volume associated with each group in the molecule so that $\overline{V}_2^\circ$ could be calculated by summing these volumes, in a way similar to that of Traube (*16*).

At temperatures of 0°, 20°, 40°, and 60° C., the volumes per methylene unit are 15.0, 15.6, 16.3, and 16.9 ml., respectively. For each alcohol, the volume associated with the end groups, $—CH_3$ and $—CH_2OH$, is calculated.

Again assuming additive volumes of groups, the $\overline{V}_2^\circ$ values for 1,3-propanediol may be used to calculate the volume associated with the $—CH_2OH$ group. Subtraction then gives the volume associated with the $—CH_3$ group.

These results suggest that water molecules are able to pack around both end groups, but especially the methyl group in a more open structure at lower temperatures.

A similar contraction with temperature has been reported by Holland and Moelwyn-Hughes (*7*) for methyl fluoride in water at low temperatures, and by Michels, Gerver, and Bijl (*11*) and Kritchevskiĭ and Ilinskaya (*9*) for several gases in water.

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Estimation of Interfacial Energy Factors of Surfactants

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Girifalco and Good (*1*) recently proposed a theory for estimating the interfacial energy of liquid-liquid systems using a function, Φ, equal to the ratio of the free energy of adhesion for the interface between phases and the geometric mean of the free energies of cohesion of the separate phases. When applied to several groups of "nonregular" systems of water-organic liquid interfaces, the accuracy of calculated interfacial tensions was 3 to 5 ergs per sq. cm. (*1*).

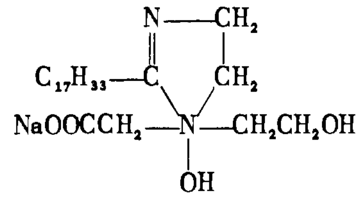
This article extends the proposed method to interfacial systems of aqueous surfactant solutions and organic liquids, the surfactant concentration level being that obtained in practical detergency.

EXPERIMENTAL

Materials. Surfactants. The following surfactants, all commercial preparations of 100% active content except where noted and all of different types, were used as received:

Surfactant	Symbol	Molecular Weight	% Active
Octyl phenyl nonaethylene glycol ether	IOPNG	602	100
tert-Dodecyl nonaethylene glycol thioether	TDNG	598	95
Tridecyl dodecaethylene glycol ether	TDG	728	100
Nonaethylene glycol monolaurate	NGML	613	100
Polyoxylethylene tall oil ester	PGTO	1050	100
Polyoxyethylene sorbitan monolaurate	PSML	1230	100
Dioctyl sodium sulfosuccinate	DOSS	444	100
Sodium *p*-dodecylbenzenesulfonate	SDBS	346	100
Lauric diethanolamide	LDA	287	100
Amphoteric agent	OMSF	1280	35

The amphoteric agent was 1-(2-sodium acetato),1-ethanol,2-heptadecenyl,4,5-dihydroimidazolium hydroxide, and possessed the following structural formula:



Since commercial surfactants usually consist of a homologous series of compounds, the molecular weights given above are mean theoretical values, in some instances supplied by the manufacturers.

Organic Liquids. The organic liquids used were as follows:

Paraffin oil. National Formulary, 28.74 centistokes at 100° F., viscosity index = 89.5, density 0.851, surface tension 29.9.

Glyceryl trioleate. Free fatty acid = 2.5%, free glycerol = 0; iodine No. = 78; saponification No. = 198; density 0.916; surface tension 31.6.

n-Octyl alcohol. Free fatty acid = 0.05%; B.P. = 194–5° C.; density 0.822; surface tension 26.9.

n-Octanoic acid. M.P. = 0–5° C.; density 0.906; surface tension 28.3.

n-Heptane. B.P. = 96–7° C.; density 0.680; surface tension 18.8.

Castor oil. C.P.; density 0.957; surface tension 34.4.

Iso-octane. 2,2,4-Trimethylpentane; 99 + %; density 0.689; surface tension 18.0.

Table I. Surfactant Surface Tensions, 25–6° C.

Surfactant	Surface Tension, Dynes/Cm. 0.005M	 0.01M	 0.02M
IOPNG	30.0	30.0	30.1
TDNG	28.3	28.3	28.4
TDG	29.6	29.3	29.4
NGML	29.3	29.1	29.2
PGTO	35.7	34.7	34.8
PSML	34.0	33.8	33.8
DOSS	28.5	27.0	25.9
SDBS	30.4	30.5	30.6
LDA	26.6	26.7	26.9
OMSF	28.9	29.4	29.9

Densities are in grams per milliliter at 25.5° C. Surface tensions are in dynes per centimeter at 25–6° C.

