was allowed to evaporate through a layer of water containing a small amount of sodium hypobromite. This method was chosen in preference to one which would introduce considerable amounts of other reagents after a control determination showed good recovery of iodine.

From the data in the table it is evident that bromine of sufficient purity for microchemical work can be prepared by the washing method. It is also evident from data on the third washing at the end of one and three hours, respectively, that considerable time must be allowed for the reaction between iodine bromide and water to take place. Water from the third washing, if separated from the bromine residue, would introduce less than 0.04 gamma of iodine into the sample per cc. of bromine water used. Saturated bromine water prepared from the bromine obtained at this stage would contain approximately one-twentieth of that amount.

Summary

A method for the preparation of iodine-free bromine for use in the micro-analytical determination of iodine is described.

PITTSBURGH, PENNSYLVANIA

THE SURFACE RELATIONS OF POTASSIUM ETHYL XANTHATE AND PINE OIL. I

BY C. C. DEWITT AND EDWIN E. ROPER

During recent years the froth flotation method for the concentration of ores has made great progress, but an actual knowledge of the mechanism of the formation of the froth and the flotation of the metallic values by the admixture of potassium ethyl xanthate and pine oil is still lacking. A program of research has been instituted from which, it is hoped, a satisfactory explanation of the phenomena may result. This paper is a brief exposition of the methods used and the results obtained in the first stage of the investigation. Generalization in the field as a whole is reserved for later papers, when more complete data on the surface relations of these materials will be available. In this report data on the surface relations of solutions of potassium ethyl xanthate and pine oil are presented, the relative values of the various data are discussed, and problems are suggested for future solution.

The surface tension of the potassium ethyl xanthate solutions was measured by the methods of Ferguson and Dowson and the interfacial tension of the xanthate–pine oil system by the method of Bartell and Miller. A series of parallel determinations was carried out on sodium car-

bonate solutions in order to determine the effect of the hydroxyl ion. Several relevant secondary phenomena were observed, the significance of which will be more thoroughly investigated, and reported in later papers.

Purification of Materials.—The xanthate as purchased was a supposedly pure product, but upon examination it gave a distinct carbon disulfide odor and showed a brownish-yellow color, and also heterogeneous lumps of darker shade; these lumps were picked out and discarded as unfit material. Considerable effort was expended in working out a suitable method of purification. Foster[1] states that recrystallization from acetone–benzene, and from acetone–petroleum ether mixtures, or from alcohol can be used to obtain pure crystals of xanthates. It is to be noted that Foster prepared his xanthates from pure materials and proceeded immediately to purification. We followed his method on a small scale and obtained a good product. For large quantities of material this method of recrystallization did not prove applicable; the xanthate thus obtained was found to decompose so readily that the product was not much purer than the original. A precipitation method was devised whereby the xanthate was exposed to the solvent and to the atmosphere for a short time only.

Because of the high specific volume of the xanthate and the large amounts of solvents necessary, a batch of 100 g. was about the maximum amount that could be handled conveniently. One hundred grams of xanthate was added to 1000 cc. of warm acetone (40°) on a water-bath and stirred for a few minutes; some of the xanthate did not dissolve—in fact, this undissolved portion appeared to be quite different from the rest, being but slightly soluble even in an excess of boiling acetone. No attempt was made to examine this insoluble portion; it was filtered off through a hot water funnel and discarded.

To the cold filtrate 4000 cc. of benzene was slowly added, with stirring, and the precipitate was filtered out on a Büchner funnel, with the aid of suction. This precipitate was then dissolved in 500 cc. of acetone and 5000 cc. of petroleum ether quickly added, with no stirring. The precipitate thus obtained was again recovered by filtration through a Büchner funnel and was washed with several 50-cc. portions of petroleum ether (40–50°). It was then transferred to a vacuum desiccator containing a small beaker of concentrated sulfuric acid and a small amount (15–20 g.) of recently heated active charcoal on a watch glass, and was kept under a vacuum of a millimeter of mercury for at least twelve hours. At the end of this time, the acid and the charcoal were exchanged for fresh portions and the xanthate was stored in the desiccator. This purified product had no odor, was of a light cream color, and gave a colorless dilute solution in water. The degree of purity of this xanthate was established by comparative determinations of sulfur content: Carius method: S calcd. 40.01; S found, 39.98. The decomposition point of the purified material on heating was $200 \pm 0.3°$. Subsequent batches of xanthate purified in the same manner were checked as to purity by the surface tension values of solutions and the density of these solutions. The decomposition point of the xanthate was found to be easily reproducible.

