[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE DEPARTMENT OF CHEMISTRY, OREGON STATE AGRICULTURAL COLLEGE]

THE STRUCTURE OF FILMS OF WATER ON SALT SOLUTIONS. II. THE SURFACE TENSION OF CALCIUM CHLORIDE SOLUTIONS AT 25°

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Introduction

The purpose of the investigation reported here is to determine the variation of the "thickness" of the water film on the solution of a salt of a divalent metal ion as the concentration of the salt is varied. Harkins and McLaughlin[1] have given an equation from which the thickness may be obtained provided that both the surface tensions and the activity coefficients for the salt at the various solutions are known. The surface tensions of solutions of calcium chloride have been determined by a number of different observers,[2] but the degree of accuracy required for the purpose of the present work is high, so that a new set of determinations is essential.

Surface Tension of Water and of Calcium Chloride Solutions at 25°

The surface tension of water at 25° was determined as 72.03 dynes per cm., while the equation obtained by T. F. Young from the best available data gives the value 72.02. The drop-weight method was used according to the direction of Harkins and Brown,[3] and their corrections were applied. Observation of the edge of the tip under a microscope showed it to be free from imperfections and extremely sharp. Its mean radius is 0.34153 cm., and it is so nearly circular as to require no corrections for its departure from this form.

Table I gives the data and the surface tensions as calculated from them.

The third column of the table gives the values of the ratio of the radius (r) of the tip to a linear dimension of the falling drop, which is taken as the cube root of the volume ($V^{1/3}$). Harkins and Brown assume that this ratio is determined by the shape of the *pendant* drop immediately before the rupture begins to occur and that the shape also fixes the fraction of this drop which falls. The fourth column (ϕ) gives the value of the function which relates the surface tension (γ) to the weight of the drop if substituted in the equation: $\gamma = (Mg/2\pi r)\phi$. Their experimental results indicate that ϕ is a single valued function for any ordinary value of

[1] Harkins and McLaughlin, THIS JOURNAL, **47**, 2083 (1925).

[2] Motylewski, *Z. anorg. Chem.*, **38**, 410 (1904). Grabowski, *Dissertation*, Königsberg, **1904**. Valson, *Compt. rend.*, **74**, 103. Stocker, *Z. physik. Chem.*, **94**, 149 (1920). Morgan and Schramm, THIS JOURNAL, **35**, 1845 (1913).

[3] Harkins and Brown, *ibid.*, **41**, 419 (1919).

TABLE I

SURFACE TENSIONS AND DENSITIES OF CALCIUM CHLORIDE SOLUTIONS AT 25° ± 0.005° (ADDITIONAL DENSITIES AT 30°)

Drop weight	m^a	$r/V^{1/3}$	ϕ	γ Surface tension, dynes/cm. at 25° C.	Density at 25° C.	30°
0.095170 .095160	0.000	0.7469	1.6570	72.03	0.99602	....
.095637 .095633	.100	.7481	1.6573	72.39	1.00502	....
.095962 .095957	.200	.7494	1.6576	72.66	1.01396	....
.096321 .096354	.300	.7504	1.6579	72.96	1.02184	....
.097050 .097067	.500	.7529	1.6585	73.54	1.03982	....
.099195 .099214 .099192	1.00_0	.7583	1.6598	75.22	1.08534	....
.104053 .104063	2.00_0	.7621	1.6606	78.94	1.15638	1.1545
.109380 .109475	3.00_0	.76385	1.66095	83.03	1.22426	....
.114772 .114821	4.00_0	.7641	1.66105	87.11	1.28546	....
.119675 .119632	5.00_0	.7643	1.6611	90.79	1.34112	1.3379
.128066 .127923 .128232	7.00_0	.7636	1.6609	97.17	1.43160	1.4281

[a] Moles per 1000 g. of water.

Measured diameters of tip: 0.68092, 0.68290, 0.68565, 0.68455, 0.68270, 0.68165 cm. This tip is much less round than those used by Harkins and Brown.

The atomic weights used are: calcium 40.07; sulfur, 32.06; hydrogen, 1.008. The densities are the weights in grams of 1 cc. of the solution in air of 50% relative humidity as determined with brass weights and a glass counterpoise for the pycnometer.

$(r/v^{1/3})$. In this work M represents the weight of the drop in grams as determined by the use of brass weights at practically the same atmospheric pressure as that which was effective during the density determinations.

The agreement between the independent determinations of the drop weight at any one concentration is to 0.03% or better for any of the solutions up to 2 M concentration. The more concentrated solutions are hygroscopic, which increases the error. Extreme care was taken to protect the solutions from the atmosphere. The temperature was determined by a thermometer calibrated within a few months by the Bureau of Standards which showed the same ice point that was given in the certificate. The solutions were made by dilution, and the concentrations of the more concentrated solutions were determined by precipitation of the chloride as silver chloride. The concentrations of a number of the more dilute solutions were checked by titration. The concentrations are sufficiently accurate for the surface-tension values.

