Report 2867

NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER
Washington, D.C. 20007

NAVAL SHIP RESEARCH AND DEVELOPMENT LABORATORY
Annapolis, Maryland 21402

APPLICATION OF A THEORY OF BINARY SOLUTION SURFACE TENSION TO INTERFACIAL TENSION PHENOMENA

By
Donald J. Cotton

MATERIALS LABORATORY

RESEARCH AND DEVELOPMENT REPORT

July 1969

Report 2867

APPLICATION OF A THEORY OF BINARY SOLUTION SURFACE TENSION TO INTERFACIAL TENSION PHENOMENA

By
Donald J. Cotton

July 1969 MATLAB 333 Report 2867

ABSTRACT

A theoretical equation which describes interfacial tension of binary solutions as a function of concentration and of the interfacial tensions and the molecular areas of the pure components has been applied to organic and aqueous systems against water and mercury.

The derived equation gives information as to molecular area and orientation of adsorbed molecules at an interface. Gibbs' equation, while applicable to all interfaces, generates no detailed structural information. The derived equation is useful for determining the interfacial structure of solutions approximating its theoretical model.

ADMINISTRATIVE INFORMATION

This research was supported by the IR/IED Program, Subproject ZR 011 01 01, Task 05600, Assignment A821-147. This report is based on a paper to be published in the Journal of Physical Chemistry.

Dr. J. L. Shereshefsky, Department of Chemistry, Howard University, Washington, D. C., was co-author of the paper on which this report is based.

TABLE OF CONTENTS

NAVAL SHIP RESEARCH AND DEVELOPMENT LABORATORY

APPLICATION OF A THEORY OF BINARY SOLUTION SURFACE TENSION TO INTERFACIAL TENSION PHENOMENA

By
Donald J. Cotton

INTRODUCTION

Liquid environments of naval machinery frequently contain dissolved polar molecules which either are deliberately incorporated to provide corrosion and wear resistance or are present as contamination. These polar molecules have a large effect upon the surfaces of immersed machinery. Therefore, it is of importance to the Navy to understand the surface properties of liquid systems.

It is the purpose of this report to show the relevance of a theory of surface tension of solutions by J. L. Shereshefsky[1] to interfacial tension of solutions and to show its application to aqueous solutions of organic acids against mercury, binary organic mixtures against mercury, and binary mixtures against water. It is important to indicate that in these systems neither component of the solution phase is appreciably miscible with the other phase which forms the interface.

THEORETICAL CONSIDERATIONS

The equation which relates the interfacial tension with the concentration of the solution and which may be derived in a manner analogous to that of the surface tension is given by

$$\sigma = \sigma_{13} - \frac{\Delta\sigma_0 \, X_{2b} e^{\Delta F_s/RT}}{1 - X_{2b}(e^{\Delta F_s/RT} - 1)} \qquad \ldots(1)$$

Designating the phase forming the interface with the solution with Subscript 3, and the solvent and solute with the customary Subscripts 1 and 2, respectively, σ is the interfacial tension at mole fraction X_{2b}, and σ_{13} is the tension in the interface

[1] Superscripts refer to similarly numbered entries in Appendix A.

between pure solvent and Phase 3. The terms $\Delta\sigma_0$ and ΔF_s are defined by the expressions

$$\Delta\sigma_0 = \sigma_{13} - \sigma_{23} \qquad .....(2)$$

and

$$\Delta F_s = \Delta\sigma_0 \, A_2/t \qquad .....(3)$$

where σ_{23} is the tension between pure solute and Phase 3, A_2 is the area per mole of solute in a unimolecular layer, and t is the number of layers in the interface. It is seen that ΔF_s represents the change in the free interfacial energy when a mole of solute of area, A_2/t, and interfacial tension, σ_{23}, displaces an equal are of interfacial tension, σ_{13}.

The reciprocal form of Equation (1) which lends itself to easier application is given by

$$\frac{X_{2b}}{\Delta\sigma} = \frac{1}{\Delta\sigma_0} \, e^{-\Delta F_s/RT} + \frac{X_{2b}}{\Delta\sigma_0} \left(1 - e^{-\Delta F_s/RT}\right) \qquad .....(4)$$

where $\Delta\sigma$, the change in the interfacial tension, is given by

$$\Delta\sigma = \sigma_{13} - \sigma \qquad .... (5)$$

The constants, ΔF_s and $\Delta\sigma_c$, of Equation (4) are evaluated from the slope, m, and intercept, b, with the aid of the expressions

$$m/b = e^{\Delta F_s/RT} - 1 \qquad .....(6)$$

and

$$m + b = 1/\Delta\sigma_0 \qquad .....(7)$$

TEST OF THE DERIVED EQUATION WITH INTERFACIAL TENSION DATA

The derived equation was tested with interfacial tension data in literature for solutions of dimethylaniline in heptane and in benzene[2], of hexanoic and of octanoic acid in benzene[3], and of decanol and octanol in benzene[4] against water. A linear relationship was obtained for each data set (see Figures 1 and 2), and $\Delta\sigma_o$, ΔF_s, and A_s were calculated from a least square fit of the data. Results are summarized in Table 1.