Boundary Tensions. Surface and interfacial tensions (Tables I and II) were determined with a du Nouy interfacial tensiometer at 25–6° C. using the Harkins and Jordan correction factors (*2*). Interfacial tensions were determined at a 6-minute age of interface between the organic liquids and aqueous solutions of the surfactants. The organic liquids were not treated (saturated) with surfactant prior to measuring the interfacial tensions. Table III lists the free energy of adhesion for each surfactant.

RESULTS

The values of the Girifalco and Good function, Φ, of all ten surfactants with glyceryl trioleate as the organic liquid phase were in close agreement, averaging 0.991 for all concentrations (Table IV). Calculated interfacial tensions and free energies of adhesion for the triolein systems using the value of 0.991 agreed

Table II. Interfacial Tension, 25–6° C.

(Ergs per sq. cm.)

Surfactant	Molar Concn.	Paraffin Oil	Iso-octane	Octyl Alcohol	Octanoic Acid	Glyceryl Trioleate	*n*-Heptane	Castor Oil
IOPNG	0.005	2.6	3.3	5.5	6.5	0.7		3.3
	0.01	2.5	3.0	4.8	5.8	0.3	2.9	2.8
	0.02	2.3	2.6	4.7	5.6	0.5		2.4
TDG	0.005	5.0	4.1	3.5	5.3	0.4		4.0
	0.01		3.8			0.4	3.9	3.8
	0.02	4.4	3.6	2.3	5.4	0.4		3.5
SDBS	0.005	4.5	3.5	4.0	3.8	0.4		4.1
	0.01	4.3	3.7	3.0	2.3	0.2	3.0	3.5
	0.02	4.4	3.7	2.4	1.9	0.3		3.1
NGML	0.005	4.7	5.8	5.0	6.0	3.1		5.7
	0.01	4.0	5.1	4.9	5.2	2.3		5.4
	0.02	4.2	4.3	4.7	5.6	1.4		4.0
PGTO	0.005			4.6	4.2	1.2		
	0.01			4.5	4.3	1.0	6.3	
	0.02			4.2	3.8	0.9		
PSML	0.005	5.4	5.2	1.9	4.2	1.5		4.7
	0.01	4.9	4.9	1.5	3.6	0.5	4.8	4.7
	0.02	4.4	4.6	1.4	3.6	1.0		4.3
TDNG	0.005	2.4	2.7	5.1	5.9	0.6		3.8
	0.01	2.0	2.3	3.8	5.0	0.3	2.4	2.7
	0.02	1.7	1.9	4.1	5.7	0.4		2.3
DOSS	0.005		2.6	3.9	3.5	0.4		5.4
	0.01		1.8	2.9	2.8	0.3	1.4	4.3
	0.02	2.4	1.1	2.5	2.4	0.3		3.1
LDA	0.005			6.0	4.2	0.7		
	0.01			5.6	4.0	0.4	0.2	
	0.02			5.5	3.9	0.3		
OMSF	0.005			2.8	3.9	0.1		
	0.01			2.5	3.6	0.2	3.6	
	0.02			2.1	3.7	0.2		

Table III. Free Energy of Adhesion, 25–6° C.

(Ergs per sq. cm.)

Surfactant	Molar Concn.	Free Energy of Adhesion, 25–6° C. Paraffin oil	 Iso-octane	 Octyl alcohol	 Octanoic acid	 Glyceryl trioleate	 *n*-Heptane	 Castor oil
IOPNG	0.005	57.3	44.7	51.4	51.8	60.9		61.1
	0.01	57.4	45.0	52.1	52.5	61.3	45.9	61.6
	0.02	57.7	45.5	52.3	52.8	61.2		62.1
TDG	0.005	54.5	43.5	53.0	52.6	60.8		60.0
	0.01		43.5			60.5	44.2	59.9
	0.02	54.9	43.8	54.0	52.3	60.2		60.3
SDBS	0.005	55.8	44.9	53.3	54.9	61.6		60.7
	0.01	56.1	44.8	54.4	56.5	61.9	46.3	61.4
	0.02	56.1	44.9	55.1	57.0	61.9		61.9
NGML	0.005	54.5	41.5	51.2	51.6	57.8		58.0
	0.01	55.0	42.0	51.1	52.2	58.4		58.1
	0.02	54.9	42.9	51.4	51.9	59.4		59.6
PGTO	0.005			58.0	59.8	66.1		
	0.01			57.1	58.7	65.3	47.2	
	0.02			57.5	59.3	65.5		
PSML	0.005	58.5	46.8	59.0	58.1	64.1		63.7
	0.01	58.8	46.9	59.2	58.5	64.9	47.8	63.5
	0.02	59.3	47.2	59.3	58.5	64.4		63.9
TDNG	0.005	55.8	43.6	50.1	50.7	59.3		58.9
	0.01	56.2	44.0	51.4	51.6	59.6	44.7	60.0
	0.02	56.6	44.5	51.2	51.0	59.6		60.5
DOSS	0.005		43.9	51.5	53.3	59.7		57.1
	0.01		43.2	51.0	52.5	58.3	44.4	57.1
	0.02	53.4	42.8	50.3	51.8	57.2		57.2
LDA	0.005			47.5	50.7	57.5		
	0.01			48.0	51.0	57.9	45.3	
	0.02			48.3	51.3	58.2		
OMSF	0.005			53.0	53.3	60.4		
	0.01			53.8	54.1	60.8	44.6	
	0.02			54.7	54.5	61.3		