The densities were determined by the use of a pycnometer of a volume of 22 cc. and with a single neck of about 1 mm. diameter. This is essentially a short thermometer stem with an extremely large and well-seasoned bulb sealed on below and is the same pycnometer that was used by Harkins and Hayes.[4]

Purification of the Salt

A large amount of Baker and Adamson's C. P. fused calcium chloride was washed with a stream of pure water. The remaining salt was then dissolved in a relatively small amount of warm water. A portion of the salt separated on cooling in a freezing mixture and this was removed from the mother liquor. This process was repeated four times and until only a very small fraction of the original material remained. This was used to make up the solutions.

Thickness (t) of the Film of Water

Table II gives the *mean* thickness of the film of water on aqueous calcium chloride solutions of different concentrations.

TABLE II

PROVISIONAL VALUES FOR THE MEAN THICKNESS OF THE FILM OF WATER ON AQUEOUS SOLUTIONS OF CALCIUM CHLORIDE

Moles of $CaCl_2$ per 1000 g. of H_2O	0.1	0.5	1.0	2.0	3.0
Thickness in Å	4.5	3.9	3.3	2.8	2.5

The film is somewhat thicker at low concentrations than that on a sodium chloride solution as determined by Harkins and McLaughlin,[1] and also thicker at all concentrations than on a lithium chloride solution as determined in work still unpublished.

The calculations for the two most dilute solutions were made by the use of Equation 1, and for the others by the equivalent Equation 2.

$$t = -\frac{1000\alpha}{3RT}\left[\frac{\partial\gamma}{\partial(\alpha m)}\right]_{T,A} \quad (1) \qquad t = -\frac{1000}{mRT}\left(\frac{\partial\gamma}{\partial \ln a}\right)_{T,A} \quad (2)$$

where α is the activity coefficient of the salt, and a the activity.

The values for the thickness of the film are termed provisional because the activity coefficients for calcium chloride were calculated from data which were in some cases not very accurate, but it seems probable that the thicknesses are nearly correct. The results of the activity calculations will be presented in a later paper.

A very high degree of exactness is required in the determination of the thickness of the film for a 0.1 M solution, so the value given for this con-

[4] Harkins and Hayes, THIS JOURNAL, **43**, 1815 (1921).

centration is somewhat uncertain. It is quite exact if the surface tension is a linear function of the molality in this region, as seems to be indicated by the adjacent portion of the curve and almost all other measurements on salt solutions. However, this may not be the case, since if it is assumed that the activities of the dilute solutions are the same as those given by Lewis and Randall for solutions of barium chloride, this linear interpolation gives a thickness of 4.05 Å. at 0.0001 *M*, and of 4.26 Å. at 0.001 *M* which is thinner than that indicated at 0.1 *M* (4.5 Å.). The thickness for these dilute solutions should be obtained from measurements of the highest exactness possible with the capillary-height method. This work is now in progress in the Kent Chemical Laboratory and it is hoped that sufficient accuracy will be attained to warrant a comparison with the predictions of the Debye-Hückel theory which concern the variation of the surface tension of such dilute salt solutions.

Summary

Careful measurements of the surface tension of water and of aqueous solutions of calcium chloride at 25° have been made at concentrations up to 7 moles of salt per 1000 g. of water. From the surface tensions and the values of the activity coefficients for calcium chloride calculated from data found in the papers of various investigators, the mean thickness of the water film on the calcium chloride solutions is calculated.

The thickness of the film at 1.25 *M* is 3.1 Å., which is the cube root of the volume of a water molecule. At lower concentrations the film is thicker and at higher concentrations *thinner*, but up to 3 or 4 *M* (at least) it is essentially a monomolecular water film.

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THE PHOTO-CHEMICAL INACTIVITY OF INFRA-RED RADIATION WITH SPECIAL REFERENCE TO THE DECOMPOSITION OF NITROGEN PENTOXIDE

BY FARRINGTON DANIELS

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The decomposition of nitrogen pentoxide is a valuable reaction for testing theories of the mechanism of chemical reaction. Not only is it a homogeneous gas reaction but, according to three different researches, it now appears to be truly unimolecular.[1,2,3] As such, it has been supposed to be uninfluenced by collision, and experiments have shown that its

[1] Tolman and White, THIS JOURNAL, **47**, 1240 (1925).

[2] Hirst, *J. Chem. Soc.*, **127**, 657 (1925).

[3] Hunt and Daniels, THIS JOURNAL, **47**, 1602 (1925).