Table 1
Surface Energy and Surface Area Constants
of Several Binary Systems Against Water

System	Figure	$\Delta\sigma_o$ erg/cm²*	$\Delta\sigma_o$ (Obs) erg/cm²	ΔF_s erg/mole x 10^{-9}	A_s Å²	A_s (Dens) Å²
Dimethylaniline-heptane/H_2O	1	22.0 (9.1)	24.8	58.95 (7.4)	31.8 (13.4)	35.4
Dimethylaniline-benzene/H_2O	1	7.6	9.1	20.8	37.7	35.4
Hexanoic acid-benzene H_2O	2	19.6	30.5	98.7	83.6	35.2
Octanoic acid-benzene H_2O	2	17.2	27.5	105.0	101.2	42.6
Decanol-benzene/H_2O	2	19.9	29.5	95.5	81.2	45.5
Octanol-benzene/H_2O	2	18.8	27.5	111.2	98.0	40.9

Obs - Observed Dens - Density

Interfacial tensions were measured between mercury and aqueous solutions of butanoic, isobutanoic, pentanoic, hexanoic, and heptanoic acid and solutions of nitro-benzene in heptane and benzene.

A capillary rise method described by Bartell and Miller[5] was used to determine the interfacial tensions between mercury and the solutions of interest. A diagram of the apparatus with approximate dimensions appears in Figure 3. Two such apparatuses made entirely of Pyrex glass were used simultaneously for each interfacial tension measurement. Equation (8) was used to obtain interfacial tensions between mercury and the solutions without determining solution density.

*Abbreviations used in this text are from the GPO Style Manual, 1967, unless otherwise noted.

$$\sigma_{ij} = (r_m r_n \rho_{ig}/2)\,(h_{im}h_{jn} - h_{in}h_{jm})/(r_m h_{jm} - r_n h_{jn}) \qquad .....(8)$$

where

σ_{ij} = interfacial tension between Phases i and j

ρ_i = density of i-th phase

r_m = radius of m-th apparatus

g = gravitation constant

h_{im} = height of i-th phase in m-th apparatus.

Equation (8) was obtained by solving simultaneously the equations, described by Equatior (9), which resulted from making measurements with the same solutions in different apparatuses.

$$\sigma_{ij} = (r_m g/2)(h_{im}\rho_i - h_{jm}\rho_j) \qquad .....(9)$$

The radii of the capillaries were determined bv an optical method using a microscope equipped with a movable stage, a filar screw micrometer eyepiece of 6X magnification, and an objective of 10X magnification. The eyepiece micrometer was calibrated against a precision stage micrometer. With the optics described, 1-scale division was equivalent to 0.388 mm, and the eyepiece micrometer could be read to 0.001 scale division. Consequently, maximum precision was 0.388 micron.

The radii were measured at intervals along the length of the capillary. Equation (10) was used to correct for magnification by the cylindrical walls of the capillary[6]

$$r = R/n \qquad .....(10)$$

where

r = actual radius

R = apparent radius

n = index of refraction of the walls of the capillary.

Solutions, made by weight, were introduced into the higher reservoir of each apparatus, and pure mercury was placed into the other. The apparatus was placed into a constant temperature water bath at 25° C, maintained to within ±0.01° C. After the stopcock had been opened, the solution was allowed to come to equilibrium for 1 hour before meniscus and reservoir heights were measured with a cathetometer to within ±0.001 centimeter.

Doubly demineralized water was used to make all aqueous solutions. All organic compounds used were Eastman Kodak chromophotography grade chemicals. The mercury was allowed to drop from a capillary through a 1 meter long 10% nitric-acid column and then double distilled under vacuum for purification

Interfacial tensions were calculated from the meniscus and reservoir heights data by applying Equation (8). The value of 375 erg per cm^2 for the interfacial tensions of water against mercury at 25° C, obtained by Bartell[7] and coworkers, was used to obtain the difference between the interfacial tensions of the solutions and pure water. Interfacial tension differences were then used in the derived equation to calculate $\Delta\sigma_0$, ΔF_s, and A_2 with the derived equation. The data are summarized in Figures 4 through 6.