The pine oil, obtained from the Hercules Powder Company, was a triply distilled commercial product with a clear, light yellow color. This material consisted mainly of a mixture of pinene, fenchyl alcohol, α-terpineol, dipentene, terpinolene and borneol. No attempt was made to purify it other than to remove most of the water. This was accomplished by allowing the oil to stand for one month or longer in contact with granular, anhydrous calcium chloride. The density dropped no lower after this interval, indicating that all the water which could be removed by this method was taken out.

[1] Foster, "Preparation of Xanthates and Other Organic Thiocarbonates." University of Utah, Tech. Paper No. 2, 1928.

All other materials were purchased as c. p. reagents and were purified by recrystallization methods.

Thermometric Standards.—Thermometers used were checked against the melting points of triply distilled water, purified naphthalene, benzoic acid, urea, diphenylurea and anthracene. The values of these melting points were taken from "International Critical Tables."

Determination of Surface Tension.—The selection of a simple and reliable method of determining surface tension presents considerable difficulty. The capillary rise method, as has been shown by other workers[2] in this field, is difficult to apply properly. Its great disadvantage is in the difficulty of obtaining even a short length of capillary tubing with a uniform bore; Harkins and Brown[2b] examined 500 feet of capillary, and Richards and Carver[2c] a like amount before they found a short piece suitable to their needs.

The method of Ferguson and Dowson[3] was used in measuring the surface tension values reported in this paper. This method makes use of the fact that if a capillary tube is immersed vertically in the liquid for which the surface tension is to be evaluated and if the meniscus is forced down to the exact end of the capillary by applied pressure, then the value of the surface tension, γ, may be expressed in terms of six factors: (1) the height of the manometric liquid, h_m; (2) the density of the manometric liquid, ρ_m; (3) r', the radius of the capillary at the extreme end of the immersed portion; (4) ρ_c, the density of the liquid under investigation; (5) h_c, the depth of immersion of the capillary; and (6) the contact angle, θ, between the experimental liquid and the capillary.

Some contact angles have been measured and found to be zero for a water–glass interface. A contact angle of 6° will give rise to an error of about 1% in the value of the surface tension of water. The most concentrated xanthate solution used was 1.3 molal, and if the contact angle were formed by the addition of the solute, it would probably necessitate but a small correction.

For this type of apparatus, Ferguson and Dowson have given the mathematical relationship connecting surface tension and the six factors mentioned. However, their final equation, while correct, is not clear in its definition of terms nor in the assumptions made. In particular, their densities as written should mean the density of the liquid minus the density of the saturated vapor.

According to Dr. N. E. Dorsey[4] the equation for the surface tension should be

$$\gamma = \frac{g\,r'}{2}\,[(\rho_m - \sigma_m)h_m - (\rho_0 - \sigma_0)h_0] + \frac{1}{6}\,r'^2\,(\rho_0 - \sigma_0)g \tag{1}$$

---

[2] (a) Richards and Coombs, THIS JOURNAL, **37**, 1656 (1915); (b) Harkins and Brown, *ibid.*, **41**, 502 (1919); (c) Richards and Carver, *ibid.*, **43**, 638 (1921).

[3] Ferguson and Dowson, *Trans. Faraday Soc.*, **17**, 384 (1921).

[4] Dr. N. E. Dorsey, private communication.

in which g is the acceleration due to gravity, σ_c is the density of the vapor immediately over the meniscus in the capillary, and σ_m is the density of the vapor immediately over the meniscus in the arm of the manometer. The remaining symbols have been defined.

