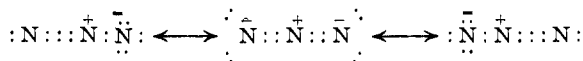


symmetric azide ion, this configuration of which can be satisfactorily represented by the three structures



PASADENA, CALIF.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

The Effect of Surface Tension and Electrical Potential on the Stability of Mercury Emulsions

By V. SIVERTZ, W. H. NAYLOR AND H. V. TARTAR

In the preparation of mercury emulsions in water the function of certain ions as emulsifying agents has been attributed largely to the lowering of the interfacial tension between the two liquids.¹

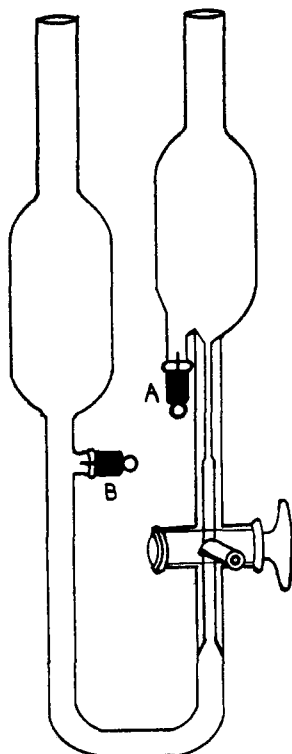


Fig. 1.—The capillaritymeter.

In addition to this, the emulsifying agent has also been supposed to exert a stabilizing influence through the production of an electrical effect: the preferential adsorption of ions at the interface produces an electrical potential difference which tends to prevent coagulation.

The work presented in this paper was undertaken to determine the influence of different emulsifying agents on the interfacial tension and electrical potential of a given pair of liquids. For this purpose, mercury emulsions were used because these systems are well adapted for the direct measurements required. It is unnecessary to give here any extensive review of the general literature on mercury emulsions or on the influence of electrolytes on the potential at a mercury-water interface.

Experimental

Purification of Materials.—Distilled water from the laboratory supply was further purified by distillation from alkaline permanganate in an apparatus of Pyrex glass

(1) Svedberg, "Colloid Chemistry," Chemical Catalog Co., 2nd edition, 1928, p. 28.

which had been seasoned by use. The water was received slightly below the boiling temperature in Pyrex bottles to minimize the amount of dissolved gases.

The salts used were of analyzed reagent grade and were tested for purity. Some were first purified by recrystallization. The sodium lauryl sulfonate was prepared by R. M. Reed.²

The mercury was first washed with benzene to remove grease. Then it was shaken with nitric acid (containing a small amount of mercurous nitrate) and air drawn through for several hours. The nitric acid was then removed by thorough washing with distilled water and the mercury dried. This product was further purified by repeated distillation *in vacuo* in a Pyrex still.

Emulsifying Agents.—A number of substances (listed in Table I) were used as emulsifying agents. A concentration of 0.025 *N* was adopted because this concentration gave satisfactory electrical conductivity for e. m. f. measurements. In general, former workers have favored lower concentrations. Nordlund³ considered 0.0025 *N* the optimum concentration. It was found, however, that when a material was an emulsifying agent at the lower concentration, it also functioned when the concentration was increased to 0.025 *N*. Solutions were also used of certain electrolytes which were not emulsifying agents.

Apparatus.—A sketch of the capillaritymeter used for the interfacial tension measurements is given in Fig. 1. It was made of Pyrex glass with sealed-in tungsten electrodes, A and B, which were protected externally by a metallic sheath of special design. In designing the apparatus, careful adherence was made to specifications of Richards and Coombs⁴ and of Bartell, Case and Brown⁵ for capillary tubes for surface tension measurements. The tubing was tested for uniformity of bore both before and after sealing to the other parts of the apparatus. The radius was $0.03374 \pm 3 \times 10^{-6}$ cm. at 25°.