DISCUSSION OF RESULTS

In reference to Table 1, the deviations of $\Delta\sigma_0$ from $\Delta\sigma_0$ (observed) apparently reflect the degree of orientation of solute molecules in the surface region; the deviations of A_2 from A_2 (density) support this conclusion. Dimethylaniline molecules in benzene against water either change their orientation or their packing density in the surface region at higher concentrations, which is evidenced by the existence of different linear relationships in different concentration regions. Consequently, two different values for $\Delta\sigma_0$ and ΔF_s, and A_2 were obtained for this system. In Table 1, the values in parentheses were obtained in the region of higher concentration; $\Delta\sigma_0$ in this region is the same as $\Delta\sigma_0$ (observed) which indicated little orientation, and the small magnitude of ΔF_s supports this conclusion. However, A_2, which is approximately one-third the molecular surface area obtained in the dilute region, suggests that the surface layer is three molecules thick in the concentrated region.

The experimental molecular areas for hexanoic and octanoic acids and those of decanol and octanol imply that these molecules are oriented with their long axes parallel to the interface The difference between the molecular surface area of hexanoic and octanoic acids is 17.6$Å^2$, and of decanol and octanol is 16.8$Å^2$.

Since the molecular surface area of the members of each pair, oriented with major axis parallel the surface, differ by the surface area of two methylene groups, the average molecular area of a methylene group is determined as 8.6Å^2.

The progressive increase in molecular surface area, A_2, for butanoic, pentanoic, hexanoic, and heptanoic acids, obtained by interfacial tension against mercury measurements (see Table 2), suggests that these molecules were also oriented with their long axes parallel to the surface. When the molecular area per molecule was plotted versus the number of methylene or methyl groups in the molecule, a straight line resulted (see Figure 7) the slope of which was equal to 9.2Å^2 per group, and the intercept of which was equal to 28Å^2. The slope is equivalent to the surface area of a methylene or methyl group, and the intercept is equivalent to the surface area of a carboxyl group. This molecular area, 9.2Å^2, obtained for a methylene group in a straight chain hydrocarbon oriented with its long axis parallel to a mercury surface, is close to that obtained for similar hydrocarbons similarly oriented toward a water surface. These results demonstrate how the derived equation can be used to ascertain the size, shape, and orientation of molecules at an interface by interfacial tension measurements.

Table 2
Interfacial Energy and Area Constants
For Several Aqueous Solutions Against Mercury

Solute	$\Delta\sigma_0$ erg/cm^2	$\Delta F_s \times 10^{-9}$ erg/mole	A_2 Å^2	A_2 (Density) Å^2
Butanoic	24.6	82.4	55.7	28.9
Pentanoic	24.7	96.8	65.1	32.1
Hexanoic	24.6	109.8	74.1	35.5
Heptanoic	10.8	58.6	90.7	38.8
Isobutanoic	23.0	90.5	65.3	28.9

In Table 3, $\Delta\sigma_0$ is less then $\Delta\sigma_0$ (observed) for nitrobenzene dissolved in heptane, and $\Delta\sigma_0$ (calculated) approached $\Delta\sigma_0$ (observed) for nitrobenzene dissolved in benzene.

Table 3
Interfacial Energy and Area Constants
For Nitrobenzene Solutions Against Mercury

Solvent	$\Delta\sigma_o$ erg/cm^2	$\Delta\sigma_o$ (Observed) erg/cm^2	$\Delta F_i \times 10^{-9}$ erg/mole	A_a Å^2	A_a (Density) Å^2	t
Heptane	16.4	29.0	22.5	22.8	30.8	2
Benzene	9.6	9.09	20.5	45.8	30.8	1

This implies that there is a greater change in surface energy, due to orientation at the interface, for the heptane than for the benzene solution. It is reasonable to assume that the orientation of the nitrobenzene molecule in the interface is predominantly influenced by the mercury phase. From this follows that the area of the molecule in the heptane-mercury interface should be the same as in the benzene-mercury interface. This condition is obtained when t for the heptane-mercury interface is equal to 2, and for the benzene-mercury interface is equal to unity. The area per molecule, namely, 45.6Å^2, thus obtained corresponds approximately to the area of the benzene molecule (41Å^2) when oriented parallel to the surface[8]. The different thicknesses of the interfacial region are very likely due to the different miscibilities of nitrobenzene in heptane and benzene, the thickness being favored by lower miscibility.

