aqueous layer becoming less. In most cases the aqueous layer will disappear before the critical composition is reached and then the distillation curves undergo a sharp change. The composition of the liquid (heavy layer) now moves along a practically straight line, joining the point at which the solution left the heterogeneous area and the apex of the triangle, toward the base of the triangle; the composition of distillate (vapor phase) follows along what is practically the same straight line but with much higher water content (see the first point marked "homogeneous" in Table V). If the composition of the heterogeneous mixture is such that the critical composition is reached without exhaustion of the aqueous layer, the behavior is qualitatively the same. The composition of the boiler liquid turns sharply downwards toward the base of the triangle and eventually only anhydrous phenol–aniline is left. The vapor composition curve passes out of the area of heterogeneity some time before the liquid mixture has become homogeneous, the aniline content of the vapor falling as low as 1.8% at one point. The last point in Table V, referring to a system from which all the water had distilled, shows a composition of vapor very close to that of liquid.

The existence of a maximum vapor pressure on the curves below the heterogeneous area might be thought to determine the direction of the distillation curves to the left or the right, but while this is true in a binary system it is not necessarily so in a ternary system. It must be remembered that the system represented by the base line, *viz.*, phenol–aniline, is one of low vapor pressure and all mixtures rapidly arrive on it, after leaving the heterogeneous area.

From a practical point of view, it is of some importance to observe that almost any heterogeneous mixture of phenol, aniline and water, will, on being submitted to distillation, give rise to an eventual residue free from water and, usually, richer in phenol than aniline. The distillate will be at first rich in aniline, poor in phenol, but its composition will change during distillation, the aniline content falling to a minimum of 1.8% (after which it will rise again) and the phenol content rising progressively.

Summary

The following have been investigated experimentally for the system phenol–aniline–water:

1. The isotherms for 8.6, 25.4, 48.0, 66.3, 69.6 (partially) and 96.7°. The investigations include, besides the mutual solubility curves, the equilibria with solid phases, where solid phases exist.
2. The ternary eutectics.
3. The vapor pressure isotherms for 96.7, 66.3 and 48.0°.
4. The distillation curves.

The above data are discussed.

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[CONTRIBUTION FROM DIVISION OF INSECTICIDE INVESTIGATIONS, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Surface Tensions of Calcium Chloride Solutions at 25° Measured by their Maximum Bubble Pressures

BY H. L. CUPPLES

The surface tensions of calcium chloride solutions have been determined by a number of observers.[1] As calcium chloride is very soluble in water, it is possible to measure large values of the surface tension of the solution minus that of the pure solvent ($\Delta\gamma$), and a comparison of measurements by different methods affords an excellent test of the precision and comparability of the respective methods when applied to aqueous solutions of high surface tension. Harkins and Gilbert used the drop-weight method according to the directions of Harkins and Brown.[2] Belton[3] measured the surface tension of calcium chloride solutions by the method of maximum bubble pressure, but his results cover only a minor fraction of the available range of concentrations. It was considered to be of much interest to measure the surface tensions of these solutions by the method of maximum bubble pressure, and to compare the results with those obtained by Harkins and Gilbert and other investigators.

Experimental

The determination of surface tension by measuring the minimum pressure required to blow a bubble from the bottom of a tube extending vertically downward to or below the surface of a liquid, named by Sugden[4] the "method of maximum bubble pressure," was first suggested by Simon.[5] It was developed by Cantor[6] and by Jaeger.[7] Important and fundamental improvements were made by Sugden.[4] The theory and application of the method is described by Adam.[8]

These observations were made by the Sugden meth of maximum bubble pressure, using a capillary tip,

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[1] W. D. Harkins and E. C. Gilbert, THIS JOURNAL, **48**, 604–607 (1926).

[2] W. D. Harkins and F. E. Brown, *ibid.*, **41**, 499–524 (1919).

[3] J. W. Belton, *Trans. Faraday Soc.*, **32**, 1717–1721 (1936).

[4] S. Sugden, (a) *J. Chem. Soc.*, **121**, 858–866 (1922); (b) **125**, 27–31 (1924).

