in form with equation (1). In case of an expansion taking place at higher concentrations, the entire curve for the volume changes may be given with a surprisingly high degree of accuracy simply by the addition of a positive linear term.

A relationship such as the one suggested would require that all non-electrolytes give salting out curves of the same sequence. As already mentioned this does not seem to be the case. It should be stressed, however, that the probable errors in a substantial portion of the data in Table II are very large and a really precise study of the whole field is very much needed.

Summary

The solubility of helium and argon in various salt solutions at 25° has been studied. The salting out constants obtained have been found to have the same order of magnitude as those of any other non-electrolyte studied. A short discussion of the salting out studies that have been presented in the literature shows the need for an investigation of real precision.

NEW HAVEN, CONN. RECEIVED APRIL 20, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

The Change in the Surface Tension of a Solution of Methyl Acetate Due to Hydrolysis[1]

BY BENJAMIN H. HANDORF AND E. ROGER WASHBURN

The possibility of measuring the rate of hydrolysis of ester solutions by measuring the changes in surface tension which accompany hydrolysis has been suggested.[2] It was the purpose of this study to carry out such an investigation. The rate of change of the surface tension of a 2 molar solution of methyl acetate was compared with the rate of hydrolysis as measured by titration with standard barium hydroxide.

Purification of Materials and Preparation of Solutions

Methyl acetate of C. P. grade was further purified by the method used by Young[3] in the preparation of samples for the determination of its physical constants. The intermediate fractions distilling over within less than 0.5° range in temperature were used in making up the solutions. The specific gravity of the methyl acetate used was d^{25}_4 0.9275 ± 0.0003 as compared with the value in the literature.[4] d^{25}_4 0.9273.

Synthetic methyl alcohol of a high degree of purity was fractionally distilled through an efficient fractionating column to remove minute traces of water. The specific gravity of the purified alcohol was d^{25}_4 0.7867 ± 0.0001 as compared with the value in the literature.[4] d^{25}_4 0.7867.

Acetic acid of C. P. grade was purified by repeated fractional crystallization and then by fractional distillation through an efficient fractionating column. The specific gravity of the acid used was d^{25}_4 1.0446 ± 0.0001 as compared with the value in the literature.[4] d^{25}_4 1.0443.

Conductivity water was used for making up the solutions.

Barium hydroxide solutions, standardized by means of benzoic acid and phenolphthalein, were used for titrating the liberated acetic acid.

Measurement of Surface Tension and Percentage Hydrolysis

The ring method of measuring surface tension was used in this investigation to determine the surface tension of the solutions. One purpose for its choice was for testing its accuracy and applicability as a means of following the changes in the surface tension of hydrolyzing solutions containing ingredients of varying volatility.

In measuring the surface tension the force required to break the ring from the surface was determined by means of a chainomatic balance especially constructed for surface tension measurements. The magnitude of the force was read directly in grams. The ring was constructed of platinum wire. 0.31 mm. in diameter. The circumference of the ring as calculated from its measured diameter, 1.272 cm., was 3.996 cm. The surface tension measurements were made at suitable intervals of time on samples withdrawn from the solutions in a constant temperature bath. A suitable quantity of solution from each sample was titrated with standard barium hydroxide for determining the percentage hydrolysis. During the titrations the solutions being titrated were kept in ice water to retard the hydrolyzing effect of the barium hydroxide on the methyl acetate. Data beyond the equilibrium point between methyl acetate and water and methyl alcohol and acetic acid were obtained by studying the methyl alcohol–acetic acid solutions as the acid and alcohol reacted to form the ester and water.

In making the surface tension measurements the precautions recommended by Harkins[5] were observed with one exception. the instrument was not immersed in a thermostat. and constant temperature was not maintained in the instrument during succeeding measurements. During a

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(1) Presented at the Twelfth Midwest Regional Meeting of the American Chemical Society, May 4, 1934, at Kansas City, Missouri.

(2) Bigelow and Washburn, *J. Phys. Chem.*, **32**, 321 (1928).