CONCLUSIONS

It has been shown how the derived equation can be employed to generate information as to molecular area and orientation of adsorbed molecules at an interface. Consequently, the derived equation can be a powerful aid in further understanding the interaction of polar molecules at the surfaces of naval machinery. Predictions, for example, can be reliably made as to the behavior of additive molecules in a lubricant medium in which naval machinery is immersed.

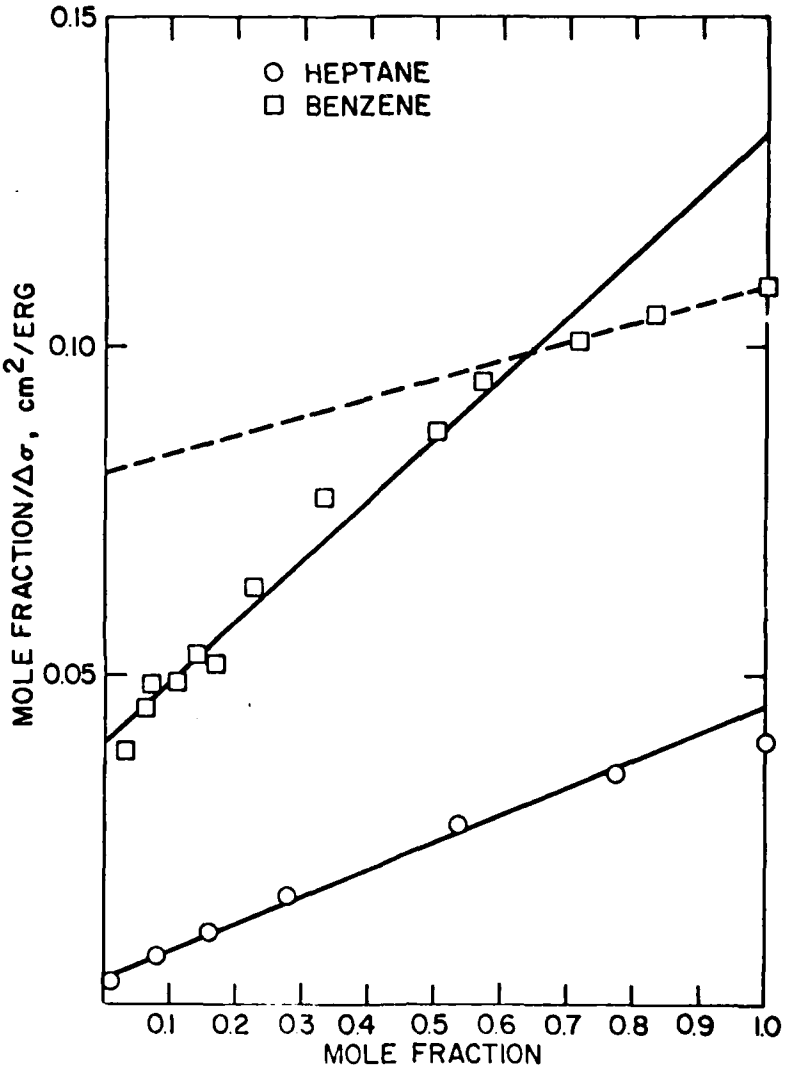

Figure 1
Mole Fraction Divided by Δσ Versus Mole Fraction for Solutions of Dimethylaniline in Heptane and in Benzene at 25° C Against Water