In all of our determinations water was used as the manometric liquid and since the vapor pressure lowering due to the solute is negligible (mole fraction of xanthate at the highest concentration is 0.02), we may use as an approximation

$$\sigma_o = \sigma_m \tag{2}$$

To neglect σ_m will limit our accuracy to about 0.5% at values of $\gamma = 70$ dynes per centimeter. Since this order of accuracy was suitable, σ_m was entirely neglected. In the second term on the right-hand side of (1) $r'^2 \sigma_c$, being of the second order, may be neglected without influence on the results.

The simplified equation now becomes

$$\gamma = \frac{g\,r}{2}\,[\rho_m h_m - \rho_o h_o] + \frac{1}{6}\,r^2\,\rho_c g \tag{3}$$

This is the equation which Ferguson and Dowson give and is that which Edwards[5] used to calculate his results.

In equation (3) it will be noticed that we have substituted r for r', where r is the "effective" radius of the immersed end of the capillary. This change was adopted for our convenience; it will be explained later in connection with standardization.

For ease in computing values of γ from experimental data we can write

$$\gamma = A\Sigma(\rho h) + B\rho_o \tag{4}$$

where

$$A = \frac{g\,r}{2};\ \Sigma(\rho h) = (\rho_m h_m - \rho_o h_o);\ B = \frac{g\,r^2}{6}\ . \tag{5}$$

It can be seen that A and B are constants for a given apparatus.

The apparatus in its final form is shown in Fig. 1. It consisted of Pyrex glass with all joints fused, except the short length of rubber tubing K. The beaker, D, was at least 45 mm. inside diameter; all the experimental liquid was immersed in the thermostat, with the capillary tip 4–5 cm. below the experimental liquid surface. The manometer, the air reservoir and the connecting lines were all immersed in the thermostat liquid wherever possible. The pressure necessary to force down the meniscus was applied to the tip through a column of water NAKF and was varied by raising or lowering the reservoir N by means of the rod L, which operated a rack and pinion gear. The arm LP for operating the elevating mechanism of the reservoir, N, extended back to the cathetometer, a distance of about 150 cm., in order that the pressure might be varied, and the result observed through the cathetometer telescope. This connecting arm, operating in bearings at 75-cm. intervals, provided a means of delicate adjustment of the pressure.

Stopcock B was used in cleaning the tip. During this cleaning, stopcock A was closed and the open arm of the manometer was plugged with a cork. When a deter-

[5] Edwards, *J. Chem. Soc.*, **127**, 744 (1925).

mination was to be made, the positions of the stopcocks were reversed and the cork removed.

The aquarium thermostat had two plate glass sides and contained 48 liters of a colorless mineral oil (Finol). In Fig. 1, a cross sectional view is given. The remaining walls of the tank were of sheet copper, with a 5-cm. layer of insulating material on the outside.

Both the copper tank and the stirrers and metal stands within the bath were grounded through a switch. After equilibrium of the meniscus was attained the switch was opened to discover whether any electrical effect on the meniscus could be observed. No disturbance of the meniscus level could be observed when the switch was left open while equilibrium was being established and then closed.
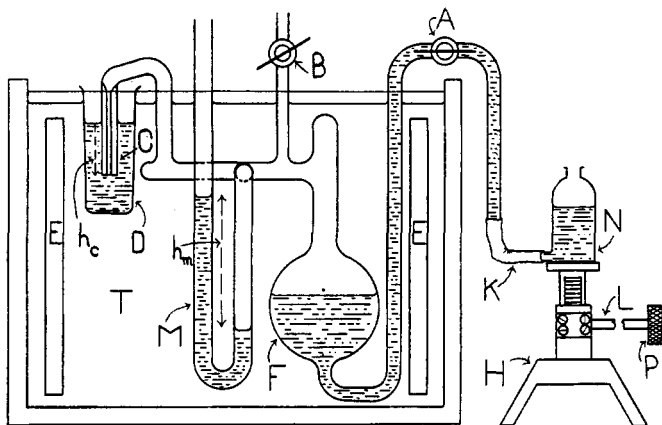

Fig. 1.—Ferguson apparatus for determining surface tension by balanced pressure.

