

The Adsorption of S³⁵ Labelled Sodium Tetradecyl Sulphate at the Solution-Air Interface of Solutions Containing Sodium Tetradecyl Sulphate and Sodium Dodecyl Sulphate

GÖSTA NILSSON and OLE LAMM

Division of Physical Chemistry, Royal Institute of Technology, Stockholm, Sweden

Using surface tension-concentration measurements and the Gibbs adsorption equation the surface excess for systems containing one or two¹ surface-active substances has been calculated. In these calculations one usually approximates the activities of the solutes with their concentrations. This is perhaps accurate below the C.M.C. (critical micelle concentration) but not at higher concentrations². At concentrations greater than the critical the surface excess calculated using this approximation will be smaller than the true one. This can be demonstrated by the following calculation using Gibbs' adsorption equation for one component in its exact (1) and approximate (2) forms where γ is the surface tension in dyn/cm and Γ the surface excess in mol/cm².

$$d\gamma = -\Gamma_a \cdot 2 RT \, d \ln (f_{\pm} \cdot c) \quad (1)$$

$$d\gamma = -\Gamma_c \cdot 2 RT \, d \ln c \quad (2)$$

The two equations give

$$\Gamma_c/\Gamma_a = 1 + \frac{c}{f_{\pm}} \cdot \frac{df_{\pm}}{dc} \quad (3)$$

where $df_{\pm}/dc < 0$. This shows that the calculated surface excess (Γ_c) is smaller than the true one (Γ_a). The true surface excess can however be measured directly by application of a tracer technique using radioisotopes³⁻⁹.

The tracer technique is as follows: Sodium tetradecyl sulphate was labelled with S³⁵ and the activity from its solution was then measured with an end-window Geiger-Müller tube. Because of the relatively large range of beta particles from S³⁵ one does not only measure the activity from the surface-adsorbed molecules but also from those which are

dissolved to a depth of about 0.3 mm (beta particle range in water) below the surface. To correct for this extra activity, solutions with different concentrations of the S^{35} labelled sulphuric acid used in the synthesis were prepared. Since this acid has exactly the same specific activity as the synthesized compound but is not surface-active in this concentration range¹⁰, the activity from such a solution is the same as the activity from the interior of the surface-active solution at the same concentrations of the labelled substances when measured under the same conditions. From these two measurements the activity from the adsorbed molecules was determined.

The surface excess in mol/cm² was then calculated from a measurement of the specific activity, defined as the activity which one mol of the labelled substance would show under the same conditions of measurement as the adsorbed molecules.

Though the method is not yet very accurate its advantage lies in its application to systems with concentrations above the critical or to systems with many solutes. Gibbs' adsorption equation would in the first case be too inaccurate in its approximate form and in the second case it would be too complicated to handle.

EXPERIMENTAL

Pure *n*-dodecanol and *n*-tetradecanol, kindly supplied by Dr. Stenhagen of Upsala, were sulphated according to a method described elsewhere⁸. The *n*-tetradecanol was sulphated with S^{35} labelled sulphuric acid from Oak Ridge.

It is found¹¹ that if the alkyl sulphate contains 1 % of a normal alcohol with the same number of carbon atoms, then the alcohol will constitute 50–80% of the mixed surface film. When the C.M.C. for the soap is reached such a mixture will give a very sharp minimum in the surface tension-concentration curve¹². Even as small amounts of alcohol as 0.05 % cause the minimum to appear¹¹. The purifying of alcohol sulphates, where the most probable impurity is unsulphated alcohol, is therefore very important and the surface tension versus concentration measurements can be used as a very sensitive method for the indication of impurities.

