production is "abnormal" in that no such mass effect is evident. This contrast suggests that ethane production is the result of excess translational energy in the methyl radical while methane production may be the result of excess internal energy. However, this proposal cannot be regarded seriously until further evidence is available.

When a hydrogenous substance is present during the photolysis of methyl iodide, that substance may act as a moderator and also give rise to methane through a hot radical reaction. By use of deuterium, this product may be distinguished from that arising from reaction 2. From the yields given in Table I for systems containing deuterium, equation 9 yields $k_{4a}/k_4 = 0.35$ for methane production and 0.15 for ethane production. For systems containing methane-d_4, equation 9 yields $k_{4a}/k_4 = 1$

for methane production and $k_{4a}/k_4 = 0.33$ for ethane production. It is evident that methane-d_4 is by far the best moderator of methane production, but not unusual in moderation of ethane production.

The production of methane-d in the presence of deuterium or methane-d_4 is clearly a hot radical reaction, since it occurs with relatively good efficiency even in the presence of iodine. The production of methane-d is especially efficient from methane-d_4.

NOTRE DAME, INDIANA

Surface Tension of Ammonia and of Solutions of Alkali Halides in Ammonia

BY R. A. STAIRS AND M. J. SIENKO

The surface tension of liquid ammonia from −75 to −40° and of solutions in ammonia of sodium chloride and bromide and potassium bromide and iodide at −40° were measured by the method of maximum bubble pressure and checked by a few measurements by the capillary rise method. The surface tension of ammonia may be represented by the equation $\gamma = 23.41 - 0.3371t - 0.000943t^2$ with a standard error of 0.15 dyne/cm. from −75 to −40°. The results obtained with the salt solutions may be expressed in the form $\Delta\gamma = Ac + Bc^2$ where c is the concentration in moles per liter. The A coefficients decrease regularly with increase in the polarizabilities of the ions, as they do in aqueous solutions. An argument is presented relating the B coefficients to the Bjerrum theory of ionic association.

The theories of the surface tension of salt solutions due to Oka[1] and Onsager and Samaras[2] are in agreement in predicting the approximate magnitude of the effect of KCl on the surface tension of water. They also agree in predicting an inverse dependence of the magnitude of the effect on the dielectric constant. The measurements of Kosakevich[3] on solutions of several salts in a number of solvents appear not to demonstrate the expected relationship. Kosakevich noted that the order of the effects of different salts in a given solvent was usually different from that found in water.

As was pointed out by Onsager and Samaras, neither of these theories takes account of higher order electrostatic forces between the ions and the surface that would be expected to arise from the polarizability of the ions. That different salts of a given charge type do not have the same effect on the surface tension of water is well known. For example, for LiCl (where the sum of the ionic polarizabilities[4] is equal to 3.01 Å.[3]) the surface tension increment over that of the pure solvent in one molar solution in water[5] is approximately twice that of KI ($\Sigma\alpha = 7.44$ Å.[3]). Onsager and Samaras showed that an effect of this magnitude would not be expected to result from differences in size alone, so the observed effect presumably arises from the polarizability differences. Though the amount of scatter

is considerable, there seems to be a linear relationship between the surface tension increment and the sum of the ionic polarizabilities.

The experiments to be described were designed to find out whether a similar relationship between the surface tension increment and the polarizability exists in liquid ammonia, and to examine further the dependence of the surface tension increment on the dielectric constant. It proved necessary also to make some measurements of the surface tension of pure liquid ammonia, as existing data were few.

Experimental

The method chosen was Sugden's modification of the maximum bubble pressure method.[6] As a check, however, a few measurements were also made by capillary rise. Since the diameters of the precision-bore capillary were measured only at both ends and the heights of the liquid in the capillaries were measured through the walls of a clear Dewar flask, the highest accuracy attainable by the capillary rise method was not achieved.