The temperature of the bath was set at 25°. Near the center of the bath variations of 0.01° were rare.

The capillary tip C was kept immersed in a chromic anhydride-sulfuric acid mixture when not in use; just before a determination the tip was thoroughly cleaned and immersed in the experimental liquid contained in D. (The complete glass apparatus could be moved vertically on a slide.)

After thermal equilibrium was attained, air, forced out of the tip by the raising of N, gave a fresh surface; the meniscus was then pulled into the capillary for about a millimeter to wet the walls and was then forced down to the end of the tip. The horizontal cross hair of the cathetometer telescope was set on the end of the tip. After drainage had ceased, the final adjustment of bringing the meniscus into coincidence with the cross hair was accomplished, and h_0 was measured. Next h_m was measured, and finally each height was checked.

Tip No. E was standardized by finding the $\Sigma(\rho h)$ in equation (4) for pure water at 25°. The values were substituted in equation (3) and the resulting quadratic was solved for r, the value of γ being taken as 71.97 dynes per cm.[6] The mean of six determinations gave the average value of r as 0.017915 cm. with a maximum deviation of 0.2%. This method gives the value of r, while a comparative reading would give r'. The quantity r can be given the significance of a mean, integrated radius, which,

[6] "International Critical Tables," Vol. IV, p. 447.

when substituted in equation (3), gives a correct value of ($\gamma = \pm0.5\%$), but this r is not necessarily the actual radius that would be obtained by physical measurements.

As a check on this value of r, the same procedure was carried out using purified benzene as the experimental liquid, the value of γ for benzene at 25° being taken as 28.22 dynes,[6] and the average value of r was found to be 0.01792 cm., with a maximum deviation of 0.2% from the mean.

Using the value of 0.01792 cm. for r, we calculated the values of the constants A and B in equation (4)

$$\gamma = 8.7898 \ \Sigma(\rho h) + 0.0526 \ \rho_0$$

The value of g for this locality has been found to be about 981 dynes. The values for the densities of water and benzene were taken from "International Critical Tables."

Determination of Interfacial Tension.[7]—The method of Bartell and Miller[7] was used for determining the tension at the interface of the two liquid phases. The method is adequately treated by the authors in their original article, which can be consulted for details.

The radii of the cell capillaries were standardized with water and as a check the interfacial tension of the system benzene–water at 25° was determined. A maximum deviation of +0.17% from the accepted value of 34.56 dynes per cm. was observed for cell No. 2, and a deviation of −0.17% for cell No. 1.

The density of the solutions was determined by the pycnometer method, using 25-cc. pycnometers. These were placed in a smaller water-bath which was then immersed in the main oil-bath. No difficulty was experienced in obtaining results accurate to the fourth decimal place.

Results

The values of γ^{25} for xanthate solutions were determined; these data are given in Table I and are presented graphically in Fig. 2. On the same graph is plotted the surface tension of sodium carbonate solutions, the values being taken from "International Critical Tables."

TABLE I

THE SURFACE TENSION OF AQUEOUS POTASSIUM ETHYL XANTHATE SOLUTIONS AT 25°

m, molality of xanthate	N_2, mole fraction of xanthate	d_4^{25}, g./cc.	γ^{25}, dynes/cm.
0.0000	0.0000	0.9971	71.97
.2700	.0048	1.0145	71.36
.6510	.0116	1.0374	69.44
.9430	.0167	1.0512	68.10
1.3020	.0229	1.0679	65.95

The values obtained for the interfacial tension of pine oil–xanthate solutions represent mutual saturation to such an extent as saturation took place at the interface after the two phases had been in the cell. Attempting