MATLAB 333

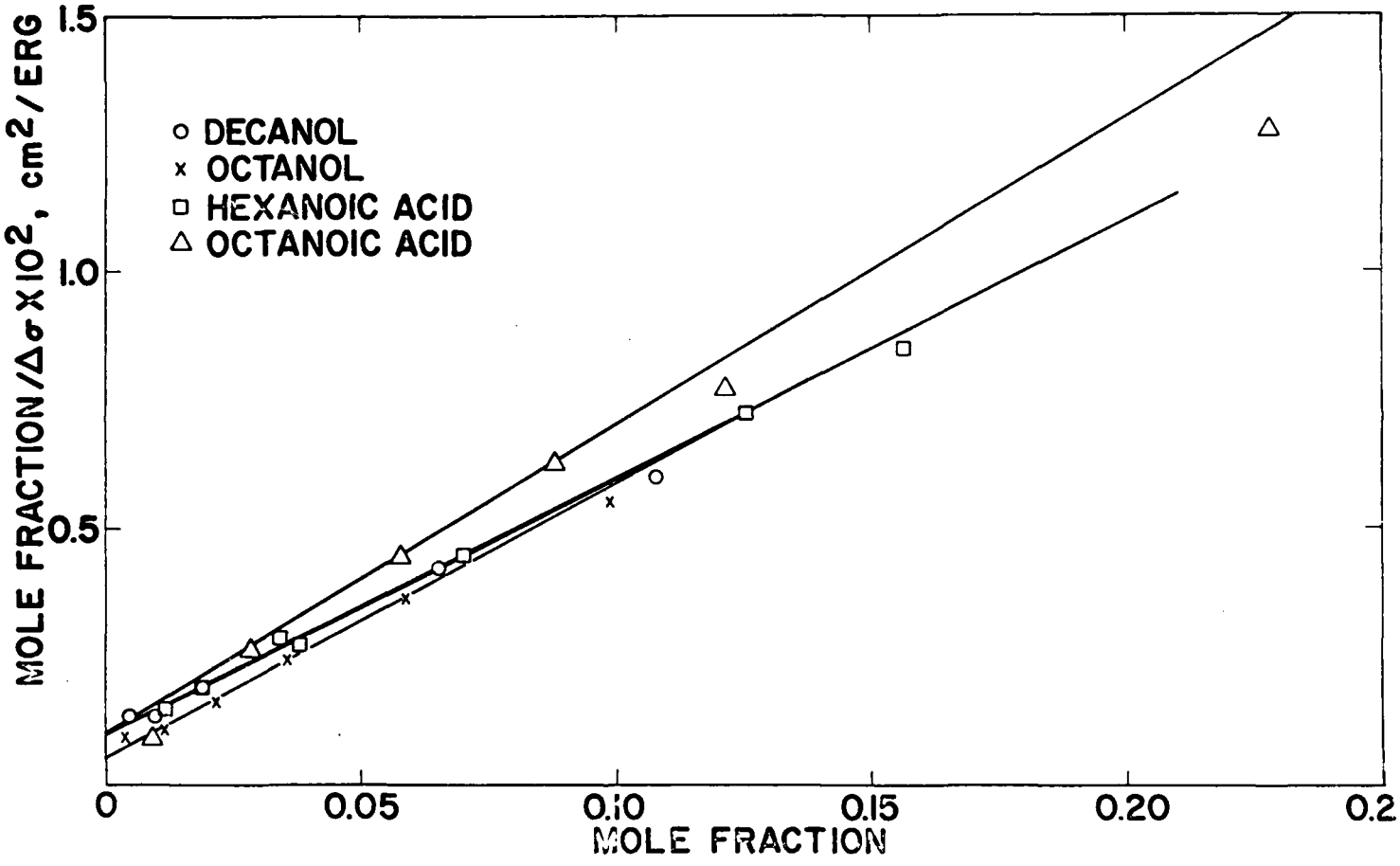

Figure 2
Mole Fraction Divided by Δσ Versus Mole Fraction for Solutions
of Some Organic Compounds in Benzene at 20° C Against Water