The soap may be purified by ethyl ether extraction¹², foamextraction^{13,14} or emulsion-extraction^{13,14}. The two substances were extracted with diethyl ether in a micro extraction device and recrystallized several times from ethanol. As shown from the surface tension-concentration curves in Fig. 1, measured at $22 \pm 2^\circ \text{C}$, the large depression in the sodium dodecyl sulphate curve has disappeared but the values are 1–3 dyn/cm lower than those of Miles and Shedlovsky¹². Hence it is possible that traces of impurities ($\ll 0.05\%$) remain in the soap. The sodium tetradecyl sulphate curve still shows a minimum of about 0.6 dyn/cm. It seemed to be impossible to purify this substance completely with this method. Some of the other methods may perhaps have been more effective, but because the loss of material is rather large with these methods they could not be used.

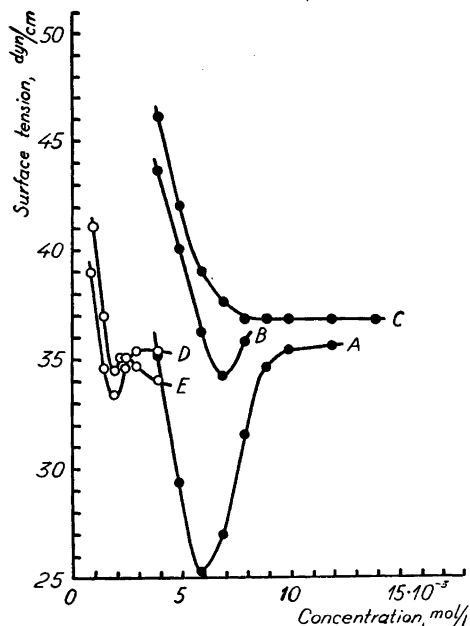


Fig. 2. The measuring device. A is the G.-M tube, B the aluminium tube and C the lucite cuve.

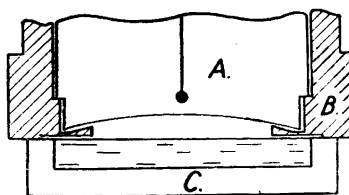


Fig. 1. Surface tension curves.
A, B and C = sodium dodecyl sulphate.
(A before and C after purifying.)
D and E = sodium tetradecyl sulphate.
(D before and E after purifying.)

In the purifying process the minimum in the surface tension-concentration curve decreases and at the same time moves to higher concentrations (Fig. 1 the curves A and B). This may be explained by the fact that in the presence of an alcohol the C.M.C. is reduced¹⁵ and that this reduction is a function of the alcohol concentration.

The measuring device is schematically shown in Fig. 2. The tube A is an Amperex 200-CB end-window Geiger-Müller tube with a window thickness of 1.4 mg/cm^2 . A correction curve for the dead time of the tube was determined using J^{128} according to Kohman¹⁶. The tube rests on the flange of the aluminium tube B and the latter rests on the edges of the lucite cuve C. The bottom flange of the aluminium tube forms a screen for the beta particles coming from the edges of the cuve where the conditions are less defined because adsorption on the cuve may take place or the surface of the solution may be curved. The distance from the center of the curved G.-M window to the surface of the solution is 2.8 mm and the inner radius of the G.-M tube is 16 mm. With these figures and assuming that the sensitive volume of the G.-M tube starts 4 mm behind the window, the geometry is approximately 30% (a point source in the centre of the surface of the solution according to Burt¹⁷). The cuve is 2 mm deep and has a radius of 17.5 mm. It was filled to the brim with the solutions and the geometry was exactly reproduced except for small differences (about 0.2 mm) in the distance from the G.-M window to the surface of the solution. Experiments have however shown that these differences have no measurable influence upon the activity from the surface.

All measurements have been carried out in an air-thermostat, which at the same time protected the solutions from dust. With regard to the solubility of the sodium tetradecyl

sulphate, the temperature of the thermostate was held at 30 ± 1 °C, and to avoid evaporation from the solutions the air in it was kept at a relative humidity between 85 and 95 %.