Bartell and Miller, THIS JOURNAL, **50**, 1961 (1928).

mutual saturation earlier gave rise to an emulsion. The character of each phase adjacent to the interface in the cells indicated saturation. A slow change of tension with time was noted but was not investigated thoroughly.
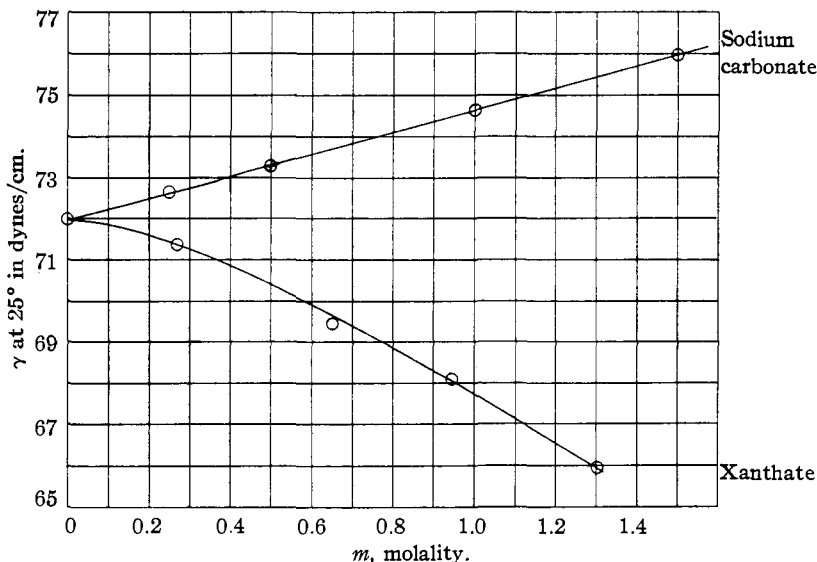

Fig. 2.—Surface tensions of Na_2CO_3 and $KS(S)COC_2H_5$ at 25°; values for Na_2CO_3 from "I. C. T.," Vol. IV, p. 446.

The values given for S represent the interfacial tension at zero time of contact of the two phases, since they are either the values obtained as soon as

TABLE II

INTERFACIAL TENSION OF PINE OIL AGAINST AQUEOUS POTASSIUM ETHYL XANTHATE SOLUTIONS AT 25°

m molality of xanthate	d_4^{25}, density of xanthate solutions	$S_{2,3}$, interfacial tension (dynes/cm.)
0.00000	0.9971	10.88
.0370	.9992	11.63
.0750	1.0018	11.97
.1110	1.0041	12.19
.1470	1.0064	12.36

TABLE III

INTERFACIAL TENSION OF PINE OIL AGAINST AQUEOUS SODIUM CARBONATE SOLUTIONS AT 25°

m molality of Na_2CO_3 solution	d_4^{25}, density of Na_2CO_3 solution	$S_{2,3}$, interfacial tension (dynes/cm.)
0.0000	0.9971	10.88
.0228	.9996	10.16
.0584	1.0034	9.75
.1480	1.0128	8.88

The density of our sample of dried pine oil was 0.9279 g./cc.