A special sighting device was made to facilitate the determination with a cathetometer of the height of the wide mercury surface in the capillaritymeter. A fine platinum wire with a minute bead on the exposed end was sealed into a glass tube. This in turn passed through the hole left by removing the stationary part of a micrometer caliper. The tube was cemented to the moving screw and rotated true. This device was mounted above the mercury

(2) Reed and Tartar, *THIS JOURNAL*, **57**, 570 (1935).

(3) Nordlund, Diss., Upsala, 1918; *J. Chem. Soc.*, **114**, **11**, 267 (1918).

(4) Richards and Coombs, *THIS JOURNAL*, **37**, 1656 (1915).

(5) Bartell, Case and Brown, *ibid.*, **55**, 2419 (1933).

surface. The bead and its reflection could be brought together, indicating the exact position of the surface to which the cross hair of the telescope was adjusted.

The capillarimeter was clamped to a heavy metal stand which was mounted on rubber in an air thermostat kept at $25 \pm 0.2^\circ$. The illumination was obtained from a large electric bulb immersed in water outside the thermostat to minimize temperature effects. The light entered the thermostat through a double layer of frosted glass. The capillarimeter was observed through a plate glass window. The entire set-up including cathetometer was mounted on a brick pier.

Preparation of Emulsions.—The emulsions were prepared by shaking mercury with the various solutions for several hours in Pyrex bottles. Identical results were obtained whether an atmosphere of air or of nitrogen was used. The shaking was accomplished with an electrically operated shaking machine.

Experimental Procedure.—An interfacial tension measurement was made by the following procedure. After the capillarimeter was cleaned, steamed and thoroughly dried, the mercury was poured into the left arm (Fig. 1). By tilting the apparatus, some mercury was allowed to flow into electrode A. The tube was then clamped in a vertical position and the right arm rinsed several times with the solution. The stopcock was opened during the rinsing so that the mercury flowed out of the capillary. This ensured a fresh surface of mercury when it was subsequently allowed to rise; also the solution in the capillary was of the same concentration as the bulk of the solution.

No lubricant other than the solution was used in the stopcock which had been carefully ground and polished before use. The stopcock was manipulated to let the mercury rise slowly in the capillary to form a zero (or 180°) angle of contact.⁵ It was also noted that by this procedure equilibrium was more readily established. Identical results could be obtained, however, by lowering the mercury in the capillary, provided no film formed at the interface (see later portion of this paper).

The levels were carefully read with a cathetometer first with open circuit between electrodes A and B, then with these shorted externally and finally with various electrical potentials (negative to the capillary) applied using a balanced type K potentiometer as a source of e. m. f. The potential was increased in 0.1 volt steps until the region of maximum surface tension was reached, when 0.01 volt steps were used.

The formulation used for calculating the interfacial tensions was that used by Bartell, Case and Brown.⁵

$$\gamma = \frac{rg}{2} \left[hd - h'd' + \frac{r}{3} (d - d') \right]$$

h and d refer to the height and density of mercury and h' and d' to the solution.

The value for pure water checks closely with values given in the literature. Bartell, Case and Brown⁵ obtained a value of 375 dynes per cm. by the capillary method and 374.1 by the drop weight method.

Results and Discussion

The interfacial tensions of mercury against the different solutions are given in Table I. The pH of the solutions is also included.

TABLE I
INTERFACIAL TENSION OF MERCURY AGAINST VARIOUS SOLUTIONS AT 25°

	Concn. of electrolyte	pH of solution	Surface tension dynes/cm.
Pure water	...	7.0	374.8
Non-emulsifying agents			
Potassium nitrate	0.025 <i>N</i>	7.2	380
Copper sulfate	.025 <i>M</i>	4.8	364
Emulsifying agents			
Potassium citrate	.025 <i>N</i>	7.7	388
Potassium citrate	.0025 <i>N</i>	7.6	383
Potassium tartrate	.025 <i>N</i>	7.7	377
Potassium acid tartrate	.0016 <i>N</i>	3.7	358
Potassium chloride	.025 <i>N</i>	7.3	381
Ammonium chloride	.025 <i>N</i>	6.1	373
Citric acid	.0025 <i>N</i>	below 3.0	285
Sodium lauryl sulfonate	.001 <i>M</i>	7.0	372

It was found necessary to prevent solution of gases in order to obtain consistent results. Dissolved gases lowered the interfacial tension slightly.