[5] M. Simon, *Ann. chim. phys.*, [3] **32**, 5–41 (1851).

[6] M. Cantor, *Ann. der Phys. u. Chem.*, **47**, 399–423 (1892).

[7] F. M. Jaeger, *Z. anorg. allgem. Chem.*, **101**, 1–214 (1917).

[8] N. K. Adam, "The Physics and Chemistry of Surfaces," ed. 3, Oxford University Press, London, 1941, pp. 11, 372–376.

effective radius 0.03968 cm. The capillary tip was made by breaking off squarely a piece of capillary tubing, and beveling the outer edge. Examination under the microscope showed the capillary edge to be sharp. The maximum bubble pressures were measured by adjusting the depth of immersion of a second capillary in a light grade of engine oil so that the pressure was just sufficient to cause all the bubbles to issue from the capillary tip in the test solution. The pressure-measuring capillary was fixed in position in a glass container of 40 mm. diameter, and calibrated by reading the pressures on a water manometer with varying amounts of oil in the glass container. In determining the maximum bubble pressure, the pressure was gradually increased by dropwise addition of oil until the bubbles issued from the capillary tip in the test solution. The volume of oil at this point was determined by weighing the tared container on an analytical balance. The capillary tip which was immersed in the test solution was similarly mounted in a glass container, and its depth of immersion was measured with a cathetometer. The two containers were placed side by side in a water thermostat at 25.0 ± 0.1°. The bubbles were formed with air from the laboratory compressed air supply, filtered through absorbent cotton and containing water vapor at the saturation pressure of the solution under observation. Preliminary experiments had shown that the maximum bubble pressure did not change appreciably when the rate of bubbling was varied between one bubble each five seconds and one bubble each thirty seconds, and for these measurements the rate was kept between ten and fifteen seconds per bubble. The temperature was measured with a thermometer that was compared with another standardized at the Bureau of Standards, allowing for the applicable ice-point correction. Sugden[8a] has calculated that in a vessel of radius 1.5 cm. the radius of curvature of the surface, if the liquid is water, corresponds to a pressure of 5.9 dynes per square centimeter, and that if the capillary has a radius of 0.04385 cm. the minimum correction to be added to the observed surface tension is 0.13 dyne per centimeter. The exact correction is probably somewhat greater, owing to the presence of the central capillary tube. These are approximately the dimensions of the apparatus used in the present investigation. However, the correction need not be applied to the present measurements, since the radius of the capillary was here determined by measuring the pressure due to the surface tension when the liquid was water, and assuming the surface tension of the water to be 71.97 dynes per centimeter at 25°.[9] An error in the pressure measurement due to capillarity in the containing vessel will be exactly compensated by the resulting slight change in the calculated value of the radius of the capillary when the liquid is water, and since the pressure due to capillarity in the containing vessel will be approximately proportional to the surface tension of the liquid, it will be approximately compensated at any other value of the surface tension. Accordingly, if the correction for capillarity in the containing vessel is small, as in the present measurements, it may be neglected when the radius of the capillary is determined by calibration against a liquid of known surface tension.

The water was prepared from the laboratory distilled water by treatment with acid potassium permanganate and double redistillation. The calcium chloride was of analytical-reagent grade. The concentrations were determined from the densities, using the concentration-specific gravity table given by Hodgman.[10] In the case of the most concentrated solution it was necessary to dilute it, by weight, and calculate the concentration from that of the diluted solution. Solution densities were determined with a 25-ml. specific-gravity bottle, weights being reduced to vacuum. The capillary tip was calibrated from nine independent pressure measurements made at different times during the course of the experiments, by averaging the pressures, assuming $\gamma = 71.97$, and calculating the radius with the aid of the tables prepared by Sugden (see Adam[8]). The pressure corresponding to the surface tension was found to be 3653 ± 2 dynes per square centimeter. At each concentration several independent measurements of the maximum bubble pressure were made. The individual measurements, converted to surface tensions, and their averages, are given in Table I, in which D_{25} is the density at 25.0° in grams (*in vacuo*) per cc., M is the concentration in moles of calcium chloride per liter of solution at 25.0°, F is the concentration in moles of calcium chloride per 1000 g. (*in vacuo*) of water, and γ is the surface tension at 25.0° in dynes per centimeter.