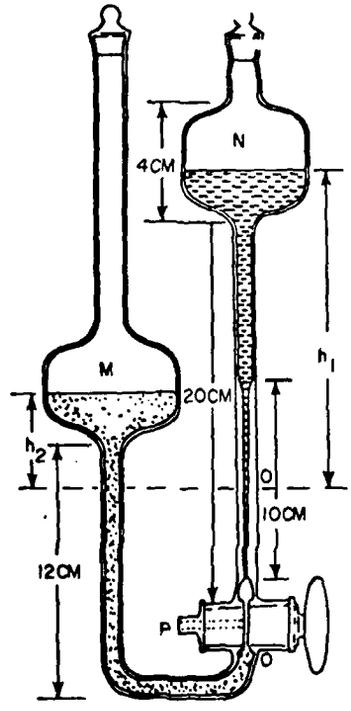

Figure 3
Interfacial Tension Apparatus

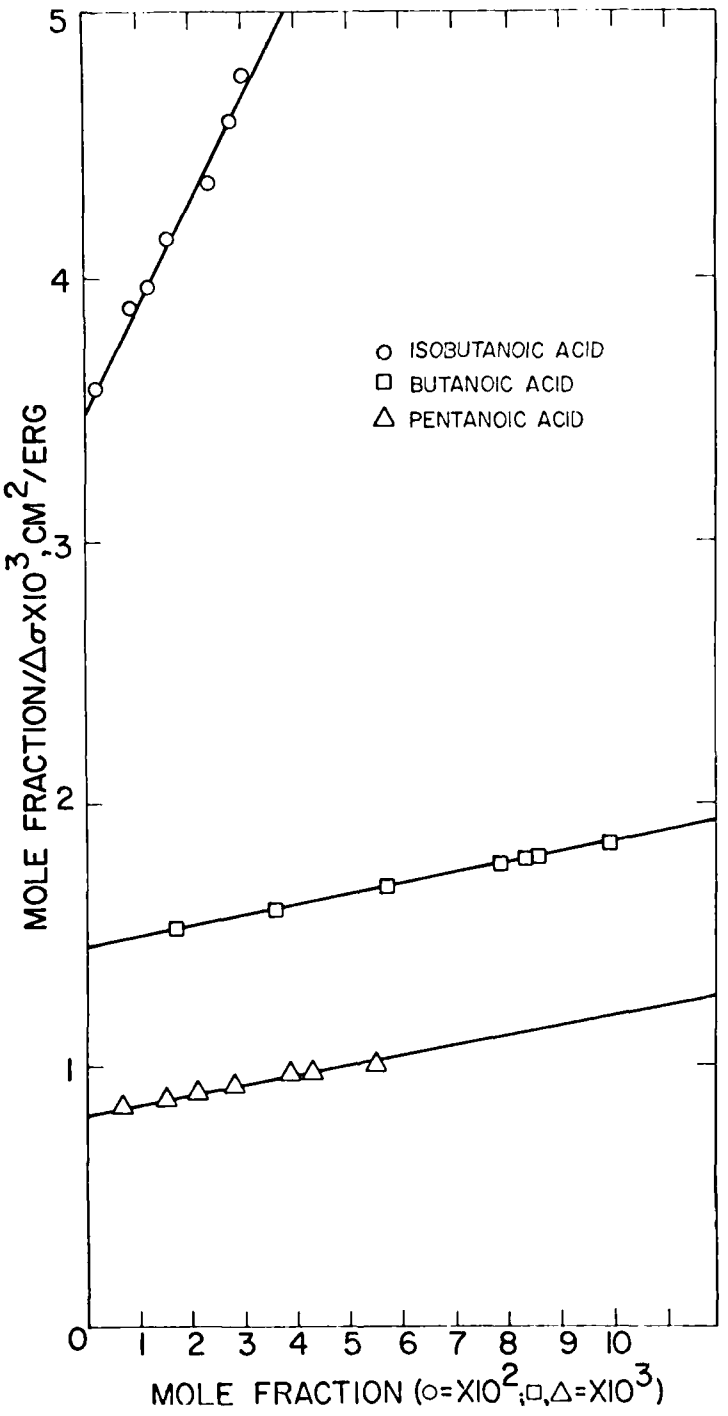

Figure 4
Mole Fraction Divided by Δσ Versus Mole Fraction for Aqueous Solutions of Isobutanoic, Butanoic, and Pentanoic Acid Against Mercury at 25° C