In the first measurements it was found that water vapour condensed on the G.-M window and formed small droplets. To avoid this the G.-M tube was heated with a spiral of kanthal wire to 5° C above the temperature of the thermostate. This is very important because a water film of only 0.5μ thickness reduces the activity by 1 %. Macaulay and Carson^{18,19} have found that when, as in this case, the mica surface is not clean or the water vapour pressure is close to the saturation pressure it will be covered with a water film. The thickness of this film may however be regarded as constant under constant humidity and temperature, which is not the case for the film of water droplets. These droplets were never observed, when the tube was heated.

It was found that the activity from the solutions of sodium dodecyl sulphate and sodium tetradecyl sulphate decreased with time and after about 60 minutes reached a constant value, which was between 93 and 96 % of the initial one. The cuve was covered the whole time by the G.-M tube. If however the tube was taken away from the cuve the activity increased in five minutes to its initial value. If the cuve was covered with a glass plate, when the tube was taken away, the activity had not changed when measured again after five minutes. This indicates that the decrease in activity does not depend upon water vapour condensation on the G.-M window but has something to do with the evaporation from the surface of the solutions. This was supported by the fact that in all cases when water vapour condensed upon the glass plate the activity had increased when measured again after five minutes. These effects were not found in the measurements on S³⁵ labelled sulphuric acid. Lottermoser and Stoll²⁰ have found that the surface tension of sodium tetradecyl sulphate at constant concentration decreases with decreasing temperature and from their curves it is seen that dy/dc at the same time increases. But an increase in dy/dc and a decrease in temperature gives, according to Gibbs' adsorption equation an increase in the surface excess and consequently an increase in the activity from the solution. This may explain the effect of increasing activity because evaporation from the solution decreases the temperature of the surface layer. This effect may also influence surface tension measurements and give lower absolute values than those obtained from a solution in equilibrium with its saturated vapour. The evaporation effect here discussed was obtained although the relative humidity in the air thermostate was between 85 and 95 %. Care was taken not to make measurements before equilibrium was obtained (*i.e.* constant value of the activity).

Before each measurement of the activity the surface of the solution was cleaned with the aid of a platinum wire mesh. The wire-mesh was put below the surface and then raised slowly. When the mesh broke the surface, the surface layer adhered to it and was

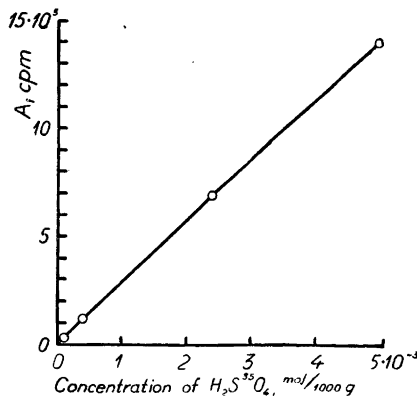


Fig. 3. The activity from the interior of the solution.

thus easily removed. A fresh prepared solution generally gave the lowest values of activity. When used several times the activity from the surface increased, sometimes as much as 20%, perhaps due to the accumulation of impurities. Cleaning of the surface had in these cases only a little effect. For this reason a solution could be used for no more than one single measurement.

To determine the activity from the interior of the solutions different concentrations of the S³⁵ labelled sulphuric acid used in sulphating the alcohol was carefully titrated and the activity measured in the same way as the activities from the surface active solutions. The activity versus concentration curve was almost a straight line (Fig. 3). The activity from the surface calculated as the total activity minus the activity from the interior of the solution has in these experiments only been between 4 and 19% of the total activity.

To determine the specific activity as earlier defined 0.1 ml of a 0.110 M solution of the S³⁵ labelled sulphuric acid was evaporated in the centre of a lucite plate and the activity measured. In this measurement the lucite plate replaced the cuve in the measuring device and had its surface at the same level as that of the solutions. The specific activity so measured was $2.39 \cdot 10^{11}$ cpm/mol.

