that the temperatures of zero conductance are almost the same as those of infinite viscosity.

SUMMARY

1. The changes in electrical conductivities and viscosities with temperature of the negatively charged colloidal solutions of ferric vanadate, ferric molybdate, ferric tungstate, ferric borate, ferric arsenate, and ferric phosphate have been investigated.

2. The temperatures of zero conductance of the various sols have been extrapolated by plotting conductivity against temperature and extrapolating from the curve the temperature at which the conductivity reduces to zero.

3. It has been shown that the temperatures of zero conductance of the various sols are always higher than −39°C. The values lie between −16°C. and −28.5°C.

4. The temperature coefficients of conductivity per 1°C. of the various sols have been calculated, and it is observed that the values are always less than 2 per cent of the conductances at 35°C.

5. The temperatures of infinite viscosity of the various sols have also been extrapolated by plotting $1/\eta_s$, where η_s is the viscosity of the sol, against temperature and extrapolating from the curve the temperature at which $1/\eta_s$ reduces to zero. The values lie between −17°C. and −28°C.

6. It has been shown that the temperatures of zero conductance of the various sols are nearly the same as those of infinite viscosity.

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SURFACE TENSION OF ALUMINUM SULFATE SOLUTIONS

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This paper presents measurements of the surface tension of solutions of hydrated aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, within the range 0.0287 to 1.063 molal concentration. This compound was chosen for study because of its valence type, and because values for the surface tension of its solutions over a range of concentrations were not available in the literature.

Analytical reagent-grade hydrated aluminum sulfate was twice recrystallized from water. Its solutions were prepared in water purified from the laboratory distilled water by treatment with acid potassium permanganate and double redistillation. The concentrations were determined by measurements of the specific gravity at 15°C. with a 25-ml. specific gravity bottle, and by reference to concentration–specific gravity tables (2). Appropriate corrections were made for the buoyancy of air. Determinations were also made of the specific gravity at 25°C.

The surface tension was measured by the method of maximum bubble pressure, using the tables prepared by Sugden (1) for correcting for deviations of the meniscus from the spherical form. The capillary jet, effective radius 0.05477 ± 0.00003 cm., was calibrated against water at 25°C. from sixteen pressure measurements made at different times during the course of the experiments, assuming $\gamma = 71.97$. Pressures were read on a water manometer of 1.5 cm. bore, using a cathetometer with vernier reading to 0.01 cm., estimates being made to 0.005 cm. The liquid under examination was contained in a crystallizing dish of 12 cm. inside diameter, covered with an inverted Petri dish, through the center of which was bored a hole large enough for free entrance of the capillary jet. For each measurement of the maximum bubble pressure the capillary jet was carefully lowered by means of a smoothly operating rack and pinion until it just touched the liquid surface. Capillarity causes the liquid surface to rise slightly upon the outside surface of the jet and thus permits measurement of the maxi-

TABLE 1

Surface tensions and densities of aluminum sulfate solutions at 25.0°C.

d_{15}	d_{25}	M	m	γ
1.0090	1.0068	0.0286	0.0287	71.87, 71.87, 72.01 Av. = 71.92
1.0191	1.0168	0.0584	0.0585	72.00, 72.13, 72.00 Av. = 72.04
1.0404	1.0378	0.1217	0.1218	72.31, 72.33, 72.33, 72.33 Av. = 72.33
1.0617	1.0588	0.1859	0.1863	72.86, 72.99, 72.99, 72.99 Av. = 72.96
1.0829	1.0798	0.2510	0.2517	73.12, 73.25, 73.52, 73.25 Av. = 73.29
1.1060*	1.1025	0.3227	0.3242	73.52, 73.63, 73.76, 73.76 Av. = 73.67
1.1530	1.1490	0.4721	0.4761	74.45, 74.45, 74.45 Av. = 74.45
1.2000	1.1958	0.627	0.636	75.34, 75.61, 75.74 Av. = 75.56
1.2547	1.2503	0.810	0.829	77.42, 77.42, 77.42 Av. = 77.42
1.3172	1.3123	1.027	1.063	80.82, 80.82, 80.69 Av. = 80.78

* This concentration was prepared with the analytical reagent-grade hydrated aluminum sulfate, which was not recrystallized before use.

mum bubble pressure within the body of the liquid. There is produced a slight lowering of the "free" liquid surface, resulting in a negative pressure at the jet, amounting to approximately −1 dyne per square centimeter for water. Temperature was controlled by immersion in a water bath at 25.0°C. ± 0.1°. The rate of bubble formation was kept between 10 and 15 sec. per bubble. The bubbles were formed with air from the laboratory compressed-air supply and filtered through absorbent cotton. They contained water vapor at the saturation pressure of the test solution.

At each concentration several measurements were made of the maximum bubble pressure. The individual measurements, converted to surface tensions, and their averages, are given in table 1. d_{15} and d_{25} are the densities at 15.0°C. and 25.0°C., respectively, in grams (*in vacuo*) per cubic centimeter; M is the concentration in moles per liter of solution at 25.0°C.; m is the concentration in moles per 1000 g. (*in vacuo*) of water; and γ is the surface tension at 25.0°C. in dynes per centimeter.

TABLE 2

Surface tensions of aluminum sulfate solutions at 25.0°C.