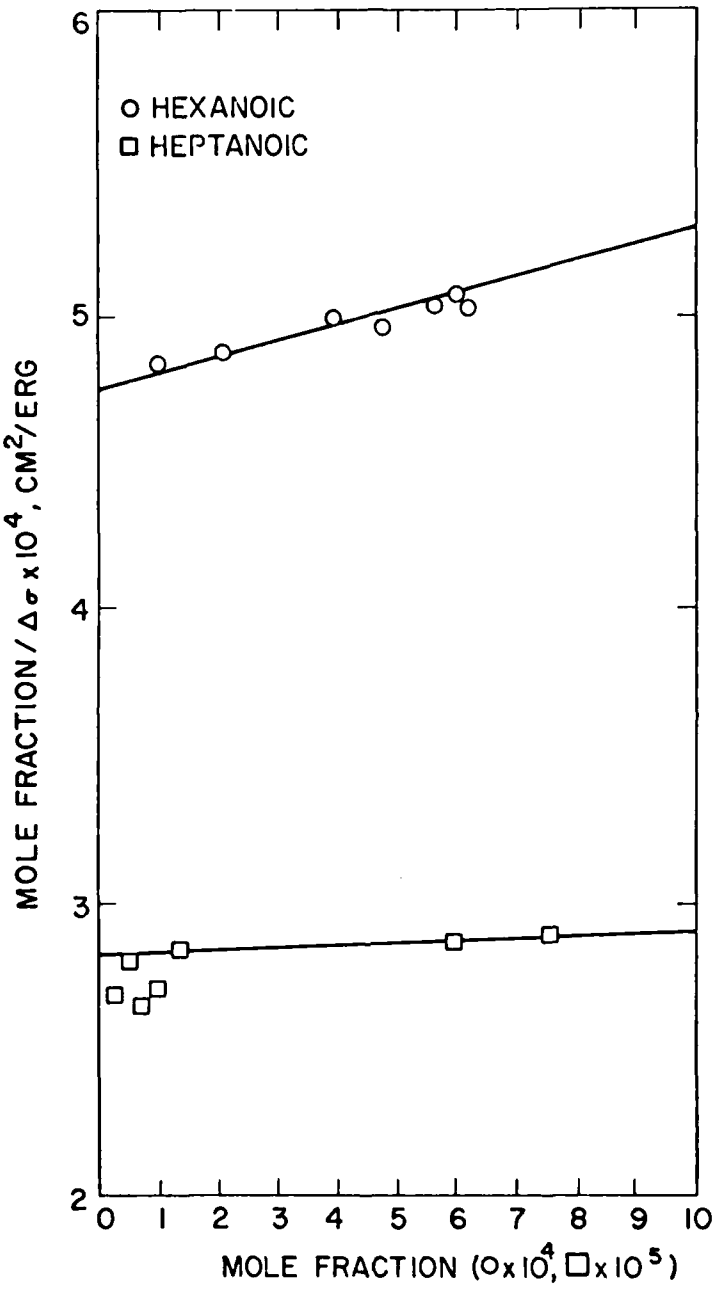

Figure 5
Mole Fraction Divided by Δσ Versus Mole Fraction for
Aqueous Solutions of Hexanoic and of Heptanoic
Acid Against Mercury at 25° C

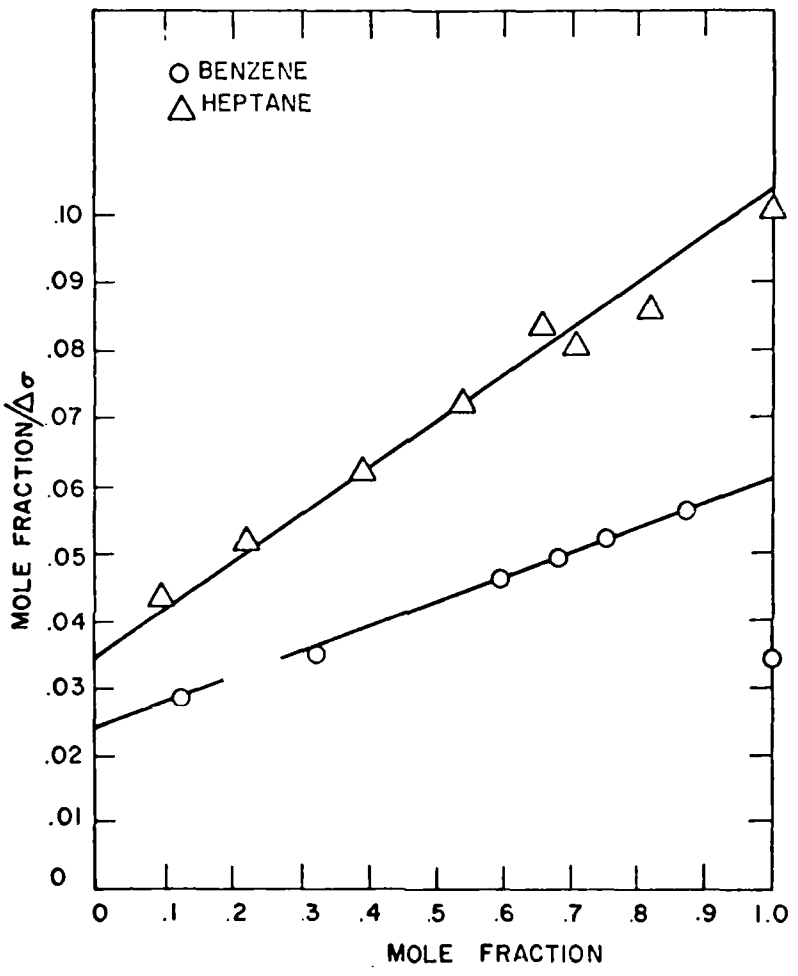

Figure 6
Mole Fraction Divided by $\Delta\sigma$ Versus Mole Fraction For Solutions of Nitrobenzene in Benzene and in Heptane Against Mercury at 25° C