The question now is if this measuring technique gives the specific activity according to the definition on page 2. For this to be true the measuring conditions for surface adsorbed molecules and the sulphuric acid molecules must be the same. The specific activity of the surface adsorbed and the sulphuric acid molecules is the same and they are measured in the same geometry in the same measuring device. The surface adsorbed molecules form an infinitely thin layer on a water layer as backing material whereas the layer of sulphuric acid is formed of droplets with an estimated thickness of about 1 μ on a backing layer of lucite. The thickness of the backing material is in both cases enough to give saturation backscattering. The average atomic number of water is 7.2 and of lucite 6.2. The backscattering factors are therefore almost the same. The monolayer may be considered to have no self-adsorption and no self-scattering. This is however not the case for the sulphuric acid layer.

If it were possible to make thin ($d < 1.5 \text{ mg/cm}^2$) uniform layers of the S^{35} labelled sulphuric acid the value of the specific activity at $d = 0$ ("zero" thickness) could be found from an extrapolation of a specific activity versus d curve. At present only an estimation can be made.

When the surface density of the source is below the order of 5 % of the beta particle range (in this case 1.5 mg/cm^2) the specific activity in cpm/mol is found to increase instead of decrease with increasing surface density^{16,21}. This means that the measured cpm/ d versus d curve passes through a maximum. This phenomenon is termed self-scattering¹⁶. It depends upon the forescattering effect as defined by Zumwalt²² and upon a difference in backscattering power between the source and the source supporting material. The forescattering effect is a focusing effect of the beta particles in the direction of the tube from an absorbing layer on the top of the active layer. The increase in counting rate due to this effect is at small surface densities greater than the decrease due to absorption in the focusing layer. The forescattering effect increases with increasing atomic number of the source. The backscattering effect also increases with the atomic number of the backing material. Because the average atomic number of sulphuric acid is 10.4 whilst that of the lucite plate only 6.2 a layer on the top of the source may, because of backscattering, show a greater activity than one on the bottom. So in this case we may expect that the forescattering effect and the increase in backscattering makes the measured specific activity slightly higher than that measured from an infinitely thin layer, but it is not possible to estimate the increase.

All activity values have been corrected for background, decay and dead time of the tube. The background was measured with the cuves filled with water.

The surface excess can then be calculated from the following equation also used by Aniansson⁸:

$$\Gamma = \frac{A_y}{s \cdot 2\pi \int_0^r r \eta(r) dr} = A_y \cdot 0.01 \cdot 10^{-10} \text{ mol/cm}^2 \quad (4)$$

where A_y is the activity from the surface in cpm, s the specific activity in cpm/mol measured at $r = 0$, where r is the radius of the surface from which the activity is measured, and $\eta(r)$ is the counting efficiency of the tube as a function of r , measured with the aid of a point source (Fig. 4). The integral was calculated numerically.

The surface tension measurements were made by means of the ring method using a du Nouy tensiometer. The values were corrected according to Harkins and Jordan²³. In all solutions (also in the radioactive measurements) water, purified using a mixed bed ion exchange column²⁴ and having a specific conductivity of about $8 \cdot 10^{-7} \text{ ohm}^{-1}\text{cm}^{-1}$, was used. Since only relative values are needed it was sufficient to ensure that the surface tension measurements were made in a reproducible manner with a definite time of waiting before each single measurement.

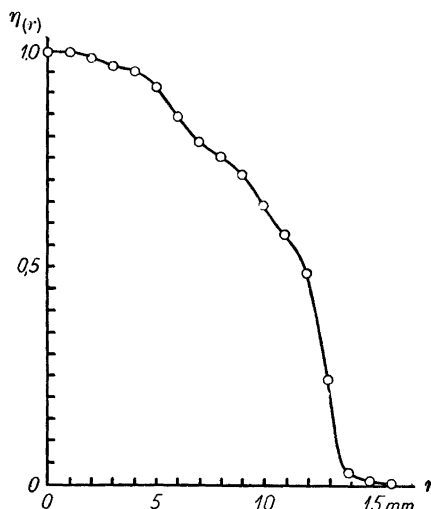


Fig. 4. The counting efficiency.