The maximum bubble pressure method has the advantage of being virtually independent of contact angle and it is less sensitive to small amounts of dirt than other methods by virtue of the continual formation of new surface. Long and Nutting[7] demonstrated that, at least with ionic solutions, it appears to yield the true "static" value of the surface tension at reasonable bubbling rates. The apparatus was calibrated using benzene as a standard liquid, and the bubble pressures were measured with a manometer containing m-xylene. Both liquids were Baker and Adamson Reagent grade, refluxed in the presence of sodium, and distilled through a short column in all-glass apparatus. The hydrogen used to blow the bubbles was Matheson electrolytic grade, further purified over hot copper and dried with

(1) S. Oka, Proc. Phys. Math. Soc. Japan, 14, 233, 469 (1932).
(2) L. Onsager and N. N. T. Samaras, J. Chem. Phys., 2, 46 (1934).
(3) P. P. Kosakevich, Z. physik. Chem., 136, 195 (1928).
(4) C. J. F. Böttcher, Rec. trav. chim., 65, 19 (1946).
(5) "International Critical Tables," Vol. IV, McGraw–Hill Book Co., Inc., New York, N. Y., 1928, p. 464 ff.

(6) S. Sugden, "The Parachor and Valency," George Routledge and Sons, Ltd., London, 1930, p. 208 ff, p. 220.
(7) F. A. Long and G. C. Nutting, THIS JOURNAL, 64, 2476 (1942).

barium oxide. The ammonia, Matheson Anhydrous, was twice distilled over sodium, degassed by repeated freezing and evacuation, and a middle fraction was distilled into a measuring bulb, the contents of which were totally distilled into the cell. The salts used, NaCl, NaBr, KBr and KI, were Baker and Adamson Reagent or Mallinckrodt Analytical Reagent grade, of rather large crystal size (1 to 2 mm.) so as not to stick in the addition tube. They were used without further purification but were predried at 110° for some hours and vacuum-dried in the addition tube at 60° overnight.

In addition to the cell which is described below, the apparatus consisted of a vacuum system for the purification, handling and storage of ammonia and hydrogen, a manometer filled with *m*-xylene, thermostats for the cell and the manometer, and a cathetometer to read the manometer.

Figure 1 is a diagram of the maximum bubble pressure cell, showing the magnetically operated reciprocating stirrer and the side tube for the addition of solid solutes. The larger of the two bubble tips was cut from 5 mm. o.d. Pyrex tubing. A number of pieces were cut and selected by direct and microscopic examination, and by measurement of the inner diameter at six orientations, for squareness, regularity and most nearly circular inner shape. The radius of the large tip (needed to apply Sugden's correction, discussed below) was of the order of 0.170 ± 0.001 cm. The smaller tips were made by drawing out 3 mm. o.d. Pyrex tubing and cutting off the drawn-out portion with a chip of boron carbide. The radius of a suitable tip was about 6 × 10⁻³ cm., but no attempt was made to measure it exactly.

The temperature of the cell was controlled by a thermostat consisting of a large Dewar vessel filled with methanol, cooled by a copper coil through which circulated methanol chilled in another coil surrounded by Dry Ice and acetone. The circulating pump was operated intermittently through a relay by a bimetallic thermoregulator. With this arrangement the bath temperature could be held within less than a tenth of a degree at any temperature from 0 to −65°. Temperatures below this were maintained manually by the addition of small pieces of Dry Ice to cold acetone substituted for the alcohol in the thermostat vessel. A thermostat of conventional design was used to control the temperature of the manometer.

The cell and manometer bath temperatures were measured by means of iron–constantan thermocouples using a Leeds and Northrup portable precision potentiometer. Each thermocouple was calibrated against evaporating Dry Ice, freezing mercury, melting ice, the sodium sulfate transition, boiling benzene and boiling water. The cell thermocouple was also calibrated in the vicinity of −40° against an ammonia vapor pressure thermometer prepared according to the directions given by Sanderson.[8] The two calibrations disagreed by 0.04° at the temperature of freezing mercury. The ammonia thermometer was used throughout the work on the salt solution as an additional check on the temperature of the cell thermostat. It could be read to 0.01° at −40°, and the largest fluctuation noted during all the runs in which it was in use was 0.04°.