The interfacial tension of water against mercury is actually increased by the addition of potassium citrate, which functions as a good emulsifying agent. The interfacial tensions with solutions of the various emulsifying and non-emulsifying agents indicate that raising or lowering the interfacial tension has no relation to emulsification of mercury in water.

The hydrogen-ion concentration of the solutions (determined colorimetrically) also does not seem to have any appreciable influence on the emulsification. However, in every case studied, those solutions with pH greater than 7 show interfacial tensions greater than that of pure water, while those with pH less than 7 show interfacial tensions less than that of water.

It is believed by the authors that the lowering of the interfacial tension of pure water against mercury due to dissolved gases is connected with the lowered pH due to dissolved carbon dioxide.

The data for the electrocapillary curves are given in Table II and Fig. 2.

The maximum interfacial tensions obtained are given in column two with the corresponding impressed electrical potentials in column three. In Fig. 2 the interfacial tension is plotted as a function of the potential. These curves are, in most instances, of the usual type. In some cases the maxima are not sharply defined and a considerable increase in potential was necessary to start the lowering of the interfacial tension beyond the maximum.

TABLE II
ELECTROCAPILLARY DATA AND ELECTRODE POTENTIAL
FOR VARIOUS SOLUTIONS AGAINST MERCURY

Solution		Surface tension at maximum, dynes/cm.	Potential at maximum, volts	Electrode potential (normal hydrogen electrode = 0) volts
Non-emulsifying agents				
Potassium nitrate	0.025 N	438	0.86	0.421
Copper sulfate	.025 M	404	no return	...
Emulsifying agents				
Potassium citrate	.025 N	438	0.60	0.362
Potassium citrate	.0025 N	443	.80	...
Potassium tartrate	.025 N	417	.70	...
Potassium acid tartrate	.0016 N	437	.80	...
Potassium chloride	.025 N	437	.63	0.372
Ammonium chloride	.025 N	436	.63	.370
Citric acid	.0025 N	423	.63	...
Sodium lauryl sulfonate	.001 M	418	no return	...

There is no observable correlation between the emulsifying property of a solute and the nature of the electrocapillary maxima since both the non-emulsifying potassium nitrate and potassium

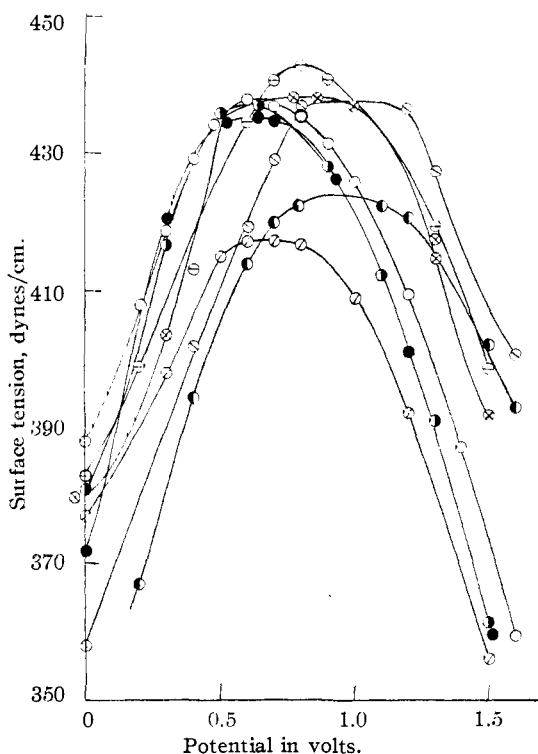


Fig. 2.—○, 0.025 N K citrate; ⊖, 0.0025 N K citrate; ⊙, 0.025 N K tartrate; ⊗, 0.0016 N KH tartrate; ●, 0.025 N KCl; ⊗, 0.025 N KNO₃; ●, 0.025 N NH₄Cl; ⊙, 0.0025 N citric acid.