A few measurements of conductivity using a Philip's measuring bridge and a small conductivity cell have also been made.

RESULTS

In one series of measurements the total concentration of dodecyl and tetradecyl sulphate was constant ($5 \cdot 10^{-3}$ mol/1 000 g) throughout, but the proportions between the two substances varied. The activity values for different concentrations of surface active agent are given in Table 1, and in Table 2 for diff. conc. of S^{35} labelled sulphuric acid.

Table 1. Activity values from the first series of measurements.

C_{14} mol/1000 g	C_{12} mol/1000 g	$A_y + A_i$ cpm	A_y cpm	Rel. error in A_y %
$0.32 \cdot 10^{-3}$	$4.69 \cdot 10^{-3}$	1144 ± 2	154 ± 8	5.2
0.60	4.40	2068 ± 3	228 ± 10	4.4
0.90	4.10	3043 ± 3	328 ± 11	3.4
1.20	3.80	3982 ± 4	382 ± 12	3.1
1.60	3.40	5205 ± 4	455 ± 13	2.9
1.90	3.10	6121 ± 4	501 ± 15	3.0
2.04	2.96	6650 ± 5	640 ± 15	2.3
2.18	2.82	7075 ± 5	655 ± 16	2.4
2.51	2.50	8055 ± 5	705 ± 17	2.4
3.10	1.90	9817 ± 6	817 ± 19	2.3
3.11	1.89	9918 ± 6	878 ± 19	2.2
4.00	1.00	12521 ± 7	1041 ± 20	1.9
4.50	0.50	14037 ± 7	1187 ± 20	1.7

C_{14} = sodium tetradecyl sulphate.

C_{12} = sodium dodecyl sulphate.

A_y = activity from the surface.

A_i = activity from the interior of the solution.

Table 2. The activity from the interior of the solution.

$\text{H}_2\text{S}^{35}\text{O}_4$ mol/1000 g	A_i cpm
$0.110 \cdot 10^{-3}$	355 ± 2
0.396	1203 ± 7
2.380	6975 ± 16
4.948	14077 ± 23

These values are shown in Fig. 3. The curve so obtained was used in calculating the values of A_y in Table 1. The surface excess of sodium tetradecyl sulphate calculated from equation (4) is shown in Fig. 5.

In the second series of measurements the concentration of sodium tetradecyl sulphate was $0.5 \cdot 10^{-3}$ mol/1 000 g throughout and the concentration of sodium dodecyl sulphate was increased from 0 to $9 \cdot 10^{-3}$ mol/1 000 g. A_i is in this case constant. Its value (1617 ± 9) is taken from Fig. 3. Table 3 gives the activity values in this case.

Table 3. Activity values from the second series of measurements.

C_{12} mol/1000 g	$A + A_y$ cpm	A_y cpm	Rel. error in A_y %
$0.00 \cdot 10^{-3}$	2010 ± 3	393 ± 10	2.5
2.01	1933 ± 3	316 ± 10	3.2
3.91	1906 ± 3	289 ± 10	3.5
5.05	1813 ± 3	196 ± 10	5.1
5.99	1785 ± 3	168 ± 10	6.0
6.95	1738 ± 3	121 ± 10	8.3
7.98	1716 ± 3	99 ± 10	10.1
8.97	1685 ± 3	68 ± 10	14.7

The surface excess of sodium tetradecyl sulphate calculated from equation (4) together with a surface tension and a specific conductivity curve are given in Fig. 6.

DISCUSSION

The C.M.C. for sodium dodecyl sulphate is about $6 \cdot 10^{-3}$ mol/l and for sodium tetradecyl sulphate about $2 \cdot 10^{-3}$ mol/l at 30°C . Fig. 5 shows that the surface excess of sodium tetradecyl sulphate increases greatly when its proportion in the mixture increases and that this is the case also when the C.M.C. for the mixture is passed. The largest surface excess measured gives an area of 12.7 \AA^2 per molecule of tetradecyl sulphate. Because dodecylsulphate molecules also are present the true area per molecule will be smaller.

