graphically. It may be noted that the same thing is accomplished analytically by equation (4) above.

A proof of the tangent theorem is as follows. From the above mentioned familiar property of the intercepts at $x_2 = 0$ and $x_2 = 1$, it follows that the equation of the tangent in Fig. 1, *i. e.*, in Description 1, is

$$h = (g_2 - g_1)k + g_1$$

The elimination of k from this equation by means of the above condition

$$r = (1 - k)/k$$

gives

$$h = (rg_1 + g_2)/(1 + r) \qquad (6)$$

But by equation (4) the right side of (6) equals g_2'. Q. E. D.

If, instead of the gram, the mole is used as the unit of mass, the above relations assume the following form:

Description 1.—Components A and B, mole fractions N_1 and N_2, partial molar quantities G_1 and G_2, molar quantity G.

Description 2.—Components A and A_sB (*i. e.*, s moles of A to one mole of B), quantities N_1', N_2', G_1', G_2', G.

The transformation equations in terms of the parameter s become

$$\begin{aligned} N_1' &= (N_1 - sN_2)/(1 - sN_2) \\ N_2' &= N_2/(1 - sN_2) \\ G_1' &= G_1 \\ G_2' &= sG_1 + G_2 \\ G' &= G/(1 - sN_2) \end{aligned}$$

The tangent theorem becomes

$$G_2' = h/k \text{ if } s = (1 - k)/k$$

that is, G_2' is not given directly by the intercept of the tangent but by the quotient of the intercept by its abscissa.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY, CALIFORNIA

RECEIVED DECEMBER 23, 1935

[CONTRIBUTION FROM THE CHEMICAL AND OCEANOGRAPHIC LABORATORIES OF THE UNIVERSITY OF WASHINGTON]

Equilibria in the Saturated Solutions of Salts Occurring in Sea Water. I. The Ternary Systems $MgCl_2$–KCl–H_2O, $MgCl_2$–$CaCl_2$–H_2O, $CaCl_2$–KCl–H_2O and $CaCl_2$–$NaCl$–H_2O at 0°

BY IVER IGELSRUD WITH THOMAS G. THOMPSON

Sea water is a complex solution containing, in addition to small quantities of the ions of a large number of other substances, the four major cations Mg^{++}, Ca^{++}, Na^+ and K^+ and the two major anions Cl^- and $SO_4^{=}$. To these six ions may be added the ions of carbonic acid, for the carbonates are important constituents of many oceanic sediments. In the saturated solutions of the major salts derived from the sea, the carbonates are of minor importance. Because of their insolubility the influence they exert upon the solubilities of the other salts is small. In the natural evaporation of sea water, for example, they precipitate in the early stages of the concentration and are thus removed from the solution before it becomes saturated for any other salt, calcium sulfate excepted. As a first approximation then, sea water may be considered a six-component system composed of water and five independent salts.

A survey of the solubility data for the salts found in the sea, contained in the "International Critical Tables," together with data published since their appearance, shows the considerable gaps which exist. The solubilities of the individual salts are known except for calcium sulfate, down to their eutectic temperatures. Considerable is also known, but very incompletely, about the mutual solubilities of two or more salts. Sixteen ternary systems may be formed, each containing water and two different salts. Only five have been completely determined from above 100° down to the eutectic temperature. Of the remainder, six have been investigated with some degree of completeness above 0°, ten have not been investigated below 0° and one, the system $MgSO_4$–$CaSO_4$–H_2O, very incompletely at 25° only. Of the fourteen quaternary systems, consisting of three independent salts and water, only five have been worked out completely between 0 and about 100°. Fragmentary data at one or more temperatures exist for some of the others. Four have not been studied in any manner. Of the six quinary systems, one, the system consisting of water and the chlorides and sulfates of magnesium, sodium and potassium, has been determined in the temperature range of 0 to 83°. For two others, there are incomplete data and three have not been investigated at all. The six component system formed by water and the four major cations and two major anions of the sea water salts has been investigated by van't Hoff and associates. Complete data, however, are lacking and none are available for the equilibria involving the chloride-containing calcium salts. No one of the four, five or six component systems has been investigated below 0°.

A beginning in the study of some of these systems at 0° and lower temperatures has been made in this Laboratory. Preparatory to study of the quaternary system $MgCl_2$–$CaCl_2$–KCl–H_2O, data have been obtained for the 0° isotherms for the associated ternary systems as well as for the system $CaCl_2$–$NaCl$–H_2O.