possible after the cell was filled or the values obtained by the extrapolation of the S–time curve to zero time. The value of dS/dT was negative for the xanthate–pine oil system and positive for the sodium carbonate–pine oil system. Tables II and III give the collected data, both sets being graphed on Fig. 3.
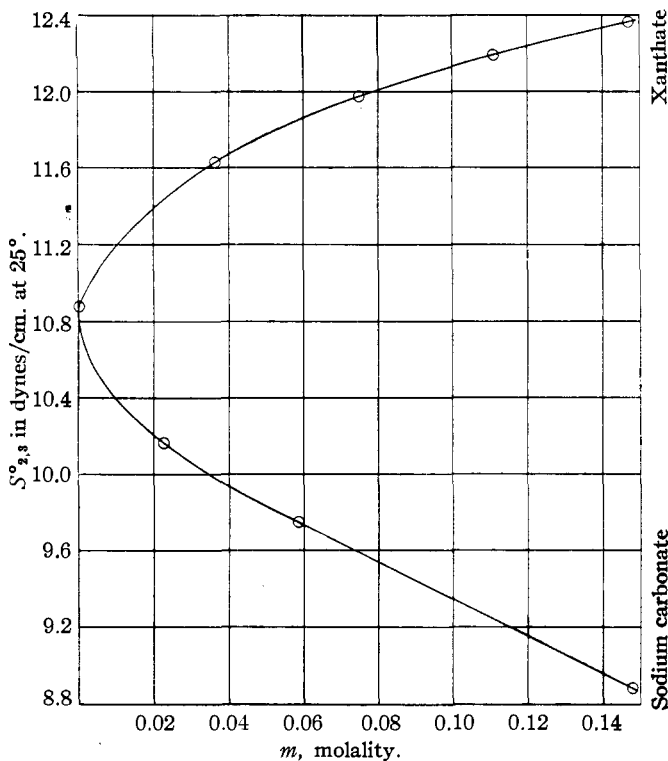

Fig. 3.—Interfacial tension of aqueous solutions against pine oil at 25°.

In the initial stage of the experimental work it was noticed that the xanthate solutions changed color upon standing. In view of this, all determinations were made upon freshly prepared solutions. In order to investigate the effect upon the physical properties being measured, these properties were determined on different solutions over a period of a month. Table IV shows some typical results obtained on one solution.

Thus it can be seen that the appearance changes markedly after one day of standing, the density shows practically no change within the limits of experimental error, and the interfacial tension against pine oil shows a slight minimum at the time of turbidity, or translucence.

This translucent state became evident from eight to forty-eight hours

TABLE IV

CHANGES IN POTASSIUM ETHYL XANTHATE SOLUTIONS, 0.037 MOLAL, KEPT IN A GLASS-STOPPERED PYREX FLASK AT ROOM TEMPERATURE

Interval after preparation, days	Appearance	Odor	d_4^{25}, g./cc.	$S_{2,3}$, dynes/cc.
0	Clear, very light yellow	None	0.9992	11.97
1	Translucent, yellow	None	.9990	11.38
8	Clear, brownish-yellow	CS$_2$	.9989	11.68
28	Clear, brownish-yellow	CS$_2$	.9990	11.63

after the solution had been prepared, the time being roughly proportional to the concentration of the xanthate solution. This cannot be due to the presence of residual solute, for then it should make its appearance upon preparation of the solution, and should be permanent, since the xanthate solution was not removed from the flask, except for the amounts necessary for determinations. No separation either of a liquid or a solid phase was observed. An examination of the P_H values at different times showed that there was a distinct and continuous change in hydrogen-ion concentration as the change proceeded.
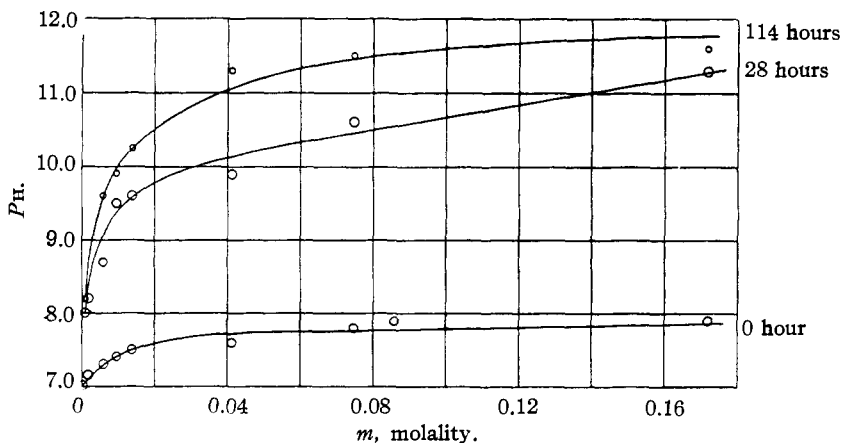

Fig. 4.—Variation of P_H of xanthate solution.