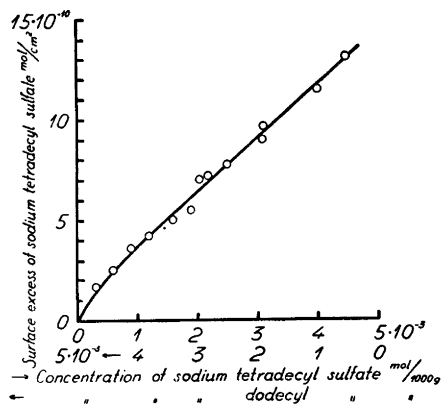


Fig. 5. The surface excess of sodium tetradecyl sulphate measured on a solution of this substance and sodium dodecyl sulphate.

The total concentration was constant
 = $5 \cdot 10^{-3}$ mol/1000 g.

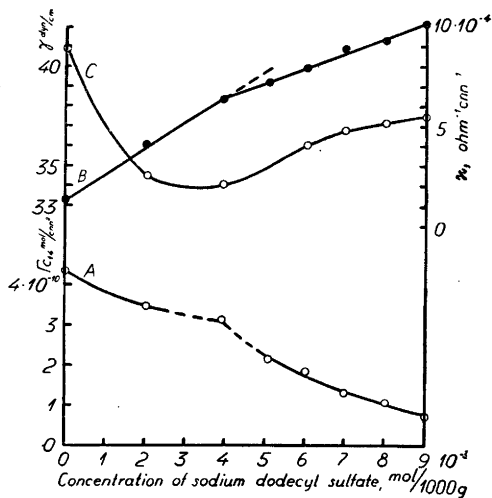


Fig. 6. The concentration of sodium tetradecyl sulphate is constant but the concentration of sodium dodecyl sulphate increases.

A = surface excess of sodium tetradecyl sulphate.

B = conductivity curve.

C = surface tension curve.

Since a molecule with a straight carbon chain in a monolayer occupies an area not smaller than 20.5 \AA^2 the result will indicate that more molecules than the number needed to form a monolayer are present in the surface. The same was found by Dixon *et al.* concerning di-*n*-octyl sodium sulphosuccinate³ and Aerosol SE⁹.

The surface tension and the conductivity curves in fig. 6 indicate that the C.M.C. for sodium dodecyl sulphate in this case appears between 3 and $4 \cdot 10^{-3}$ mol/1 000 g due to the presence of tetradecyl sulphate. The surface excess curve shows that as the concentration of dodecyl sulphate is increased the concentration of tetradecyl sulphate in the surface decreases and that this is more pronounced when the C.M.C. is passed. The latter statement is however only based on one measurement. What happens may be the following:

As the concentration of dodecyl sulphate increases it will replace tetradecyl sulphate in the surface. The total amount of surface active molecules in the surface increases however with the bulk concentration and so the surface tension decreases. When the C.M.C. for the mixture is reached micelles begin to form and tetradecyl sulphate is solubilized in these micelles. The result

of this is that the surface excess of tetradecyl sulphate decreases faster, while the conductivity increases slower than before, and the surface tension begins to increase up to values corresponding to a solution containing only dodecyl sulphate.

The statistical errors in the activity from the surface varied between 1.7 and 5.2 % in the first experiment and between 2.5 and 14.7 in the second one. These large errors are essentially due to the small activity from the surface compared with the total activity from the solution. It would have been possible to make these errors smaller by measuring the activities for longer times. Such an increase in accuracy was not possible however because the measuring conditions were not constant enough over long periods of time. In this work the times of measurement were not longer than 4 hours, the measuring device being checked with a reference source before every measurement.