Table I

Surface Tensions and Densities of Calcium Chloride Solutions at 25.0°

D_{25}	M	F	γ
1.4437	5.823	7.301	97.18, 97.20, 97.22 Av. 97.20 ± 0.05[a]
1.3183	3.995	4.566	88.48, 88.40, 88.66, 88.42 Av. 88.49 ± 0.04
1.2294	2.809	3.062	82.77, 82.71, 82.95 Av. 82.81 ± 0.05
1.1537	1.851	1.952	78.40, 78.24, 78.34 Av. 78.33 ± 0.05
1.1107	1.323	1.372	76.24, 76.26, 76.24 Av. 76.25 ± 0.05
1.0810	0.966	0.992	74.70, 74.79, 74.61 Av. 74.70 ± 0.05
1.0657	0.784	0.801	74.40, 74.46, 74.20 Av. 74.35 ± 0.05
1.0491	0.589	0.599	73.69, 73.57, 73.51 Av. 73.59 ± 0.05
1.0322	0.394	0.399	73.05, 73.08, 73.05 Av. 73.06 ± 0.05
1.0152	0.202	0.203	72.38, 72.50, 72.42 Av. 72.43 ± 0.05

[a] The mean errors of the averages are calculated from all 31 experiments on the assumption that the mean error of each experiment is uniform throughout the range of concentrations.

If γ is plotted as ordinate against F as abscissa, the points may be fitted by a straight line up to the concentration $F = 0.992$, and by a second straight line in the concentration range $F = 0.992$ to 4.566, but the point at $F = 7.301$ falls considerably below the extension of this second straight line. However, if γ is plotted against M, the curve is slightly convex toward the M axis up to the concentration $M = 1.851$, and is a straight line in the concentration range $M = 1.851$ to 5.823. Using the γ–M relationship, the surface tensions throughout the entire concentration range may be accurately expressed by the two equations

For the range 0 to 1.851M

$$\gamma = 71.970 + 2.41004M + 0.57715M^2 \qquad (1)$$

For the range 1.851 to 5.823M

$$\gamma = 69.492 + 4.7562M \qquad (2)$$

Curve (1) was adjusted to pass through the point $\gamma = 71.970$ at $M = 0$; it fits the experimental

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(9) "International Critical Tables," Vol. IV, p. 447.

(10) C. D. Hodgman, ed., "Handbook of Chemistry and Physics," Cleveland, Ohio, 1939, ed. 23, p. 1159.

points with a maximum deviation of 0.14 dyne per centimeter and with a standard error of estimate of 0.08 dyne per centimeter. Curve (2) was fitted by the method of least squares; it reproduces the experimental points with a maximum deviation of 0.04 dyne per centimeter and a standard error of estimate of 0.03 dyne per centimeter.

As surface tension data are usually reported in the literature with concentrations expressed as moles of solute per 1000 g. of solvent, it is desirable for comparative purposes to have a convenient method for transforming concentrations in terms of moles of calcium chloride per 1000 g. of water (F) into concentrations expressed as moles of calcium chloride per liter of solution, at 25° (M). This may be done with facility with the following two equations, in which $R = M/F$.

For the range 0 to 0.992F

$$R = 0.9970 - 0.022211F \qquad (3)$$

For the range 0.992 to 7.301F

$$R = 1.0026 - 0.028021F \qquad (4)$$

Equation (3) was adjusted to pass through the point $R = 0.9970$ at $F = 0$; it fits the F–M data of Table I with a maximum deviation of 0.26% (at $F = 0.203$). Equation (4) was fitted by the method of least squares; it reproduces the data with a maximum deviation of 0.10%.

The mean error of the average at any concentration, based upon an average of three experiments, is indicated in Table I to be ±0.05 dyne per centimeter, or approximately 0.06%. This may be regarded as the precision of measurement at a given concentration. The mean error (accuracy) of the pressure measurements is estimated to be ±0.16%, or better. The mean error (accuracy) of the concentrations is estimated as ±0.05%. Assuming that equations (1) and (2) yield calculated values of γ which are at least as accurate as the points to which they are fitted, the mean error (accuracy) of values of γ calculated from equations (1) and (2) is estimated to be ±0.15 dyne per centimeter.