[a] See Table IV.

Table IV. Girifalco Function, Φ

Surfactant	Molar Concn.	Paraffin Oil	Octyl Alcohol	Octanoic Acid	Glyceryl Trioleate	Iso-octane	*n*-Heptane	Castor Oil
IOPNG	0.005	0.957	0.905	0.889	0.989	0.962		0.951
	0.01	0.955	0.917	0.901	0.996	0.968	0.966	0.959
	0.02	0.962	0.919	0.905	0.992	0.977		0.965
TDG	0.005	0.916	0.939	0.909	0.994	0.942		0.940
	0.01				0.994	0.947	0.942	0.943
	0.02	0.926	0.960	0.906	0.988	0.952		0.948
SDBS	0.005	0.925	0.932	0.936	0.994	0.960		0.939
	0.01	0.929	0.950	0.962	0.997	0.956	0.967	0.948
	0.02	0.927	0.960	0.968	0.995	0.957		0.954
NGML	0.005	0.921	0.912	0.896	0.950	0.903		0.913
	0.01	0.932	0.913	0.909	0.963	0.918		0.918
	0.02	0.929	0.917	0.903	0.978	0.936		0.940
PGTO	0.005		0.936	0.941	0.984			
	0.01		0.935	0.937	0.986		0.924	
	0.02		0.940	0.945	0.988			
PSML	0.005	0.917	0.976	0.937	0.978	0.946		0.931
	0.01	0.925	0.982	0.946	0.993	0.951	0.948	0.931
	0.02	0.933	0.983	0.934	0.985	0.957		0.937
TDNG	0.005	0.959	0.908	0.896	0.992	0.966		0.944
	0.01	0.966	0.932	0.912	0.997	0.975	0.969	0.962
	0.02	0.971	0.926	0.900	0.995	0.984		0.968
DOSS	0.005		0.930	0.938	0.995	0.969		0.912
	0.01		0.946	0.949	0.998	0.980	0.985	0.937
	0.02	0.959	0.953	0.956	0.999	0.991		0.958
LDA	0.005		0.888	0.924	0.992			
	0.01		0.896	0.928	0.997		1.011	
	0.02		0.898	0.930	0.998			
OMSF	0.005		0.951	0.932	0.999			
	0.01		0.957	0.938	0.997		0.949	
	0.02		0.964	0.937	0.995			