For a measurement, pressure in the left arm of the cell was decreased by withdrawal of mercury so that hydrogen bubbles formed no faster than one every five seconds. The maximum bubble pressure (up to 30 cm. xylene) was measured by a manometer connected across the two arms of the cell. The difference in xylene levels, read with a cathetometer to ±0.05 mm., was determined first with the stopcock S (Fig. 1) open, so that bubbles came from the larger tip, then with S closed, then open again, to ensure that no change in conditions had taken place during the change from one tip to the other. The difference between the pressures required to detach a bubble from the two tips, converted to dynes/cm.², was used to calculate the surface tension or, in calibration runs, the apparatus constant. The formula used for this calculation is that given by Sugden[6]

$$\gamma = AP\phi$$

where A is the apparatus constant as determined by calibration, P is the difference in the maximum pressures observed with the two tips, and ϕ is a correction factor given by

$$\phi = 1 + 0.69 g r_2 \rho / P$$

(8) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 119.

where g is the acceleration due to gravity, r_2 is the radius of the larger tip, and ρ is the density of the liquid under examination.

The following runs were made with pure liquids: (a) calibrations with benzene; (b) ten determinations of the surface tension of ethanol over a range of temperatures from about −80° to room temperature, as a check on the method; and (c) eighteen determinations of the surface tension of ammonia between about −75 and −40°. With ammonia solutions of the four salts, a sample of salt was placed in the addition tube and vacuum dried at 60° and 10⁻⁵ mm. pressure overnight. Ammonia was distilled into the cell and the procedure carried out as above. Then the addition tube was rotated so that the salt fell into the cell and the stirrer operated long enough to ensure solution and uniform mixing. The same procedure was then carried out with the solution. The surface tension increment $\Delta\gamma$ was calculated from the formula

$$\Delta\gamma = \gamma_0(\Delta P / P_0)$$

where the subscript zero refers to the pure solvent, and Δ refers to the change in passing to the solution. It was found that the change in ϕ made only a negligible difference. The value of γ_0 was taken from the results obtained earlier.

The solutions were analyzed for both ammonia and halide ion. The ammonia was determined by allowing it to bubble into standard acid solution and the excess acid titrated with sodium hydroxide to the methyl red end-point. A relatively constant error, due to ammonia left in the system, was reduced to a minimum by chilling a portion of the tubing near the bubbler outlet to condense most of the residual ammonia and then shutting off most of the system before re-evaporation through the bubbler. After evacuating the cell to remove traces of ammonia, the halide was determined by titration with silver nitrate solution using dichlorofluorescein as an adsorption indicator.[9] In the most dilute solutions the quantity of halide present was too small to be conveniently determined by the adsorption indicator method, so the Mohr method[9] using chromate ion as indicator was used. An appreciable blank correction was necessary with this method. The density data of Johnson and Martens[10] were used to calculate the concentrations in moles per liter.

Results

The results of the measurements of the surface tension of ammonia by the maximum bubble pressure method are listed in Table I. They can be

TABLE I

SURFACE TENSION OF NH₃ BY MAXIMUM BUBBLE PRESSURE

t, °C.	γ, erg/cm.²	t, °C.	γ, erg/cm.²	t, °C.	γ, erg/cm.²
−75.3	43.45	−67.0	41.71	−52.0	38.18
−74.6	42.98	−63.6	41.08	−49.8	37.92
−72.6	42.98	−59.8	40.39	−43.6	36.16
−69.0	42.26	−58.3	39.65	−40.7	35.54
−67.2	41.91	−56.4	39.22	−40.1	35.47
−67.0	42.08	−52.2	38.51	−39.4	35.38

expressed by the equation

$$\gamma_t = 23.41 - 0.3371t - 0.000943t^2$$

which is valid from −75 to −39° with a standard error, σ, of 0.15 dyne/cm.