acid tartrate, a typical emulsifier, show the broad maxima. In general the same type of electrocapillary curve is shown by emulsifying and non-emulsifying agents. Figure 3 shows the electrocapillary curve for copper sulfate and sodium

lauryl sulfonate solutions whose interfacial tensions rise to a maximum but do not decrease with increase in potential in the range investigated.

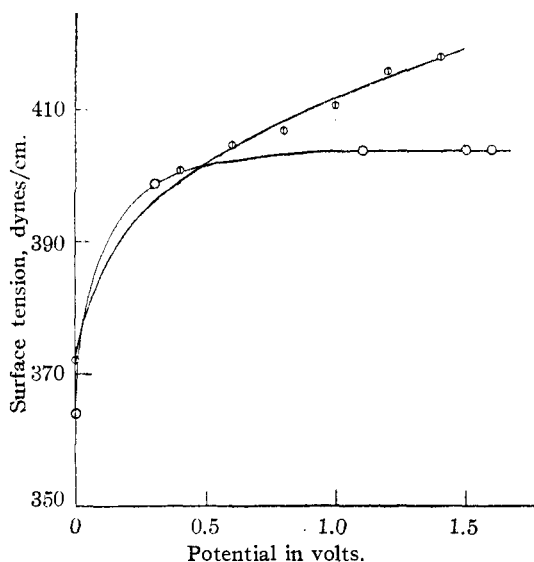


Fig. 3.—⊙, Na lauryl sulfonate 0.001 M; O, CuSO₄ 0.025 M.

Potential Measurements.—Measurements were made on the electrode potentials of four solutions shown in the last column of Table II. These were measured against the normal calomel electrode and were positive with respect to the hydrogen electrode. The values of the e. m. fs. are arbitrarily reported as positive.

Calculations made on these potentials indicate that in the case of potassium chloride and ammonium chloride, the potentials were those which would be obtained if the solution were saturated with calomel in the presence of these electrolytes. The calculations involved the assumption that $[Hg_2^{++}] [Cl^-]^2 = K$, using activities from "International Critical Tables."⁶ Usher⁷ arrived at the same conclusion using solutions of chlorides with and without the addition of hydrazine to prevent oxidation of the mercury to the mercuric state.

The potential of the solutions against mercury, shown in Table II, column four, using the normal calomel electrode as a standard, gives no indication of correlation between electrode potential and emulsification. The drifting potentials, observed before equilibrium was established, gave some indication of the phenomena of formation of mercurous ions as noticed by Usher.

(6) "Int. Crit. Tables," Vol. VII, p. 306.

(7) Usher, *J. Phys. Chem.*, **32**, 162 (1926).

In the measurement of surface tensions by the capillary method, various potential effects were noticed which, so far as could be ascertained, have not been noted in the literature. In allowing a fresh surface of mercury to rise slowly into the capillary, a negative potential was built up on the mercury in the capillary. That is to say, the capillary was negative with respect to the electrode A. This potential diminished somewhat on reaching equilibrium, but did not reach zero. If this potential was removed by shorting A and B externally, the surface tension was decreased for all the substances except citric acid, sodium lauryl sulfonate and ammonium chloride. With ammonium chloride, no decrease was noted, and with the other two, the surface tension was increased. The surface tensions for the various substances are listed in Table III. When the charge was thus removed, no subsequent building up of potential was ever observed. One could regain the original surface tension value of the solutions (excluding the exceptions noted above) by applying a small negative potential to the capillary electrode.

