

CCXXIX.—*Surface Phenomena in Sucrose Solutions.*

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THE purpose of this preliminary investigation was to discover a relation between surface tension, osmotic pressure, and adsorption at the surface of solutions of sucrose of various concentrations, with special reference to the exosmosis phenomena which have been shown by Czapek to occur in plant-cells when immersed in solutions having surface tensions 0.65 to 0.68 times that of water. It seemed possible that an explanation might be found in adsorption, and prior to the investigation of solutions the surface tensions of which were lower than that of water, examination was made of solutions of higher surface tension, in order to obtain some idea of the magnitude of the Gibbs adsorption constant.

Morse and his collaborators (*Amer. Chem. J.*, 1912, **48**, 29) found that the osmotic pressures of sucrose solutions of concentrations up to (weight) normal follow the van't Hoff gas laws. The values recorded by other investigators, however, are not concordant (Castell-Evans, *Physico-chemical Tables*, Vol. II), and therefore the surface tensions of such solutions under varying conditions of temperature and concentration have been determined, and, in addition, the relation between the density and the temperature of the various solutions.

The paper therefore divides naturally into three parts, namely, the relation between density and temperature, the determination of surface tension, and the relationship between surface tension and osmotic pressure.

Density-Temperature Curves.

These were obtained in the usual way. The pyknometer was filled with air-free, distilled water and standardised at a series of temperatures in a thermally-regulated bath. In this way, the exact volume of liquid contained by the instrument at known temperatures was ascertained, and the procedure was then repeated with sugar solutions of known strengths.

Pure white crystal sugar was used. The strengths of the solutions were determined polarimetrically, and checked against the density-concentration figures at 15° recorded by Plato (*Z. Ver. Deut. Zuckerind.*, 1900, **50**, 982).

Densities of Sugar Solutions.

The following series of sugar solutions was made up:

Per cent. by volume.	Per cent. by weight.	Normality.	d_{15}^{20} .	Polarimeter reading.
6.48	6.32	0.19	1.02511	8° 39'
13.39	12.73	0.39	1.05174	17° 49'
20.52	19.00	0.60	1.07900	27° 15'
27.67	25.01	0.81	1.10656	36° 50'
32.62	29.00	0.95	1.12491	—

The densities of these solutions were then determined.

Normality of solution.	(Water).	0.19N.	0.39N.	0.60N.	0.81N.
Density of solution.					
Temperature.					
0°	0.9999	1.027	1.054	1.082	1.110
10	0.9997	1.026	1.053	1.081	1.108
20	0.9982	1.024	1.051	1.078	1.105
30	0.9958	1.0215	1.048	1.075	1.1015
40	0.9923	1.018	1.044	1.071	1.097
50	0.9882	1.014	1.040	1.066	1.093
60	0.9834	1.009	1.035	1.061	1.087
70	0.9779	1.003	1.029	1.055	1.081

Determination of Surface Tension.

The capillary tube method was employed, the tube, attached to a finely divided scale, which was read by the aid of a pocket lens, being contained in an outer tube immersed in a constant-temperature bath. Four different strengths of sugar solutions were used, and temperature-surface tension readings taken over the range 14° to 70° ($\sigma = \frac{1}{2}rhdg$).

Normality. (water)	$d_4^{15.5^{\circ}}$	Percentage of sugar.		r (mean value in cm.).
		By vol.	By wt.	
0.20	0.9995	—	—	0.0319
0.40	1.0267	6.90	6.72	0.0362
0.61	1.0528	13.64	12.96	"
0.82	1.0805	20.91	19.36	"
	1.1071	27.93	25.23	"

The following values of the surface tension at intervals of 10° were obtained. The table contains also the calculated values of u (see below).