(3) Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

(4) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III, p. 28.

(5) Harkins, *Science*, **64**, 333 (1926).

measurement the pointer of the surface tension balance was kept at the zero mark. This was accomplished by lowering the platform supporting the liquid at a suitable rate as more force was placed upon the ring. This procedure for detaching the ring from the liquid surface was found best for giving reproducible values.

Discussion and Results

Four different two molar solutions of methyl acetate and three different solutions, two molar with respect to methyl alcohol and acetic acid, were studied in this investigation. Because the results from the different solutions of the same materials were merely confirmatory, it was considered unnecessary to list the results from more than one solution of each type. The data for the two molar methyl acetate solution are recorded in Table I, while Table II contains similar data for the solution two molar with respect to methyl alcohol and acetic acid.

The force, F, in grams required to pull the ring from the surface of the liquid has been converted into surface tension expressed in dynes per cm. by means of the equation $FG/2r = \gamma$; where G is acceleration due to gravity = 980.1 cm. sec.$^{-2}$, r is the circumference of the ring = 3.996 cm., and γ is surface tension.

It is generally recognized that the ring method gives slightly higher values than the capillary height method, and all of our values are presumably somewhat high on that account. However, the probable error in these values relative to one another is less than 0.1 dyne. The largest single source of error is believed to be the inconstancy of the temperature. Any error caused by evaporation must have been small because the solutions were practically covered by the two glass plates during the measurements.

When the surface tensions of the solution are plotted against the percentages of the hydrolysis, the points lie on a straight line within about $\pm 1\%$, and in cases where the more direct, accurate determination is impracticable, the degree of hydrolysis can be calculated from the surface tensions with this accuracy.

From a consideration of all the solutions studied in this investigation it was found that equilibrium was reached by the reaction mixture when approximately 79.6% of the ester was hydrolyzed, or in the case of the methyl alcohol–acetic solutions, when 20.4% of the alcohol and acid had reacted to form the ester. The original quantity of water present in the 2 molar ester solutions was 47.555 moles per liter. From the above data the equilibrium constant was calculated for the hydrolysis reaction

methyl acetate + water $\rightleftharpoons$ methyl alcohol + acetic acid

$K = 0.135$. The reciprocal of 0.135 is 7.40. Therefore 7.40 $= K_r$, the equilibrium constant for the reaction written in the reverse direction.

TABLE I

Elapsed time, hours	Temp. of soln. during S. T. measurement	Hydrolysis, %	Surface tension, dynes/cm.
1.0	23.6	0.00	38.27
147.8	23.6	0.74	38.30
435.5	24.8	7.95	39.23
603.5	23.5	15.35	40.26
733.5	23.2	21.22	40.91
841.0	24.1	27.62	41.52
959.0	24.2	34.20	42.23
1128.0	24.2	43.47	43.31
1273.0	24.7	50.84	44.06
1438.8	23.8	58.15	44.92
1609.0	24.9	64.10	45.44
1776.8	24.5	68.55	46.00
2017.8	25.7	73.31	46.38
2281.0	24.6	75.55	46.85
2520.0	25.3	77.10	46.96
3072.0	25.4	78.55	47.13

TABLE II

Elapsed time, hours	Temp. of soln. during S. T. measurement	Hydrolysis, %	Surface tension, dynes/cm.
1.5	23.4	99.55	49.61
119.0	23.0	94.09	48.83
238.0	24.2	90.41	48.24
383.3	24.0	87.24	47.91
550.8	24.4	84.77	47.58
741.5	24.7	83.16	47.37
935.5	24.8	82.22	47.18
1150.5	25.3	81.57	47.13
1416.5	24.7	80.97	47.12
1749.3	24.6	80.38	47.12
2159.0	25.0	80.30	46.99
2878.0	25.5	80.02	46.99
3700.0	25.5	79.88	47.10

Summary

1. A study has been made of the change in surface tension with hydrolysis of a two molar methyl acetate solution from 0 to 100% hydrolysis, arriving at the equilibrium mixture from both directions. A straight line relationship was found to exist between the surface tension and the percentage hydrolysis.