Discussion and Comparison of Results

Using equations (3) and (4) to convert concentrations in moles of calcium chloride per 1000 g. of water (F) to concentrations in moles per liter of solution at 25°, (M), equations (1) and (2) have been employed to calculate the surface tensions as measured in this investigation at the concentrations reported from other sources. The deviations of the present experimental results and the experimental results of other investigators, from the values given by equations (1) and (2), are plotted against concentration in Fig. 1.

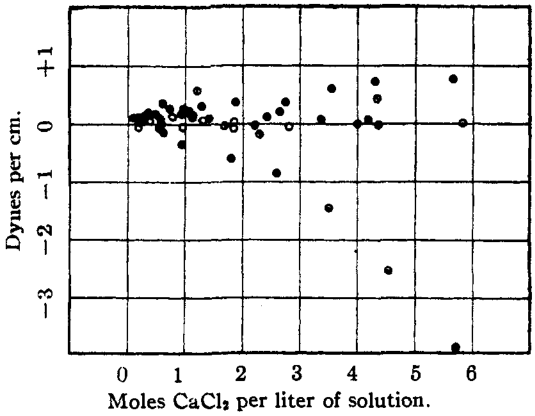

Fig. 1.—Deviations of experimental values of $\Delta\lambda$ from those calculated by equations (1) and (2): ⊙, This paper; ●, Harkins and Gilbert; ◓, Belton; ◒, Morgan and Schramm; ⊖, Stocker; ⦶, Grabowsky; ⊘, Sentis; ⊗, Volkmann.

The values of $\Delta\gamma$ observed in this investigation are lower than those reported by Harkins and Gilbert throughout the entire concentration range, the difference ranging systematically from 0.12 dyne per centimeter at $F = 0.100$ to 0.76 dyne per centimeter at $F = 7.000$. The cause of this divergence is not readily apparent. A small part of it may be due to errors in the determination of solution concentrations. For instance, at $F = 5.000$ as reported by Harkins and Gilbert, the concentration $F = 5.030$ is obtained by using their density value, corrected to vacuum, and reading the concentration from the concentration–specific gravity tables used in this investigation; this would reduce the difference between the $\Delta\gamma$ values at this solution density from 0.73 to 0.63. The evidence does not indicate that the divergence is due to an impurity in the salt. A surface tension reduction due to such an impurity would be expected to increase in magnitude with increase in concentration more rapidly than is observed. Moreover, the surface tensions here observed agree almost within experimental error with those of Harkins and Gilbert up to the concentration $F = 0.50$, and they agree within experimental error with those of several other investigators. Analytical reagent grade chemicals have been used for the most precise measurements of surface tension with no purification other than a fusion.[11] To avoid any doubt concerning the present measurements, a portion of the calcium chloride was fused in platinum and from it a 5.788 M solution was prepared. The surface tension calculated from equation (2) is 97.02 dynes per centimeter, while an average of three determinations gave the value 96.95 dynes per centimeter. There is thus no indication of the presence in the unfused salt of an impurity which reduces the surface tension. It appears that the divergence between the observations may be due to errors of instrumentation, to slight errors in Harkins and Brown's correction factors when applied to aqueous solutions of high surface tension, or to a slight departure of the experimental conditions in the maximum-bubble-pressure

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[11] F. A. Long and G. C. Nutting, THIS JOURNAL, 64, 2476–2482 (1942).

method from the fundamental assumptions underlying the theory.

The observations of Belton,[3] by the method of maximum bubble pressure, agree with those herein reported within experimental error at the highest concentration measured by him, and the agreement is reasonably good at the lower concentrations. At the higher concentrations the results of Morgan and Schramm,[12] by the drop-weight method, are several dynes lower.