Norm- ality. (Water).		0.20 N.		0.40 N.		0.61 N.		0.82 N.	
Temp.	σ .	σ .	$u \times 10^9$.	σ .	$u \times 10^9$.	σ .	$u \times 10^9$.	σ .	$u \times 10^9$.
10°	74.0	74.5	6.1	75.0	12.0	75.5	18.5	76.1	24.8
20	72.2	72.8	5.9	73.2	11.6	73.7	17.9	74.2	23.9
30	70.6	71.1	5.7	71.5	11.2	71.9	17.3	72.4	23.1
40	69.1	69.5	5.5	69.9	10.9	70.3	16.7	70.8	22.4
50	67.5	67.9	5.4	68.3	10.6	68.7	16.2	69.2	21.7
60	66.0	66.4	5.2	66.8	10.2	67.2	15.7	67.7	21.0
70	64.6	65.0	5.0	65.4	9.9	65.8	15.3	66.3	20.4

These values of σ (dynes/cm.) agree very well with those calculated from the formula, suggested by Knipp (*Physical Rev.*, 1900, **11**, 129), connecting surface tension and temperature over a limited range :

$$\sigma_t = \sigma_0(1 - At + Bt^2),$$

where t is the temperature and A and B are constants.

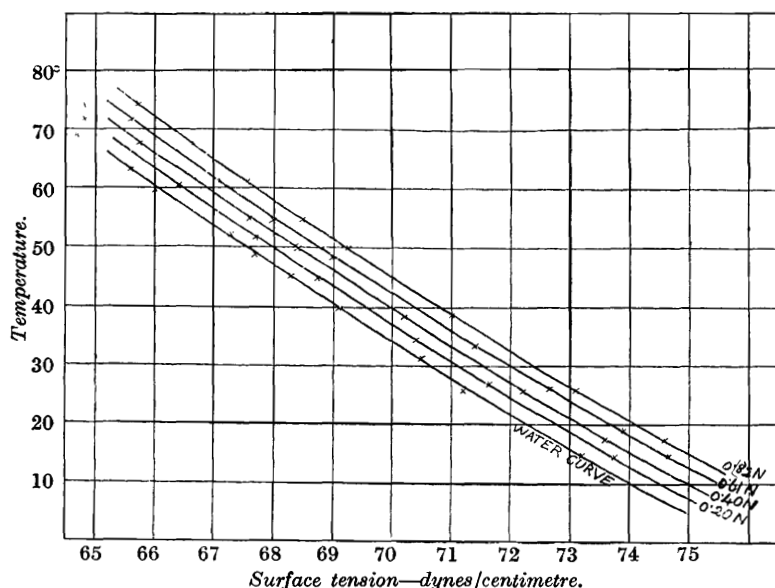
For the curves shown, the average values of these constants are $A = 0.00247$ and $B = 0.00000469$.

The accuracy with which surface tension can be determined depends on the accuracy of measurement of the height of the liquid in the capillary tube. The viscous nature of these sucrose solutions necessitated the use of a tube of somewhat wider dimensions than usual. A tube of radius 0.0362 cm. gave satisfactory results in the case of the more viscous solutions, but it should be noted that the value found for water at 25° is lower by 0.8 per cent. than that recorded by Richards and Carver (*J. Amer. Chem. Soc.*, 1921, **43**, 827).

The degree of accuracy claimed for the above figures is 0.75 per cent. The chief error arises in the determination of the position of the surface of the liquid at the place where the capillary tube enters it. The level of the bottom of the meniscus was taken in each case, probably correctly to 0.1 mm. The minimum rise measured was 3.42 cm., so that the error introduced from this source may be about 0.3 per cent.; and since the diameter of the tube and the densities are correct to three significant figures, the possible error in the final surface tension figures is as stated.

FIG. 1.

Relation between surface tension and temperature.



Quincke's attempt to connect the surface tension σ_s of a solution with the surface tension of water σ_w by the equation $\sigma_s = \sigma_w + ky$, where k is a constant, and y the number of equivalents per 100 molecules of water, was modified by Dorsey (*Phil. Mag.*, 1897, [v], 44, 369), who put y = the number of gram-equivalents per litre of solution. In the case of dilute solutions of sucrose, if y = the number of gram-molecules dissolved per litre of solution, k appears, from the experiments here recorded, to have the approximate value 2.23. It has, however, been shown by Quincke that the equation breaks down for sugar solutions of higher concentration than normal.

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The change in surface tension ($d\sigma$) can now be read directly from the curves together with the corresponding change in concentration (dc); and given the values of $d\sigma/dc$, it is possible to calculate the deficiency of solute in the surface, by the Willard Gibbs equation

$$u = -c/RT \cdot d\sigma/dc,$$

where u is the deficiency in grams per sq. cm., c is the concentration in grams per c.c., R is the gas constant, and T is the absolute temperature. For $dc = 0.21$, the values of $d\sigma$ at 30° , 40° , 50° , 60° , and 70° are 1.25, 1.25, 1.3, 1.3, and 1.25, respectively, giving a mean value of $d\sigma/dc = 6.1$. If the gram is taken as the unit of mass, $R = 8.315 \times 10^7/M$ ergs. Inserting this value in the above equation, u can be calculated in grams per square centimetre of surface. The values are given in the preceding table.

