A Note on the Theory of Surface Tension of Ternary Solutions.

By Kyozo ARIYAMA.

(Received February 5th, 1937.)

The present author has recently proposed a theory of surface tension of dilute solution of strong electrolyte,(1) and in the succeeding papers(2),(3),(4) the theory is extended to include the case of ternary solutions. More recently he has developed a theory of surface tension of aqueous solutions of inorganic acids.(5) If we have experimental data on the surface tension of ternary solutions of inorganic salt and inorganic acid, we will have a very interesting test on those theories in addition to those experimental tests which have been dealt with previously. Belton recently in his series of papers has given the experimental data on such ternary solutions.(6)

Since the surface tension of 0.1 mol hydrochloric acid is only 0.02 dynes/cm. less than that of water, it might be expected that its presence in strong solutions of salts could therefore be neglected. This would be so if the surface tension change for the mixture were the sum of the changes each solute would produce if present separately. This simple additive relation does not result however, and the effect of hydrocholoric acid increases with increasing salt concentration. Belton(6) confirmed this result with many solutions using many salts. A few examples of his results are given in the Table 1. In this Table the ratio $\Gamma_1/{}_0\Gamma_1$ stands for the ratio of the negative adsorption of the salt when the hydrocholoric acid is added to the negative adsorption of the salt when present alone in water.(4) This ratio was found to be less than one always.

This experimental fact can be accounted for theoretically by the theories mentioned above if the dielectric constant of adsorption layer is shown to be smaller than that of pure water when the inorganic acid is added.(4) We have no way of measuring the dielectric constant of the adsorption layer at present, but we can estimate it quite reasonably in the following way. When the hydrogen ions from inorganic acid are

---

(1) K. Ariyama, this Bulletin, **11** (1936), 687.

(2) *Ibid.*, **12** (1937), 32. (3) *Ibid.*, **12** (1937), 38. (4) *Ibid.*, **12** (1937), 44.

(5) *Ibid.*, **12** (1937), 109.

(6) Belton, *Trans. Faraday Soc.*, **31** (1935), 1413; **32** (1936), 1717.

positively adsorbed at the surface forming the hydrogen bond with water molecules,⁽⁵⁾ the molecules of water will be of the structure similar to ammonia molecules having three hydrogen attached to three corners of the tetrahedron. Some water molecules at the surface may carry even four hydrogen atoms on the four corners of their tetrahedrons due to the hydrogen bond. As the number of such ammonia-like water molecules increases the dielectric constant of water is expected to decrease at the surface due to the following reasons.

The H_2O molecule is of the neon type with ten electrons as are also CH_4, NH_3, and FH. The dielectric constants for these substances as well as some other similar compounds are listed in the Table 2. It is clear from this Table that as the number of hydrogen increases in molecule, the dielectric constant decreases. Thus it may be reasonable to expect that the ammonia-like water molecules will have a dielectric constant approximately the same as that of ammonia. If the number of such ammonia-like water molecules increases at the surface, it is reasonable to suppose that the dielectric constant of the adsorption layer is decreased from that of water.

Table 1.

NaCl	HCl	$\Gamma_1/{}_0\Gamma_1$	KCl	HCl	$\Gamma_1/{}_0\Gamma_2$
m_1	m_2		m_1	m_2	
1	0.1	0.91	1	0.1	0.95
2	0.1	0.91	2	0.1	0.95
3	0.1	0.91			
4	0.1	0.91	3	0.1	0.95
5	0.1	0.91	4	0.1	0.95

Table 2.

	Dielectric constant		Dielectric constant
CH_4	2.3	PH_3	—
NH_3	25.4	SH_2	5.92
OH_2	80.	ClH	8.85
FH	83.5	HOOH	92.8

Thus we can explain at least qualitatively Belton's experiments very easily.

Since it is very difficult to consider that the dielectric constant of adsorption layer is increased by the addition of inorganic acid in salt solution, the theories of the negative adsorption proposed by various other workers(7) seem to be unacceptable since they give a reverse result of the theory of the peresnt author.

In conclusion, author wishes to express his thanks to Dr. H. Erikson for his interest in the work.

Physics Department, University of Minnesota,
Minneapolis, Minn., U.S.A.

---

(7) Wagner, *Physik, Z.*, **25** (1924), 474; Shiba, *Bull. Inst. Phys. Chem. Research* (Tokyo), **13** (1934), 109; Onsagar and Samaras, *J. Chem. Phys.*, **2** (1934), 529.