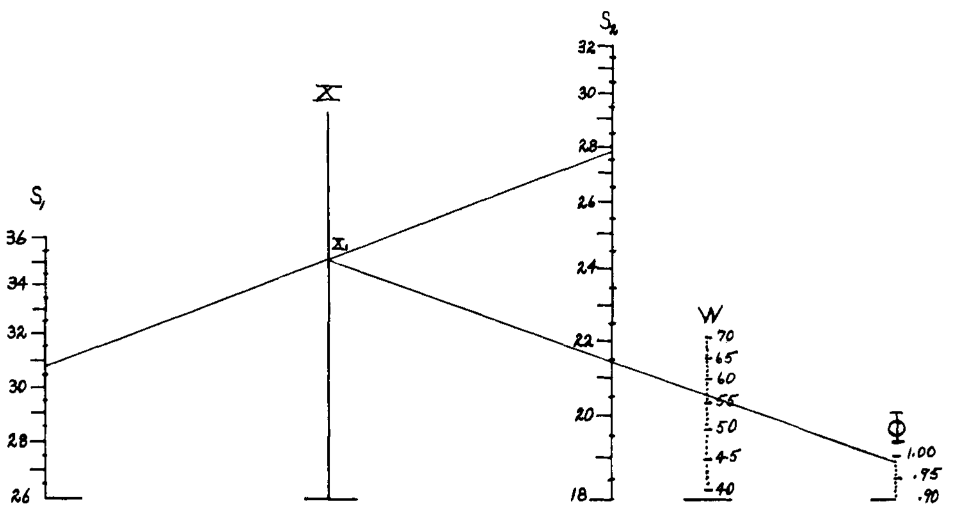


Figure 1. Nomograph for work of adhesion, W

$$W = 2\Phi[S_1S_R]^{1/2}$$

Match S_1 and $S_2 \rightarrow X_1$
Match X_1 and $\Phi \rightarrow W$

$$X = 0.5 \log S_1 + 0.5 \log S_2$$
$$X + \log \Phi = \log W + \log 0.5$$

within 0.8 erg per sq. cm. for all values except those of NGML systems. The standard deviation for the glyceryl trioleate Φ data (Table V) was 0.008.

Iso-octane and *n*-heptane system Φ values, excluding those of the NGML and PGTO surfactants, were in close agreement. A mean value of 0.963 was calculated. The standard deviation of these data was 0.015.

Table V. Interfacial Tensions and Free Energies of Adhesion for Glyceryl Trioleate Systems Using Φ = 0.991

(Ergs per Sq. Cm.)

		Interfacial Tension		Free Energy of Adhesion	
Surfactant	Molar Concn.	Exptl.	Calcd.	Exptl.	Calcd.
IOPNG	0.005	0.7	0.6	60.9	61.0
	0.01	0.3	0.6	61.3	61.0
	0.02	0.5	0.6	61.2	61.1
TDG	0.005	0.4	0.6	60.8	60.6
	0.01	0.4	0.7	60.5	60.2
	0.02	0.8	0.7	60.2	60.3
SDBS	0.005	0.4	0.6	61.6	61.4
	0.01	0.2	0.6	61.9	61.5
	0.02	0.3	0.6	61.9	61.5
NGML	0.005	3.1	0.7	57.8	60.2
	0.01	2.3	0.7	58.4	60.0
	0.02	1.4	0.7	59.4	60.1
PGTO	0.005	1.2	0.8	66.1	66.5
	0.01	1.0	0.7	65.3	65.6
	0.02	0.9	0.7	65.5	65.7
PSML	0.005	1.5	0.7	64.1	64.9
	0.01	0.5	0.7	64.9	64.7
	0.02	1.0	0.7	64.4	64.7
TDNG	0.005	0.6	0.7	59.3	59.2
	0.01	0.3	0.7	59.6	59.2
	0.02	0.4	0.7	59.6	59.3
DOSS	0.005	0.4	0.7	59.7	59.4
	0.01	0.3	0.8	58.3	57.8
	0.02	0.3	0.9	57.2	56.6
LDA	0.005	0.7	0.8	57.5	57.4
	0.01	0.4	0.8	57.9	57.5
	0.02	0.3	0.8	58.2	57.7
OMSF	0.005	0.1	0.7	60.4	59.8
	0.01	0.2	0.7	60.8	60.3
	0.02	0.2	0.5	61.3	61.0

The Φ value data of octyl alcohol and octanoic acid systems with each of seven surfactants (Table IV), excluding systems with TDG, PSML, and LDA, had standard deviations of 0.003 to 0.013.

Similarly, the Φ value data of paraffin oil and castor oil systems with each of six surfactants (Table IV), excluding only DOSS of those surfactants studied with castor oil systems, had standard deviations of 0.005 to 0.012.

It was concluded that estimations of interfacial tension and free energy of adhesion of surfactant-organic liquid systems may be made with an accuracy of about 1 erg per sq. cm. using Φ values as follows:

For glyceryl trioleate systems, Φ = 0.991.

For octyl alcohol and octanoic acid systems, the mean of the Φ values for each surfactant as given in Table IV.

For iso-octane and *n*-heptane systems, Φ = 0.963.

For paraffin oil and castor oil systems, the mean of the Φ values for each surfactant as given in Table IV.

Figure 1 is a nomograph for the determination of work of adhesion, *W*, from S_1 (surface tension of surfactant), S_2 (surface tension of organic phase), and Φ.

The systems chosen for study were intended to simulate conditions obtaining in practical detergency. Hence the 0.005 to 0.02 molal concentration range exceeds the critical micellar concentration. While the correlation found might break down at lower concentration levels, it is of practical importance that the Girifalco and Good function can be extended to the more concentrated systems of detergency.

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