The ternary system $MgCl_2$–KCl–H_2O was first studied by Löwenherz[1] in connection with the reciprocal salt pair $MgCl_2$–K_2SO_4. Van't Hoff and Meyerhoffer[2,3] investigated it polythermally from the eutectic temperature, −34.3°, to the melting point of carnallite, 265°. They made no attempt to obtain data on the isotherms but succeeded in fixing all the monovariant points of the system below about 186°. Lee and Egerton[4] give data from various sources, to supplement their own, for the 25° isotherm.

Van't Hoff, Kenrick and Dawson[5] studied the system $MgCl_2$–$CaCl_2$–H_2O between the temperatures 16.7 and 32° and fixed the lower temperature limit for the existence of tachydrite. Lee and Egerton[4] determined the 25° isotherm. The 0, −15 and −30° isotherms were obtained by Prutton and Tower,[6] who also fixed three additional monovariant points including the system eutectic point at −52.2°.

The only data existent on the system $CaCl_2$–KCl–H_2O are the isotherms at 25 and at 30° determined, respectively, by Lee and Egerton[4] and by Barbaudy.[7]

Cameron, Bell and Robinson[8] obtained the 25° isotherm for the ternary system $CaCl_2$–$NaCl$–H_2O and Pelling and Robertson,[9] the isotherms at 50 and 94.5°. A number of values for the solubility, at 25°, of sodium chloride are given by Mills and Wells.[10]

Experimental

The salts used in the solubility measurements were obtained by purification of analytical reagent grade chemicals. The magnesium, sodium and potassium chlorides were dissolved in distilled water, the solution filtered and the salts thrice recrystallized. The calcium chloride was purified by the method of Morgan and Benson.[11]

A slightly unsaturated solution was first prepared and filtered. From the filtrate was evaporated sufficient water to bring the composition of the solution to that corresponding to the hexahydrate. The solution was cooled, inoculated with a crystal of the hexahydrate and allowed to crystallize slowly. When only a small amount of liquid remained, the crystals were drained, melted and again inoculated. The salt was twice recrystallized in this manner.

The solubility tubes were large Pyrex test-tubes, 38 mm. in diameter and 30 cm. long. They were immersed in the thermostat bath to a depth of about 23 cm. and contained crystals and solution to a depth of about 15 cm. The open end of the tube was closed by a large cork. The contents of the tube were stirred by hand with an ordinary Beckman stirrer made of glass rod. The temperature of the bath and solubility tube was maintained at 0 ± 0.02°.

The solubility samples were prepared by heating the solutions in contact with the solids to about 60° in a vessel of warm water. They were then cooled to room temperature after which they were placed in the thermostat and allowed to come to equilibrium. When the tube had cooled to the temperature of the bath, the sample was inoculated with the various crystal varieties thought to be in equilibrium with the solution. Ten hours of stirring in the bath were found to be sufficient to bring the solutions in the ternary systems to equilibrium.

The presence of the proper solid phases was frequently checked during the course of a determination by removing a small sample of solid and examining it with a petrographic microscope. Potassium chloride was easily detected by its isotropic crystals. Carnallite forms short prisms with pseudo-hexagonal symmetry. It possesses very bright and characteristic interference colors under crossed nicols. $CaCl_2 \cdot 6H_2O$ separates in rod-like hexagonal crystals which dissolve very rapidly as the solutions warm and is easily distinguished from the other salts present. $MgCl_2 \cdot 6H_2O$ forms either flat or fibrous crystals. The interference colors are duller than for the other salts. They tend toward a grey if the crystals are thin.

Ten to 15-g. samples for analysis were removed with a pipet. The solution was filtered by means of a piece of heavy filter paper wrapped about the lower end of the pipet and securely tied with linen thread. For most of the samples, on account of the viscous nature of the solutions, suction was necessary. The solid phases at the bottom of the tube were sampled with a small scoop sampler made of glass, or the mixture was stirred and a sample of the mixed

---

(1) Richard Löwenherz, *Z. physik. Chem.*, **13**, 459 (1894).

(2) J. H. van't Hoff and W. Meyerhoffer, *Sitzber. preuss. Akad. Wiss., Physikmath. Klasse*, 487 (1897).

(3) J. H. van't Hoff and W. Meyerhoffer, *Z. physik. Chem.*, **30**, 64 (1899).