Solutions of different concentrations were placed in the thermostat at 25° and the hydrogen-ion concentration determined at intervals by means of a roulette comparator. At the end of 114 hours the more concentrated solutions were so highly colored that the colorimetric determination was but a very rough estimate of the P_H value. The results are shown graphically in Fig. 4.

Discussion of Results

The xanthate readily hydrolyzes in aqueous solution, since C$_2$H$_5$OC-(S)SH can be classed as a weak acid.[8] Other reactions probably occur,

[8] Halban and Kirsch, *Z. physik. Chem.*, **82**, 325 (1913); Halban and Hecht, *Z. Electrochem.*, **24**, 65 (1918).

since ethyl xanthic acid is readily decomposed at room temperature, and its low boiling point, 24°, together with its slight solubility in water, 0.02 mole per liter, would tend to shift the hydrolysis toward the acid side of the reaction, which alone would probably account for the observed change in P_H with time.

Sodium carbonate solutions were studied in experiments parallel to those of xanthate solutions to show the effect of the hydroxyl ion on γ and $S_{2,3}$, resulting from the alkali salt of a weak acid.

According to the deductions from the modified Gibbs equation

$$\Gamma = -\frac{m}{RT}\left(\frac{d\gamma}{dm}\right)_T$$

if $d\gamma/dm$ is negative, the surface or interfacial concentration of the solute, Γ, is positive, and *vice versa*. Recently the assumptions made in deriving this equation have been questioned.[9] Under any circumstances the activity of the solute should be used in place of its molality, so that the equation would be: $\Gamma = d\gamma/RT\, d\ln a$. Preliminary measurements of freezing point lowerings have been made, and the activity for xanthate solutions has been evaluated from these measurements; but before the results may be considered as final, the work is to be repeated. Qualitative results obtained from the use of the Gibbs equation are summarized in Table V.

TABLE V

SIGN OF Γ, SURFACE CONCENTRATION OF SOLUTE AT DIFFERENT INTERFACES

Liquid 2	Air–liquid 2 interface (γ)	Pine oil–liquid 2 interface ($S_{2,3}$)
K Et X (aq.)	Positive	Negative
Na$_2$CO$_3$ (aq.)	Negative	Positive
Pine oil (aq.)	Positive[a]	0

[a] Fahrenwald, *Min. Sci. Press*, **123**, 227 (1921); Gaudin, Univ. Utah Tech. Paper No. 1 (1928).

From Table V it can be seen that, qualitatively, xanthate solutions behave quite oppositely to sodium carbonate solutions. From this it would appear that the hydroxyl ion resulting from hydrolysis cannot be wholly responsible for the results obtained from xanthate solutions.

Harkins and his collaborators[10] have studied, among other substances, the surface relations of water, carbon disulfide and ethyl mercaptan. Their results show that the (SH) part of the mercaptan molecule is more polar than the divalent sulfur atom; that when the mercaptan lies in contact with water, most of the (SH) groups are turned toward the polar phase—in this instance, water; and that when these groups are pulled

[9] Harkins and McLaughlin, THIS JOURNAL, **47**, 2086 (1925); Harkins and Gans, "Colloid Symposium Monograph," **6**, 17 (1928); McBain and Davies, THIS JOURNAL, **49**, 2230 (1927).

[10] Harkins, Clark and Roberts, *ibid.*, **42**, 707 (1920).

from the water, the polarity of the group is evident in the high value of adhesional work[11] of the mercaptan and in the smaller value for carbon disulfide, which is 12.7 ergs less.

On account of the SH group the behavior of $C_2H_5OC(S)SH$ should be somewhat similar to that of mercaptan, and also to that of carbon disulfide, since the divalent sulfur atom is also present. The ether type of bonding should give rise to strong non-polar characteristics. Hence this molecule should show a non-polar end $(C_2H_5$—O—C—$)$, and a polar end, —CS— S—H. The combined effect of these four groupings—hydrocarbon, ether, disulfide and mercaptan—is rather difficult to predict.