2. The ring method of measuring surface tension was found to be suitable for determining the relative surface tensions of solutions having sur-

face tensions not differing greatly in magnitude. However, with this method absolute temperature control was found to be difficult when working with solutions of the type studied in this investigation.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Dipole Moment of Deuteroammonia[1]

BY J. M. A. DE BRUYNE AND C. P. SMYTH

Because of the accuracy with which the dipole moment of ammonia can be measured, it was selected as a suitable substance for the determination of the effect of the replacement of hydrogen by deuterium upon the dipole moment. The measurement was made possible by the kindness of Dr. J. C. Jungers, who loaned a quantity of pure deuteroammonia which he had prepared. The dielectric constants at different temperatures were measured with an apparatus previously described.[2] This apparatus had, however, been subjected to extensive alterations in the electrical circuits, which were kept at a temperature constant within 0.2° by thermostatic regulation of the air in the large shielding box enclosing them.

Preparation of Materials

Ammonia was prepared from reagent grade ammonium chloride and potassium hydroxide. The gas was passed successively over calcium oxide and potassium hydroxide and condensed in a liquid air trap. By means of liquid air, two fractionations were made on the substance, the system containing the ammonia being pumped out during the process and a small residual quantity being discarded in both fractionations.

Deuteroammonia was prepared by the action of deuterium oxide on magnesium nitride, which had been prepared by passing dry nitrogen through a silica tube containing magnesium turnings heated to about 600°. The gas was sublimed from a tube cooled with a slush of solid carbon dioxide in toluene into a trap cooled with liquid air, the system being pumped out during the sublimation. Any deuterium oxide present would have been retained in the first trap. The triple point of the substance was measured with a copper–constantan thermocouple, which had been calibrated at the boiling point of oxygen, at the freezing point of pure *n*-heptane and at the triple point of ammonia. The temperature at the triple point was found to be −73.6° and the pressure 48.6 mm.

Experimental Results

Although the moment of ammonia had been measured by other investigators, it was determined again at the beginning of this investigation. After the ammonia had been pumped out, the apparatus was rinsed thoroughly by the admission of an impure deuteroammonia and subsequently evacuated before the pure deuteroammonia was run in. The P–V–T relations determined from the equation of state found by Beattie and Lawrence for ammonia[3] were used for both gases in calculating the values of the molar polarization, $P = (\epsilon - 1)M/(\epsilon + 2)d$, where ϵ is the dielectric constant, M the molecular weight, and d the density. These values are given in Table I and are plotted against $1/T$, the reciprocal of the absolute temperature, in Fig. 1. The straight lines thus obtained give the constants a and b of the Debye equation $P = a + b/T$. Table I gives at the bottom the values of a, the induced polarization, and $b = 4\pi N\mu^2/9k$, in which N is the number of molecules per gram molecule, μ the dipole moment, and k the molecular gas constant $= 1.372 \times 10^{-16}$.

TABLE I

POLARIZATIONS OF THE AMMONIAS

Ammonia		Deuteroammonia	
T, °K.	P	T, °K.	P
273.9	53.79	274.1	54.94
309.2	48.30	304.3	49.85
334.9	45.29	333.8	45.85
363.6	41.93	363.8	42.46
394.0	39.05	394.2	39.38
423.1	36.67	425.0	37.04
$a = 5.3$, $b = 13310$, $\mu = 1.46_6 \times 10^{-18}$		$a = 4.4$, $b = 13840$, $\mu = 1.49_6 \times 10^{-18}$	

Discussion of Results

The value of the induced polarization of ordinary ammonia, 5.3, is slightly lower than those

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(1) The preliminary part of this work was done while the senior author was a National Research Fellow.

(2) McAlpine and Smyth, THIS JOURNAL, 55, 453 (1933).

(3) Beattie and Lawrence, *ibid.*, 52, 6 (1930).