(4) W. B. Lee and A. C. Egerton, *J. Chem. Soc.*, **123**, 706 (1923).

(5) J. H. van't Hoff, F. B. Kenrick and H. M. Dawson, *Z. physik. Chem.*, **39**, 27 (1902).

(6) C. F. Prutton and O. F. Tower, THIS JOURNAL, **54**, 3040 (1932).

(7) Jean Barbaudy, *Rec. trav. chim.*, **42**, 638 (1923).

(8) F. K. Cameron, J. M. Bell and W. O. Robinson, *J. Phys. Chem.*, **11**, 396 (1907).

(9) A. J. Pelling and J. B. Robertson, *S. African J. Sci.*, **20**, 236 (1923).

(10) R. V. Mills and R. C. Wells, *U. S. Geol. Survey*, Bull. No. 693, 72 (1918).

(11) J. L. R. Morgan and H. K. Benson, THIS JOURNAL, **29**, 1168 (1907).

solution and solid phase was taken with a pipet with a wide mouth. Each sample was weighed in a glass-stoppered Erlenmeyer flask, rinsed into a volumetric flask, diluted to volume and stored in glass-stoppered bottles for analysis.

In all of the systems investigated, analysis was made for chloride and this was taken as a measure of the total equivalent concentration of cations in solution. Calcium was determined in the systems containing calcium chloride; potassium in those containing potassium chloride except in the system $CaCl_2$–KCl–H_2O where it was found by difference between chloride and calcium. Sodium and magnesium were in all cases found by difference.

Chloride was determined by titration with silver nitrate, using potassium chromate as indicator.

Calcium was determined by the micro-oxalate–permanganate method of Kirk and Schmidt[12] as modified for use with a 25-milliliter sample of sea water by Kirk and Moberg.[13] The aliquot samples used in the present investigation were therefore adjusted to contain, as nearly as possible, an amount of calcium equal to that in a 25-milliliter sample of sea water.

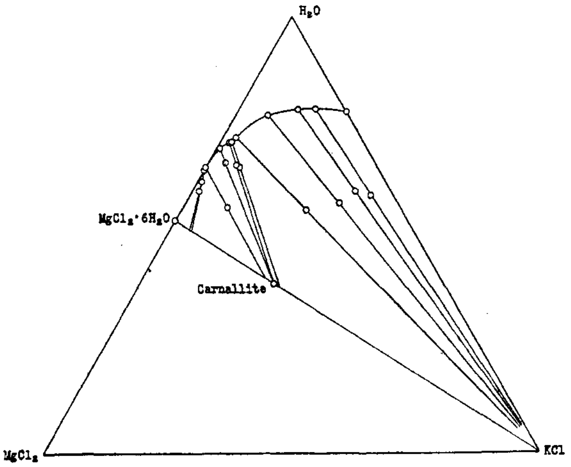

Fig. 1.—The ternary system $MgCl_2$–KCl–H_2O at 0°.

Potassium was determined by the perchlorate method as outlined by Smith[14] with only minor modifications to suit the conditions of the analysis. In most cases, except on the potassium chloride saturation curve in the system $MgCl_2$–KCl–H_2O, the amount of potassium was 2% or less of the weight of the sample. The amount of the other salt or salts was relatively high, in many cases several hundred times the potassium content. It was thus often necessary to take an entire sample for the potassium analysis.

The Solubilities of the Chlorides of Magnesium, Calcium, Potassium and Sodium in Water at 0°.—The solubilities of the various chlorides in water were determined and are given in Table I. The mean values of the "International Critical Tables" are given for comparison.

TABLE I

THE SOLUBILITIES OF THE CHLORIDES OF MAGNESIUM, CALCIUM, POTASSIUM AND SODIUM AT 0°

Salt	Solubility, % Found			"Inter. Crit. Tables"
Magnesium chloride	34.71	34.56		34.4 ± 2[a]
Calcium chloride	37.56	37.58		37.3 ± 2[b]
	37.60	37.47		
Potassium chloride	21.73	21.90	21.97	21.9 ± 0.5
Sodium chloride	26.47	26.51	26.27	26.28 ± 0.2

[a] Prutton and Tower[6] found 34.61%. [b] Prutton and Tower[6] found 37.32%.