Osmotic Pressures of Sucrose Solutions.

The following values of the osmotic pressures of the sugar solutions used in the surface-tension experiments are obtained by interpolation from the data given by Morse (*J. Amer. Chem. Soc.*, 1912, 48, 29).

Concentration. Volume normal.	Concentration. Wt. normal.	Mean osmotic pressure at :						
		10°.	20°.	30°.	40°.	50°.	60°.	70°.
0.20	0.208	5.09	5.27	5.24	5.37	5.49	5.66	—
0.40	0.434	10.63	11.00	11.17	11.50	11.64	11.79	—
0.61	0.70	17.50	18.13	18.50	18.93	19.20	19.40	19.57
0.82	1.0	25.69	26.64	27.22	27.70	28.21	28.37	28.62

There is a definite relation between osmotic pressure and the Gibbs adsorption constant u , and the slope of the curve plotted between P and u shows a nearly constant value of dP/du .

The product Pu is obviously a function of the concentration over a limited temperature range (in this case, 283° to 333° absolute). This was to be expected in the case of dilute non-dissociated solutions, since P is proportional to the concentration c , and the adsorption constant u is also proportional to c , if $d\sigma/dc$ is a constant. At a definite temperature T , or over a very small range of temperature dT , the product Pu should therefore be proportional to c^2 . The relationship will therefore take the form

$$Pu = K \times c^2,$$

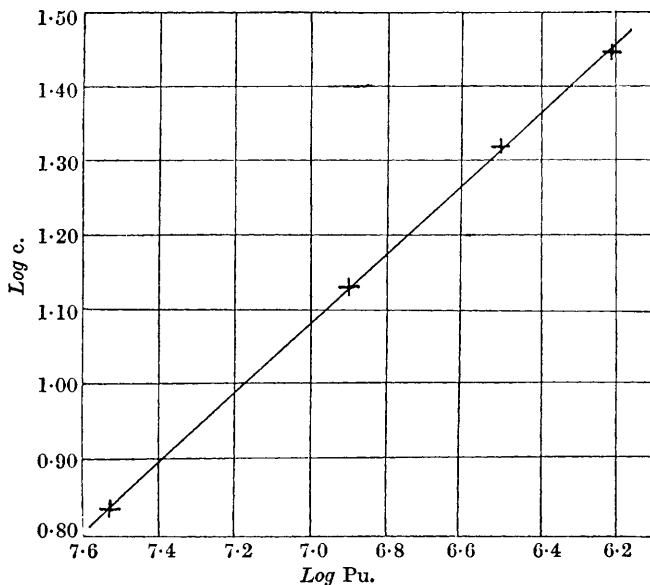
from which x can be calculated in the usual way.

If $\log Pu$ is plotted against $\log c$, all the points will be on a straight line (Fig. 2).

Concentration.		Log Pu . Mean value.	Log c .	α .
Volume normal.	Grams per 100 c.c.			
0.20	6.9	— 7.52286	0.83885	2.08
0.40	13.6	— 6.90367	1.13481	2.08
0.61	20.9	— 6.50295	1.32035	2.09
0.82	27.9	— 6.21034	1.44607	2.12

It would appear, therefore, that the relationship $Pu = Kc^2$ holds for concentrations up to approximately 20 per cent. of sucrose (grams per 100 c.c.), for a limited range of temperatures. Above that concentration, the value of α begins apparently to increase.

FIG. 2.



Whether this is due to an alteration in the value of $d\sigma/dc$ at high concentrations, or to the effect of decreasing hydration of the solute molecules, is not clear, and will be made the subject of a further paper.

If P is expressed in atmospheres, u in grams per square centimetre of surface, and c in grams of sucrose per 100 c.c. of solution, the constant K has a value lying between 5.3×10^{-10} and 5.5×10^{-10} . In view of the degree of accuracy obtainable in these experiments, it is not possible to fix the value more closely.

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