs surface excesses,  $\Gamma_2^N$ ,  $\Gamma_1$ , and  $\Gamma_2$ , which are related (9, 12) by

$$\Gamma_2^N = -\frac{X_1 X_2}{RT} \frac{\delta \sigma}{\delta X_2} = \Gamma_2 X_1 - \Gamma_1 X_2$$

The equation assumes ideal bulk behavior. The surface excess  $\Gamma_2^N$  is the excess of solute in the surface of unit area over a region in the bulk liquid containing the same number of moles of all species, and is independent of any surface model. The surface excesses  $\Gamma_1$  and  $\Gamma_2$  are the moles of component 1 or 2 per unit area in the surface and require a model of the interface and a knowledge of the individual component surface areas. Figure 2 shows the composite,  $\Gamma_2^N$  vs.  $X_2$ , and individual,  $\Gamma_1$  vs.  $X_2$ , isotherms assuming spherical molecules with surface areas at 30.1 and 35.0 sq. Å. per molecule for *p*-difluorobenzene and *p*-xylene, respectively.

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## NOMENCLATURE

- $A_e$  = fitting parameter in excess properties equation  
 $H$  = enthalpy of forming new surface, ergs per sq. cm.  
 $n$  = fitting parameter in excess properties equation  
 $R$  = gas constant  
 $S$  = entropy of forming new surface, ergs per deg. per sq. cm.  
 $t$  = temperature, °C.  
 $T$  = temperature, °K.  
 $X_i$  = mole fraction of component  $i$   
 $d$  = density, g. per cc.  
 $\Gamma_i$  = individual Gibbs surface excess of component  $i$ , moles per sq. cm.  
 $\Gamma_2^N$  = composite Gibbs surface excess, moles per sq. cm.  
 $\Sigma$  = summation sign  
 $\sigma$  = surface tension, dynes per cm. or free energy of forming new surface, ergs per sq. cm.

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# Physical Properties of Some Sulfur and Nitrogen Compounds

W. J. LANUM and J. C. MORRIS

Laramie Petroleum Research Center, Bureau of Mines,  
U.S. Department of Interior, Laramie, Wyo. 82070

**Physical properties were determined on purified samples of 38 organic sulfur compounds and 18 organic nitrogen compounds. Most of the compounds were donated by interested laboratories for augmenting the spectral data on these types of compounds. Special handling techniques to prevent contamination or decomposition were employed during purification, storage, and property measurement. Boiling point, freezing point, density at 20° C., and refractive index (sodium D and mercury g lines) at 20° C. were determined. Derived functions calculated are refractivity intercept, specific dispersion, and molecular refraction.**

**T**O SUPPLY fundamental data on the sulfur and nitrogen compounds that occur in petroleum, the Bureau of Mines prepared standard samples of organic sulfur and nitrogen compounds as reference materials and carried out intensive studies of their properties (4, 5, 6, 8).

An important adjunct of this work was a program to speed the acquisition and publication of spectral data on additional compounds of these types. A bank of over 350 sulfur and nitrogen compounds of reliable purity, ranging in amounts from a few milligrams to several grams, was accumulated. Most of the compounds in this phase of the work were donated, although a few were purchased. Spectral data on these compounds were determined by cooperating oil company laboratories and the Bureau of Mines and were published in the Catalogs of Selected Spectral Data edited by American Petroleum Institute Research Project 44 (1).

This paper reports the values for the physical properties of 56 of these small-scale samples. Included in the tables are the catalog serial numbers for the mass, ultraviolet, infrared, and Raman spectra obtained on these samples.

## EXPERIMENTAL

**Purification.** Purification procedures were similar to those reported previously by this laboratory (4, 5, 6, 8) on organic sulfur and nitrogen compounds. Three distillation columns were used: a column 30 cm. in length and 1.1 cm. in diameter packed with stainless steel helices, a spinning band column 30 cm. in length and 1.2 cm. in diameter, and a concentric tube column approximately 100 cm. in length and 1.0 cm. in diameter. Each column was vacuum-jacketed and equipped with automatic take-off and reflux ratio control.