TABLE III

INTERFACIAL SURFACE TENSION OF THE SOLUTIONS AGAINST MERCURY MEASURED BOTH NORMALLY AND WITH THE ELECTRODES SHORTED

	Concn. of electrolyte	Normal, dynes/cm.	Shorted, dynes/cm.
Pure water		374.8	374.8
Potassium citrate	0.025 <i>N</i>	388	372
Potassium citrate	.0025 <i>N</i>	383	371
Potassium chloride	.025 <i>N</i>	381	368
Potassium nitrate	.025 <i>N</i>	380	361
Potassium acid tartrate	.0016 <i>N</i>	358	340
Copper sulfate	.025 <i>M</i>	364	341
Ammonium chloride	.025 <i>N</i>	373	373
Potassium tartrate	.025 <i>N</i>	377	362
Sodium lauryl sulfonate	.001 <i>M</i>	372	373
Citric acid	.0025 <i>N</i>	285	293

If the reverse procedure was adopted, *i. e.*, letting the mercury recede into the capillary, a positive potential was obtained on the capillary mercury. If the mercury was continuous from the capillary to the fixed electrode, the potential was zero as is to be expected, but as soon as the two broke contact as the mercury settled in to the capillary, a positive potential was noticed. If the mercury was allowed to stand with a wide surface in contact with the solution for a few minutes, a film was formed on the surface. The film was invisible as long as the surface was constant, but as the surface decreased on settling into the capil-

lary, the film thickened, forming an immobile dark scum which rendered surface tension measurements impossible. This effect was obtained with the alkaline solutions and potassium chloride, but not noticeably with the acid solutions. This phenomenon may be explained as being due to the formation of hydroxide at the surface as suggested by Liebreich.⁸ If the time of standing above the capillary is not sufficient for the film formation, a position of equilibrium in the capillary is attained finally, the same as that obtained when the mercury was allowed to rise.

The potentials observed range in magnitude from 10 to 100 millivolts. They are of a drifting nature and are only approximately reproducible. By employing various modified capillarimeters it was definitely proved that these potentials are not a function of the surface of the fixed electrode nor of its relative elevation with respect to the capillary level. They are, however, dependent upon the particular capillary used as a mobile electrode. An apparatus having two capillaries gives no difference of potential when the mercury rises in both of them. They are both negative to the fixed electrode. When mercury rises in one and falls in the other, the former is negative and the latter positive with respect to the fixed electrode and to each other.

The results of Table III bring up the important question as to the true nature of the interfacial tension of the system mercury-water solution. In this investigation, with the exception of Table III, the normal unshorted values are reported and no attempt is made to arrive at the correct concept of interfacial tensions of mercury-water solution without further investigation.

Using the so-called normal values one is led to the conclusion that certain of the emulsifying solutions show an interfacial tension greater than that of pure water-mercury. In Table III, however, it is seen that all the shorted values are lower than that of pure water.

Summary

1. The interfacial tension of water against mercury, measured by the capillary rise method, is raised by the addition of either potassium citrate, potassium tartrate or potassium chloride.
2. Raising or lowering the interfacial tension of water against mercury bears no relation to its ease of emulsification in water.

(8) Liebreich, *Z. Elektrochem.*, **32**, 162 (1926).

3. For the solutions studied, those with pH greater than 7 have interfacial tensions greater than that of pure water-mercury; those with pH less than 7 have interfacial tensions less than that of pure water.

4. The pH of the solution has no direct bearing on the emulsification of mercury.

5. The electrocapillary curves of the systems

studied show that emulsifying and non-emulsifying agents give similar results with respect to maxima and form of curve.

6. Measurements of interfacial tensions made with the mercury and a fixed electrode in the solution shorted, give values less than that of pure water against mercury.