The results of Stocker,[13] by the method of vibrating liquid rays, when compared with measurements by other methods indicate that the equilibrium surface tension is established within 0.01 second. The measurements of Sentis,[14] using a hanging drop at the bottom of a capillary tube, agree well with the present results up to a concentration of 2.299 *M*, and within 0.45 dyne per centimeter at 4.353 *M*.

The results of Volkmann,[15] by the method of capillary rise, agree well with the measurements herein presented throughout the entire concentration range studied by him (up to 4.35 *M*). As Volkmann's unit of force is the gram, it has been necessary to assume a value for the gravitational constant ($g = 980$) in order to calculate comparative results. The results of Grabowsky,[16] by the method of capillary rise, are also in reasonably good agreement with those of the author.

Summary

The surface tensions of aqueous solutions of calcium chloride have been accurately determined within the concentration range 0.203 to 7.301 moles of calcium chloride per 1,000 g. of water (0.202 to 5.823 moles per liter of solution) by the method of maximum bubble pressure.

The observations are compared with those of several other investigators using the same and different methods of measurement. It is concluded that the divergence from the results of Harkins and Gilbert, amounting to a maximum of 0.76 dyne per centimeter at the highest concentration, may be due to errors of instrumentation, to slight errors in the drop-weight correction factors of Harkins and Brown when applied to aqueous solutions of high surface tension, or to a slight departure of the experimental conditions in the maximum-bubble-pressure method from the fundamental assumptions underlying its theory. The present measurements are in excellent agreement with those of Volkmann, by the method of capillary rise.

BELTSVILLE, MARYLAND RECEIVED DECEMBER 13, 1944

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(12) J. L. R. Morgan and E. Schramm, THIS JOURNAL, **35**, 1845–1856 (1913).

(13) H. Stocker, *Z. physik. Chem.*, **94**, 149–180 (1920).

(14) M. H. Sentis, *Ann. Univ. Grenoble*, **9**, 1–82 (1897).

(15) P. Volkmann, *Wied. Ann.*, N. S., **17**, 353–390 (1882).

(16) As cited by G. Zemplèn, *Ann. Physik*, [4] **22**, 391–396 (1906–1907).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Change of Surface Tension with Time. I. Theories of Diffusion to the Surface

BY SYDNEY ROSS[1]

The change of surface tension with time is here ascribed to the formation of a new phase at the surface, caused by adsorption, crystallization, denaturation or some more general chemical reaction. The rate at which equilibrium is reached has been measured for many compounds and found to vary widely: the rate is primarily characteristic of the substance and its concentration, and is indicative of the nature of the process taking place at the surface. Thus, for example, in pure liquids an extremely rapid attainment of equilibrium (within 10^{-9} second) would, if possible to observe, indicate an instantaneous reorientation at the surface to reduce the surface free energy to its minimum value. For different solutions the time to reach equilibrium ranges from a small fraction of a second to a period of several days. No single mechanism can account for all the cases and, in fact, many mechanisms have been suggested by different writers. Very few, however, have yet received mathematical treatment to predict the observed time effect. Only two are sufficiently advanced. The mechanism, originally suggested by Milner,[1a] is the same for both, namely, that the time effect is due to the time required for diffusion of the solute molecules to the surface.

The object of this paper is to compare treatments of this idea. It may be considered a work of supererogation to correlate hypotheses that, starting with similar postulates, differ only in their development. In this instance, however, predictions for certain substances are not in accord and the divergence requires an explanation.

Theory.—The theoretical treatment of Bond and Puls[2] produces the relation

$$\frac{\bar{q} - q}{\bar{q}} = e^{-\frac{2}{\sqrt{\pi}}\sqrt{\frac{t}{\tau}}} \qquad (1)$$

where q is the excess molar surface concentration at time t, during the formation of the surface layer: and $\bar{q}$ is the excess molar surface concentration at equilibrium. The quantity τ is defined by the equation

$$\tau = (\bar{q}/\bar{c})^2/D \qquad (2)$$

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(1) Bristol-Myers Co. Research Fellow, Stanford University, California.

(1a) S. R. Milner, *Phil. Mag.*, [6] **13**, 96 (1907).

(2) W. N. Bond and H. O. Puls, *ibid.*, [7] **24**, 864 (1937).