(9) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis," revised edition, The Macmillan Co., New York, N. Y., 1948, pp. 471, 473.

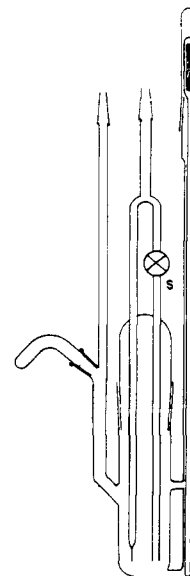(10) W. C. Johnson and R. I. Martens, THIS JOURNAL, 58, 15 (1936).

Fig. 1.—Maximum bubble pressure cell.

The data obtained by the capillary rise method are given in Table II, though less confidence is placed in them for reasons already mentioned.

TABLE II

SURFACE TENSION OF NH_3 BY CAPILLARY RISE

t, °C.	γ, erg/cm.^{2}	t, °C.	γ, erg/cm.^{2}	t, °C.	γ, erg/cm.^{2}
−64.9	41.31	−56.4	39.18	−49.5	37.72
−62.2	40.75	−54.3	39.29	−44.3	36.76
−61.1	40.37	−53.0	38.94	−37.2	34.98
−56.7	39.49	−50.1	38.04		

The results of the measurements with ethanol may be expressed by the equation

$$\gamma_t = 24.39 - 0.0846t + 0.000103t^2$$

from −80 to 25° with σ equal to 0.10.

Table III contains the data for the solutions of the four salts in liquid ammonia at −40.0°, the only temperature at which the solutions were studied.

TABLE III

SURFACE TENSION OF SALT SOLUTIONS IN LIQUID NH_3 AT −40.0°

Salt	c	$\Delta\gamma$	c	$\Delta\gamma$	c	$\Delta\gamma$
NaCl	0.023	0.07	0.086	0.23	0.131	0.23
	.042	.13	.103	.18[a]	.186	.34
	.069	.15	.130	.30[a]	.242	.32
NaBr	.031	.14	.166	.43	.392	.58
	.038	.08	.179	.36	.399	.72
	.075	.30	.270	.47	.436	.65
	.113	.26	.313	.53	.484	.78
	.137	.37	.386	.77		
KBr	.029	.11	.145	.27	.885	.77
	.047	.11	.188	.40		
	.090	.27	.421	.71		
KI	.070	.09	.246	.37	.601	1.03[a]
	.221	.32	.591	.97	.907	1.49

[a] These three values by the method of capillary rise. (Units of c are moles per liter; of $\Delta\gamma$, ergs per cm.^{2}. The surface tension of ammonia at −40.0° is 35.4 erg./cm.^{2}).

These data can be represented in the form

$$\Delta\gamma = Ac + Bc^2$$

The constants in this equation A and B, the standard error of estimate, σ, and the standard errors of the constants, σ_A and σ_B, for each of the four salts are listed in Table IV together with the sum of the ionic polarizabilities, $\Sigma\alpha$. The way this equation was fitted to the data by the method of least squares assigned equal weights to all the experimental points. Since the region of greatest interest at present is at the lowest concentrations where the theories mentioned above are expected to be most

TABLE IV

SALTS IN LIQUID AMMONIA, SUMMARY (CONSTANTS IN THE EXPRESSION $\Delta\gamma = Ac + Bc^2$ AND RELATED QUANTITIES)

Salt	NaCl	NaBr	KBr	KI
A	2.79	2.76	2.44	1.52
B	−5.96	−2.67	−1.79	+0.16
σ	0.03	0.07	0.04	0.03
σ_A	0.25	0.25	0.13	0.08
σ_B	1.28	0.64	0.17	0.11
$\Sigma\alpha$	3.22	4.48	5.22	7.44

satisfactory, it might have been more suitable to fit the data in the form $\Delta\gamma/c = A + Bc$, thereby weighting the points in proportion to $1/c.^2$ Unfortunately, the relative error at the lowest concentrations was very large, so the data would not have justified this treatment. In the absence of any better alternative, the coefficients A given in Table IV are assumed to be the correct low concentration limit of $\Delta\gamma/c$ for comparison with theory.