The Ternary System $MgCl_2$–KCl–H_2O (Fig. 1 and Table II).—The solubility curve consists of three branches. The first branch represents solutions in equilibrium with $MgCl_2 \cdot 6H_2O$. This is an extremely short curve and great difficulty was encountered in obtaining a point upon it. The amount of potassium chloride in a saturated solution of magnesium chloride at 0° is so small 0.025–0.030%, that in most attempts to prepare such a solution, one saturated for carnallite was obtained. The composition of the solution saturated for $MgCl_2 \cdot 6H_2O$ and carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$, is 34.68% $MgCl_2$ and 0.024% KCl.

TABLE II

THE TERNARY SYSTEM $MgCl_2$–KCl–H_2O AT 0°

Solution, Weight per cent. KCl	Solution, Weight per cent. $MgCl_2$	Residue, Weight per cent. KCl	Residue, Weight per cent. $MgCl_2$	Solid phases
21.87	...	...	...	KCl
15.21	5.88	36.14	4.72	KCl
11.70	9.49	32.62	7.45	KCl
6.31	16.33	30.64	11.99	KCl
2.35	25.24	24.79	19.45	KCl
2.17	26.98	...	...	KCl + Carnallite
2.05	26.64	6.58	27.79	KCl + Carnallite
2.16	26.74	...	...	KCl + Carnallite
1.68	27.03	5.68	28.20	Carnallite
0.49	29.70	3.22	30.18	Carnallite
0.028	34.74	9.71	34.99	Carnallite + $MgCl_2 \cdot 6H_2O$
0.024	34.69	0.61	37.11	Carnallite + $MgCl_2 \cdot 6H_2O$
0.027	34.62	1.14	38.65	Carnallite + $MgCl_2 \cdot 6H_2O$
0.025	34.66	0.016	35.27	$MgCl_2 \cdot 6H_2O$
....	34.63	...	...	$MgCl_2 \cdot 6H_2O$

The second branch of the solubility curve represents solutions saturated for carnallite. The position of this curve with respect to the line joining the points representing the compositions of pure water and of pure carnallite, respectively, shows that these solutions are incongruently saturated. This is characteristic of carnallite solutions at all temperatures. Advantage of this is taken in the recovery of potassium chloride from natural carnallite. The solution saturated at 0° for carnallite and potassium chloride contains, as the mean

---

[12] P. L. Kirk and C. L. A. Schmidt, *J. Biol. Chem.*, **83**, 311 (1929).

[13] P. L. Kirk and E. G. Moberg, *Ind. Eng. Chem., Anal. Ed.*, **5**, 95 (1933).

[14] G. McP. Smith, "Quantitative Chemical Analysis," 3d Ed., The Macmillan Co., New York, N. Y., 1933.

of three experiments, 2.13% KCl and 26.78% $MgCl_2$. This differs somewhat from the value given by van't Hoff and Meyerhoffer,[2,3] who obtained 2.18% KCl and 25.61% $MgCl_2$.

The third branch of the solubility curve corresponds to solutions in equilibrium with potassium chloride.

The 0° isotherm differs from that obtained at 25° by Lee and Egerton[4] only in the greater insolubility of potassium chloride and of carnallite in the saturated solutions.

Some data obtained by the authors for this system indicate the possible existence of solutions in metastable equilibrium with a double salt containing more potassium chloride than is found in carnallite. The existence of this salt has not yet been established completely and the data are therefore not reported.

The Ternary System $MgCl_2$–$CaCl_2$–H_2O (Table III).—The isotherm at 0° for this system has been determined by Prutton and Tower.[6] However, using this ternary system as a starting point in approaching the four component system $MgCl_2$–$CaCl_2$–KCl–H_2O, it was desirable to redetermine some of the points on the solubility curve. The solubilities obtained are given in Table I. Both sets of data are in good agreement.

TABLE III

THE TERNARY SYSTEM $MgCl_2$–$CaCl_2$–H_2O AT 0°

Solution Weight per cent		Residue Weight per cent		
$MgCl_2$	$CaCl_2$	$MgCl_2$	$CaCl_2$	Solid phase
...	37.55	...	...	$CaCl_2 \cdot 6H_2O$
9.81	27.17	7.27	33.51	$CaCl_2 \cdot 6H_2O$
23.81	13.97	21.16	20.65	$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$
24.07	14.03	22.53	19.41	$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$
30.89	4.51	33.70	3.76	$MgCl_2 \cdot 6H_2O$
34.63	...	...	...	$MgCl_2 \cdot 6H_2O$

The Ternary System $CaCl_2$–KCl–H_2O (Fig. 2 and Table IV).—The solubility curve for this system has two branches, one for solutions in equilibrium with potassium chloride and one for those in equilibrium with $CaCl_2 \cdot 6H_2O$. The composition of the solution in equilibrium with the two solid phases is 37.27% $CaCl_2$ and 1.96% KCl.