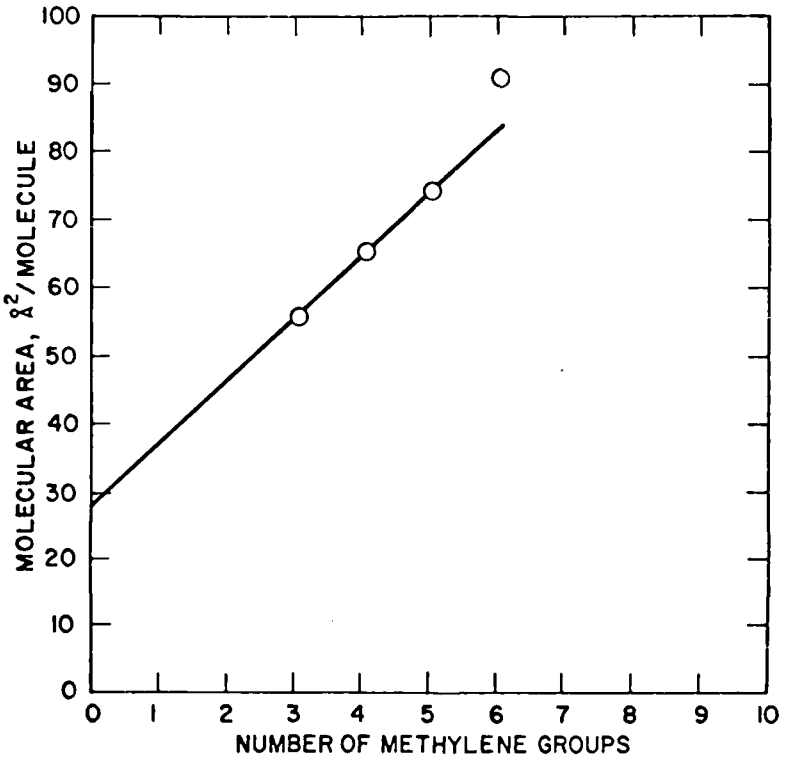

Figure 7
Molecular Area Versus Number of Methylene Groups per Molecule
for a Homologous Series of Straight Chain Acids at 25° C

Appendix A

Technical References

1 - Shereshefky, J. L., Journ. Colloid and Interface Sci., Vol. 24, 1967, p. 317

2 - Matthews, J. H. and A. J. Stamm, Journ. Amer. Chem. Soc., Vol. 46, 1924, p. 1071

3 - Hutchinson, E., Journ. Coll. Sci., Vol. 3, 1948, p. 219

4 - Pilpel, N., Journ. Coll. Sci., Vol. 11, 1956, p. 51

5 - Bartell, F. E. and F. L. Miller, Journ. Amer. Chem. Soc., Vol. 50, 1928, p. 1961

6 - Shereshefky, J. L., Journ. Amer. Chem. Soc., Vol. 50, 1928 pp. 2966, 2980

7 - Bartell, F. E., L. O. Case and H. Brown, Journ. Amer. Chem. Soc., Vol. 55, 1933, p. 2419

8 - Smith, R. N., C. Pierce and H. Cordes, Journ. Amer. Chem. Soc., Vol. 72, 1950, p. 5595

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

ORIGINATING ACTIVITY (Corporate author) Commanding Officer Naval Ship Research & Development Laboratory Annapolis, Maryland 21402	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b GROUP

3 REPORT TITLE

Application of a Theory of Binary Solution Surface Tension to Interfacial Tension Phenomena

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

Research and Development

5 AUTHOR(S) (First name, middle initial, last name)

Donald J. Cotton

6 REPORT DATE	7a. TOTAL NO OF PAGES	7b. NO OF REFS
July 1969	23	8

8a CONTRACT OR GRANT NO	9a ORIGINATOR'S REPORT NUMBER(S)
b PROJECT NO ZR 011 01 01 c Task 05600 Assignment A821 147 d	2867 9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report) MATLAB 333

10 DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
	DNL MAT 03L

13 ABSTRACT

A theoretical equation which describes interfacial tension of binary solutions as a function of concentration, and of the interfacial tensions and the molecular areas of the pure components has been applied to organic and aqueous systems against water and mercury. The derived equation gives information as to molecular area and orientation of adsorbed molecules at an interface. Gibbs' equation, while applicable to all interfaces, generates no detailed structural information. The derived equation is useful for determining the interfacial structure of solutions approximating its theoretical model.

(Author)

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

UNCLASSIFIED

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Binary solution						
Interfacial tension						
Two-phase system						
Shereshefsky's Equation						
Mercury						
Aqueous systems						
Organic systems						
Interfacial structure						