Interpolated values at even 0.1 molal concentrations

MOLALITY	SURFACE TENSION (γ)	$\Delta\gamma$
	dynes per centimeter	*dynes per centimeter*
0.1	72.32	0.35
0.2	72.92	0.95
0.3	73.51	1.54
0.4	74.11	2.14
0.5	74.71	2.74
0.6	75.30	3.33
0.7	76.06	4.09
0.8	77.07	5.10
0.9	78.30	6.33
1.0	79.73	7.76

Up to the concentration 0.636 molal the data are well fitted by the straight-line equation:

$$\gamma = 71.725 + 5.9634m \tag{1}$$

wherein m is the concentration in moles per 1000 g. of water. The maximum deviation of the average observed values from the calculated values is +0.13 dyne per centimeter, and the standard error of estimate is 0.08 dyne per centimeter. The accuracy of the average observed values is estimated to be ±0.2 dyne per centimeter.

Sentis (3) reported $\Delta\gamma$ to be 1.91 at 20.5°C. and 1.86 at 16.25°C. for a concentration of 0.561 molal. From these values one may estimate $\Delta\gamma = 1.96$ and $\gamma = 73.93$ at 25°C. This does not agree well with $\gamma = 75.07$, as calculated from equation 1.

The values of the surface tensions (γ) at even 0.1 molal concentrations, with the corresponding values of $\Delta\gamma$, are presented in table 2. Up to and including the concentration 0.6 molal the surface tensions were calculated from equation 1; at higher concentrations they were obtained by graphical interpolation.

TABLE 3

*Surface-tension increments of aqueous solutions of various inorganic salts at 20–25°C.**

COMPOUND	SURFACE-TENSION INCREMENT ($\Delta\gamma$)	
	At 0.500 *m*	At 1.000 *m*
	dynes per centimeter	*dynes per centimeter*
$Al_2(SO_4)_3$	2.7	7.8
$CaCl_2$	1.5	3.2
$MgCl_2$	1.5	3.0
Na_2SO_4	1.4	2.7
$MgSO_4$	1.0	2.1
KCl	0.7	1.4
NaCl	0.8	1.6
NaBr	0.7	1.3
$NaNO_3$	0.6	1.2

* Data for compounds other than aluminum sulfate were taken from reference 2, pp. 1320–1.

DISCUSSION OF RESULTS

It is apparent that, on a molal concentration basis, aluminum sulfate solutions have exceptionally high surface tensions. Several published values for $\Delta\gamma$ of other inorganic solutions are compared in table 3 with the values here found for aluminum sulfate.

In the compounds other than aluminum sulfate the monovalent ions are about equally effective in raising the surface tension, the divalent ions are approximately equivalent to two monovalent ions, and the effectiveness of a compound is approximately proportional to the total ionic charge of the molecule. This relationship has been commented on by others. On the basis of an extension of the same principle to a trivalent ion and to a more complex molecule, the estimated value for aluminum sulfate at a concentration of 0.500 molal would be approximately 4.2, and at a concentration of 1.000 molal, 8.4. The measured value of $\Delta\gamma$ at 0.500 molal is 2.7, considerably lower than the estimated value. The measured value of $\Delta\gamma$ at 1.000 molal is 7.8, in fair agreement with the estimated value. It will be noted that the concentration–surface tension relation for aluminum sulfate is not linear up to 1.000 molal. At concentrations higher than 0.6 molal the curve is convex toward the axis of concentration.

SUMMARY

The surface tensions of aqueous solutions of aluminum sulfate have been measured over the concentration range 0.0287 to 1.063 molal at 25°C.

The rate of change of surface tension with concentration is greater at the higher concentrations, but is approximately linear up to a concentration of 0.6 molal.

Aluminum sulfate solutions have surface tensions that are exceptionally high when compared with those of other inorganic salts on a molal concentration basis. The effectiveness of a number of compounds in this respect is approximately proportional to the total ionic charge of the molecule.

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THE VAPOR PHASE ABOVE THE SYSTEM SULFURIC ACID–WATER

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I. THERMODYNAMIC RELATIONSHIPS

The value of the vapor pressure (p_π) of H_2SO_4[1] above the liquid system sulfuric acid–water with π weight per cent H_2SO_4 is such that its molal free energy of formation[2] ($\Delta G_\pi(g)$) is equal to the partial molal free energy of formation (ΔG_π) of the liquid component $H_2SO_4(\pi)$ at the same temperature, T. If a_π is the activity of the latter, then

$$\Delta G_\pi(g) = \Delta G_\pi = \Delta G^0(g) + RT \ln p_\pi = \Delta G^0 + RT \ln a_\pi$$

$\Delta G^0(g)$ is connected with the standard free energies of formation of $H_2O(g)$ and $SO_3(g)$ by the dissociation constant, K_p, of $H_2SO_4(g)$:

$$\Delta G^0(g) = RT \ln K_p + \Delta_w G^0(g) + \Delta_\sigma G^0(g); \qquad K_p = \frac{{}_w p \, {}_\sigma p}{p}$$

Therefore,

$$RT \ln p_\pi = \Delta G(^0) - RT \ln K_p + RT \ln a_\pi$$

where $\Delta G(^0)$ is the free energy of formation of $(H_2SO_4)^0$ from $H_2O^0(g)$ and $SO_3^0(g)$:

$$H_2O^0(g) + SO_3^0(g) = (H_2SO_4)^0; \; \Delta G(^0), \; \Delta H(^0), \; \Delta S(^0), \; \Delta C(^0)$$

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[1] The sulfuric acid component, $H_2SO_4(\pi)$; the water component, $H_2O(\pi)$; the gas state, (g). Standard states are designated by a superscript cipher: sulfuric acid in its standard state, $(H_2SO_4)^0$. Values relating to water or sulfur trioxide take the index w or σ. Absence of an index indicates values relating to sulfuric acid. $\tau = 298°K$. Values for 0°K. take a left-hand top index^0. As we are dealing with a binary liquid system, all thermodynamic quantities are, of course, partial molal quantities; for the sake of simplicity the bar is omitted.

[2] The vapors are treated as ideal gases; see references 12a, 13, 74, 126.