The isotherm at 0° in this system is similar to those obtained at 25° by Lee and Egerton[4] and at 30° by Barbaudy.[7]

TABLE IV

THE TERNARY SYSTEM $CaCl_2$–KCl–H_2O AT 0°

Solution Weight per cent.		Residue Weight per cent.		
$CaCl_2$	KCl	$CaCl_2$	KCl	Solid phases
...	21.87	...	...	KCl
5.54	16.93	4.31	36.64	KCl
10.52	12.78	8.46	32.39	KCl
16.43	8.38	10.70	42.36	KCl
20.03	6.48	14.57	33.41	KCl
25.89	3.88	19.03	30.18	KCl
30.14	3.20	20.42	34.72	KCl
33.42	2.62	22.17	35.73	KCl
37.31	1.75	35.25	12.72	KCl + $CaCl_2 \cdot 6H_2O$
37.27	2.01	39.51	6.89	KCl + $CaCl_2 \cdot 6H_2O$
37.05	2.10	36.38	4.05	KCl + $CaCl_2 \cdot 6H_2O$
37.46	1.97	39.53	5.43	KCl + $CaCl_2 \cdot 6H_2O$
37.41	0.69	42.23	0.33	$CaCl_2 \cdot 6H_2O$
37.55	...	...	...	$CaCl_2 \cdot 6H_2O$

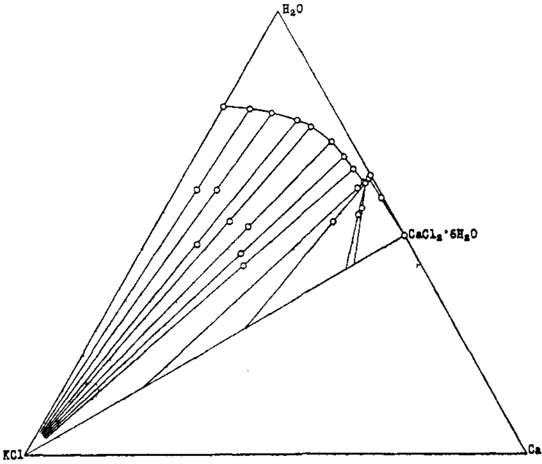

Fig. 2.—The ternary system $CaCl_2$–KCl–H_2O at 0°.

The Ternary System $CaCl_2$–NaCl–H_2O (Fig. 3 and Table V).—The stable solid phase in the system NaCl–H_2O at 0° is $NaCl \cdot 2H_2O$. The equilibrium temperature for the reaction $NaCl \cdot 2H_2O \rightleftarrows NaCl + 2H_2O$ is 0.15°. In the system $CaCl_2$–NaCl–H_2O, therefore, the first branch of the solubility curve at 0° should represent solutions of calcium chloride in equilibrium with NaCl·

TABLE V

THE TERNARY SYSTEM $CaCl_2$–NaCl–H_2O AT 0°

Solution Weight per cent.		Residue Weight per cent.		
$CaCl_2$	NaCl	$CaCl_2$	NaCl	Solid phase
...	26.42	...	...	$NaCl \cdot 2H_2O$
5.33	21.19	...	...	NaCl
9.53	17.28	9.13	22.08	NaCl
16.12	11.36	12.82	30.95	NaCl
20.60	7.78	13.46	42.28	NaCl
27.14	3.59	20.25	29.43	NaCl
35.31	0.93	25.05	30.93	NaCl
37.45	.35	37.42	8.75	NaCl + $CaCl_2 \cdot 6H_2O$
37.32	.50	39.33	16.91	NaCl + $CaCl_2 \cdot 6H_2O$
37.57	.34	40.95	2.03	NaCl + $CaCl_2 \cdot 6H_2O$
37.61	.18	34.74	15.67	NaCl + $CaCl_2 \cdot 6H_2O$
37.56	.19	41.99	0.79	NaCl + $CaCl_2 \cdot 6H_2O$
37.55	...	...	...	$CaCl_2 \cdot 6H_2O$