SEATTLE, WASH.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Silicon Compounds. I. The Use of Silicon Tetrafluoride in the Formation of Esters and Some Absorption Reactions

BY J. A. GIERUT, F. J. SOWA AND J. A. NIEUWLAND

It has been demonstrated recently in this Laboratory¹ that boron fluoride can be used to remove the elements of water and ammonia from alcohols and acids, and from alcohols and acetamide, to yield esters. Since silicon tetrafluoride resembles boron fluoride in many reactions of this type, we have studied its use in place of boron fluoride in the above reactions.

The silicon tetrafluoride was prepared either by heating to 150° a mixture of 156 g. of calcium fluoride, 300 g. (in excess) of finely pulverized silicon dioxide and 300-350 cc. of sulfuric acid, a slow stream of dry air being passed into the generator to assure a continuous flow of gas; or, more satisfactorily, by using a mixture of 100 g. of sodium fluosilicate, 15 g. of finely pulverized silicon dioxide and 250 cc. of concentrated sulfuric acid. The apparatus used was a modification of that of Adolph² with suggestions from the design of Armstrong.³

One mole each of the reacting substances was separately weighed into a 500-cc. Erlenmeyer flask fitted with a stopper carrying an outlet tube and an inlet tube which extended to within 2 cm. of the bottom of the flask. In the preparation of the benzoates, two moles of the alcohol were used to one of the acid. The amount of silicon tetrafluoride absorbed was ascertained by weighing the flask. In several cases where acetamide was used the alcohol was first saturated with silicon tetrafluoride and the acetamide then added.

The contents of the flask were refluxed for about twenty minutes. The upper layer which had then appeared was either distilled and then neutralized with a sodium carbonate solution or it was cooled and then neutralized directly. The ester layer was then separated, washed, dried over calcium chloride and fractionated.

Using acetic acid, between 0.1 and 0.3 mole of silicon tetrafluoride was absorbed per mole of methyl, ethyl, *n*- and *i*-propyl and *n*- and *i*-butyl alcohols. The yield of ester was practically quantitative for ethyl and methyl alcohol and between 20 and 60% for the other alcohols.

With benzoic acid similar amounts of silicon tetrafluoride were absorbed. A 40% yield of ester was obtained with methyl alcohol but only small yields, namely, 4-17%, with the other alcohols.

With acetamide between one-quarter and one-third of a mole of silicon tetrafluoride was absorbed with all of the alcohols and a yield between 13 and 20% of ester was obtained.

t-Butyl alcohol absorbed about 0.2 mole of silicon tetrafluoride and gave a yield of 4.3% ester with acetic acid. The phenol-acetic acid or acetamide solutions, although they absorbed some silicon tetrafluoride, gave either no ester or only a trace in all cases.

The absorption of silicon tetrafluoride by the alcohol alone was investigated using the same experimental arrangements. Methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *n*-amyl and *i*-amyl alcohols absorb about one-quarter of a mole of silicon tetrafluoride, the products being unstable addition compounds; phenol, ethyl ether, isopropyl phenyl ether, ethyl acetate and acetic acid do not absorb any silicon tetrafluoride. Acetamide absorbs about one-quarter and tributylamine about two-thirds of a mole, forming white solids.

Ammonia passed into an alcoholic solution of silicon tetrafluoride forms a white precipitate, which after removal can be sublimed without decomposition and appears to correspond to $SiF_4 \cdot (NH_3)_2$ as previously reported.⁴

It is interesting that in the case of isopropyl alcohol a white gelatinous substance began to form, indicating a possible slight dehydration of the alcohol, and indeed an absorption slightly greater than one-quarter of a mole was obtained in this case.

Summary

Various esters have been formed by treating acetic acid, benzoic acid or acetamide with alco-

(1) Sowa and Nieuwland, *THIS JOURNAL*, **55**, 5052 (1933); **56**, 271 (1936).

(2) Adolph, *ibid.*, **37**, 2500 (1915).

(3) Armstrong, *Ind. Eng. Chem., Anal. Ed.*, **5**, 315 (1933).

(4) Mixer, *Am. Chem. J.*, **2**, 153 (1881).