At the surface of an aqueous solution of xanthate, the polar end will extend into the water phase, while the non-polar end will extend into the vapor phase. Theoretically, the concentration at the surface should be greater than in the bulk of the liquid; such is shown to be the case in Table V.

At the surface of a xanthate–pine oil system, the polar end will extend into the aqueous phase and the non-polar end will certainly be repulsed by that phase. Whether it will be attracted by the pine oil phase should depend upon the polarity of that phase. From a consideration of the components of pine oil, it would seem that a majority of non-polar substances predominates. If this is a correct assumption, the concentration of xanthate should be greater in the interface than in either of the two phases, pine oil and water. The indications from the S–m curve show that dS/dm is positive, and therefore the interfacial concentration of the xanthate is less than in the bulk of the aqueous phase. However, we do not know whether we are measuring the interfacial concentration of the potassium salt, the acid or the ions; the most plausible assumption is that we are measuring the combined effect of all three.

Hence, no attempt can be made to draw logical conclusions until more interfacial data are obtained. The effect of hydroxyl ion on interfacial tension between xanthate solutions and each pure component of pine oil as the non-polar phase, must be determined. This investigation is being carried on at present.

Summary

1. The surface tensions of aqueous potassium ethyl xanthate solutions up to 1.3 molal have been measured at 25°, and $d\gamma/dm$ has been found to be negative.

2. The interfacial tension of dilute solutions of potassium ethyl xanthate against pine oil has been measured at 25°, and dS/dm has been found to be positive.

3. It has been shown by means of parallel experiments with sodium

[11] Harkins and Cheng, THIS JOURNAL, 43, 35 (1921).

carbonate, that the hydroxyl ion resulting from the hydrolysis of the alkali salt of a weak acid cannot be wholly responsible for the observed results.

HOUGHTON, MICHIGAN

THE SURFACE RELATIONS OF THE COMPONENTS OF PINE OIL AND OF POTASSIUM ETHYL XANTHATE. II[1]

BY C. C. DEWITT AND R. F. MAKENS

The object of the work here reported is two-fold: to determine the surface relations of aqueous solutions of various components found in pine oil and to extend the work of DeWitt and Roper[2] on the surface tensions of aqueous potassium ethyl xanthate solutions. The data on surface tension will be used in conjunction with wettability experiments now in progress in this Laboratory. The data on the pine oil components can also be used as a measure of the value of the several constituents as frothers for ore flotation purposes.

All surface-tension determinations were made with a drop-weight apparatus, and all interfacial tension determinations with a drop-volume apparatus. Both sets were constructed by Mr. Richard Kittel of the Kent Chemical Laboratories, the University of Chicago, under the supervision of Dr. Gans.

The drop-weight apparatus was similar to that used by Gans and Harkins[3] except for the method of raising and lowering the supply bottle. Each determination consisted of a run of thirty drops followed by a run of five drops. The difference represented the weight of twenty-five drops. Two determinations were made at each concentration. This procedure is that suggested by Harkins and used in the experiments reported in his latest paper on the subject, except that he made twenty-drop instead of thirty-drop runs. The equation used in the calculation of the surface tension is

$$\gamma = \frac{w\,g\,\phi}{2\,\pi\,r}$$

where γ is the surface tension, w is the weight of one drop, d is the density of the liquid phase, r is the radius of the tip, v is the volume of the drop calculated from the weight and density and ϕ is the reciprocal of a function of $r/v^{1/3}$.

The functions were taken from the work of Harkins and Brown.[4]

[1] These papers were presented at the Spring Meeting of the American Chemical Society at Indianapolis, Division of Physical and Inorganic Chemistry.

[2] DeWitt and Roper, THIS JOURNAL, 54, 444 (1932).

[3] Gans and Harkins, ibid., 52, 2290 (1930).

[4] Harkins and Brown, ibid., 41, 519 (1919).