$2H_2O$. The molal freezing point lowering of calcium chloride is, however, so great as to make it extremely difficult, at 0°, to obtain points on this curve or to obtain data on the isothermal monovariant point at which the saturated solution is in equilibrium with NaCl and $NaCl\cdot 2H_2O$. The necessary data for these portions of the isotherm were not obtained and the first branch of the solubility curve is therefore represented, subject to correction, as for solutions in equilibrium with NaCl. The other branch corresponds to saturated solutions in equilibrium with $CaCl_2\cdot 6H_2O$. Because of the shortness of this curve, no points upon it were obtained, but study of the associated system $CaCl_2$–KCl–H_2O and $MgCl_2$–$CaCl_2$–H_2O shows that the solid phase is $CaCl_2\cdot 6H_2O$. The composition of the saturated solution at the isothermal monovariant point is 0.31% NaCl and 37.50% $CaCl_2$.

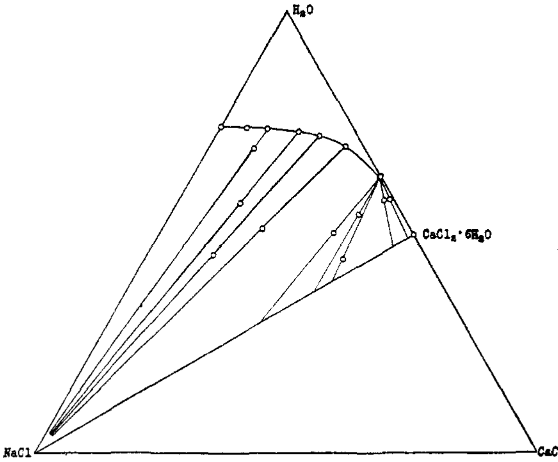

Fig. 3.—The ternary system $CaCl_2$–NaCl–H_2O at 0°.

The isotherm at 0° differs but little from the isotherms for the same system obtained at 25° by Cameron, Bell and Robinson[8] and at 50 and 94.5° by Pelling and Robertson.[9]

Summary

1. The isotherms for the ternary systems $MgCl_2$–KCl–H_2O, $MgCl_2$–$CaCl_2$–H_2O, $CaCl_2$–KCl–H_2O and $CaCl_2$–NaCl–H_2O have been determined at 0°.
2. The ternary system $MgCl_2$–KCl–H_2O, at 0°, is characterized by the extreme insolubility of potassium chloride, or of carnallite, in solutions saturated for $MgCl_2\cdot 6H_2O$.
3. Data for the system $MgCl_2$–$CaCl_2$–H_2O agree substantially with those obtained at the same temperature by Prutton and Tower.[6]
4. No evidence of double salt formation was found in the system $CaCl_2$–KCl–H_2O.
5. Because of the freezing point lowering produced by calcium chloride, it was impossible to obtain points on the solubility curve for $NaCl\cdot 2H_2O$ or data for the monovariant point where $NaCl\cdot 2H_2O$, NaCl and solution are in equilibrium. Because of the shortness of this curve, these values are probably not much different from that for the solubility of sodium chloride in pure water.

SEATTLE, WASHINGTON RECEIVED NOVEMBER 25, 1935

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

A Study of Salts of Higher Alkyl Sulfonic Acids

BY R. M. REED AND H. V. TARTAR

The salts of the higher alkyl sulfonic acids are typical colloidal electrolytes with soap-like properties, but are better than soaps for experimental studies because they are salts of strong acids and do not hydrolyze in aqueous solutions.

The preparation of the sodium alkyl sulfonates has been described by the authors in a previous paper.[1] This communication describes the preparation of certain other salts and gives the results of solubility, surface tension and interfacial tension measurements, and determinations of electrical conductivity made on aqueous solutions of various salts.

Solubility Determinations

Introduction.—It has long been known that the solubility of soaps in water increases greatly at certain temperatures.[2] The only work which has been reported on the solubility of salts of alkyl sulfonic acids is that of Murray and Hartley,[3] who studied the solubility of the cetyl derivative and its sodium, lithium and potassium salts. They found that sharp increases in solubility occurred at certain temperatures. This behavior was explained by the assumption that

---

[1] Reed and Tartar, THIS JOURNAL, **57**, 570 (1935).

[2] Krafft, *Ber.*, **28**, 2566 (1895); *ibid.*, **29**, 1328 (1896); *ibid.*, **32**, 1584 (1899).

[3] Murray and Hartley, *Trans. Faraday Soc.*, **31**, Part 1, 183 (1935).