The errors can be made smaller by increasing the activity from the surface relative to the total activity. This is attained by using a beta emitter of lower energy and a more surface active substance with greater specific activity. A calculation has shown that the use of tritium instead of S^{35} in this case would have increased the activity from the surface from on the average 10 % to 80 % of the total activity. The relative mean errors in the surface excess calculated from equation (4) are estimated to be 2–3 % greater than the relative errors in the activity from the surface.

SUMMARY

The surface excess of S^{35} labelled sodium tetradecyl sulphate has been measured at the solution-air interface of solutions containing this substance in the presence of sodium dodecyl sulphate.

The measurements show that the surface excess increases greatly when the proportion of sodium tetradecyl sulphate in the mixture increases and that this is the case also when the C.M.C. for the mixture is passed. They also show that at higher concentrations of sodium tetradecyl sulphate more molecules than the number corresponding to a monolayer are present in the surface, and that if the concentration of sodium tetradecyl sulphate is constant but the concentration of sodium dodecyl sulphate increases then the surface excess of the former substance decreases.

Also the experiments show that the radiotracer method can be used to determine quantitatively the surface excess of a selected substance in a mixture.

The authors have to express their thanks to Mr. G. Aniansson for valuable discussions, to Mr. I. Andersson for help in preparing and purifying the substances and to The Swedish Atomic Committee for financial support.

REFERENCES

1. Hutchinson, E. *J. Colloid Sci.* **3** (1948) 413.
2. Scholberg, H. M. *J. Phys. & Colloid Chem.* **54** (1950) 107.
3. Dixon, J. K., Weith, A. J., Argyle, A. A., and Salley, D. J. *Nature* **163** (1949) 845.
4. Aniansson, G., and Lamm, O. *Nature* **165** (1950) 357.
5. Judson, C. M., Argyle, A. A., Salley, D. J., and Dixon, J. K. *J. Chem. Phys.* **18** (1950) 1302.
6. Hutchinson, E. *J. Colloid Sci.* **4** (1950) 600.
7. Salley, D. J., Weith, A. J., Argyle, A. A., and Dixon, J. K. *Proc. Roy. Soc. (London)* **203** (1950) 42.
8. Aniansson, G. *J. Phys. & Colloid Chem.* **55** (1951) 1286.
9. Judson, C. M., Argyle, A. A., Dixon, J. K., and Salley, D. J. *J. Chem. Phys.* **19** (1951) 378.
10. *International Critical Tables.* **4** (First Edition) 464.
11. Hutchinson, E. *Trans. N. Y. Acad. Sci.* **11** (1949) 266.
12. Miles, G. D., and Shedlovsky, L. *J. Phys. Chem.* **48** (1944) 57.
13. Shedlovsky, L., Ross, J., and Jakob, C. W. *J. Colloid Sci.* **4** (1949) 25.
14. Shedlovsky, L. *Ann. N. Y. Acad. Sci.* **49** (1948) 279.
15. Klevens, H. B. *Chem. Revs.* **47** (1950) 1.
16. Kohman, T. P. *Anal. Chem.* **21** (1949) 352.
17. Burt, B. P. *Nucleonics* **5** (1949) 28.
18. Macaulay, J. M., and Carson, D. *J. Roy. Tech. Coll. (Glasgow)* **2** (1930) 161.
19. Macaulay, J. M. *Nature* **167** (1951) 1037.
20. Lottermoser, A. and Stoll, F. *Kolloid-Z.* **63** (1933) 49.
21. Schweitzer, G. K., and Stein, B. R. *Nucleonics* **7** (1950) 65.
22. Zumwalt, L. R. *AECU-567* (1950).
23. Harkins, W. D., and Jordan, H. F. *J. Am. Chem. Soc.* **52** (1930) 1751.
24. Kunin, R., and Myers, R. J. *Ion Exchange Resins.* John Wiley and Sons, Inc., New York (1950) 109.

Received October 2, 1951.