Discussion

Pure Liquids.—The values of the surface tension of ethanol reported by Tonomura and Ishahara[11] (capillary rise) at low temperatures tend to agree with those of Lalande[12] (du Nouy method) and of Ramsay and Shields as corrected by Sugden[13] near room temperature. They are 1.0 to 1.5 dynes per cm. above those of Jaeger[14] who used the maximum bubble method with a single tip as an absolute method. It appears probable that Jaeger's results are too low owing to certain difficulties in the method as he used it. The present results agree within about 0.1 dyne per cm. with those of Tonomura and Ishahara in the range −70 to −40° but appear to depart from them at higher and lower temperatures. On the other hand, the corrected values[15] of Morgan, et al., tend to support the present results at the higher temperatures. A fair estimate of the accuracy of these results is probably about ±0.2 dyne per cm. at least in the range −70 to −40°, so this accuracy is assumed for the data on liquid ammonia also. This may be compared to their precision as given above.

As an independent test of the results with ammonia, the parachor was calculated for four temperatures in the range of these measurements, using values of the surface tension taken from the least-squares curve, as well as three values measured by Berthoud[16] at higher temperatures. The densities used were taken from Cragoe and Harper[17] and Holst.[18] The parachor, essentially constant at 60.5 from 40° to about 0°, drops off to 60.0 at −70°, thus showing the expected decrease at low temperatures characteristic of hydrogen bonded liquids.[19]

The Solutions.—It was mentioned above that Kosakevich found that the order of the effects of various salts in a non-aqueous solvent was not usually the same as in water. This is true in liquid ammonia as indicated by the order at 0.1 mole per liter, KI < KBr, NaCl < NaBr, and at 0.2 mole per liter, KI, NaCl < KBr, NaBr. However, extrapolating to very low concentrations by means of the expression $\Delta\gamma = Ac + Bc^2$—that is, comparing the values of A—the order of decreasing polarizability KI < KBr < NaBr < NaCl is obtained.

(11) T. Tonomura and K. Ishahara, Bull. Chem. Soc. Japan, 9, 439 (1934).
(12) A. Lalande, J. chim. phys., 31, 583 (1934).
(13) S. Sugden, J. Chem. Soc., 125, 37 (1924).
(14) F. M. Jaeger, Z. anorg. allgem. Chem., 101, 1 (1917).
(15) Reference 5, Vol. IV, p. 449.
(16) A. Berthoud, J. chim. phys., 16, 429 (1918).
(17) C. S. Cragoe and D. R. Harper, Bur. Stand. Sci. Papers, 420, 313 (1921).
(18) "Landolt-Börnstein Tabellen," Fifth edition, IIw. I, p. 272.
(19) S. Glasstone, "Textbook of Physical Chemistry," Second edition, D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 527.

In Fig. 2 the values of A found for the four salts in ammonia are compared with the corresponding quantities in water. The vertical bars represent twice the standard errors of the separate A values estimated by the usual statistical method from the original data. As was predicted by both the Oka and the Onsager–Samaras theories, the value of A for each salt in ammonia lies above that found in water. The exact dependence on the reciprocal of the dielectric constant predicted by Oka's theory was not found but rather a weaker inverse dependence as is suggested by the form of the Onsager–Samaras limiting law. While no theory has yet been worked out to explain the slopes of the lines in Fig. 2, since the forces involving polarizabilities should depend inversely on the dielectric constant, the slope should be greater in ammonia than in water as was found.
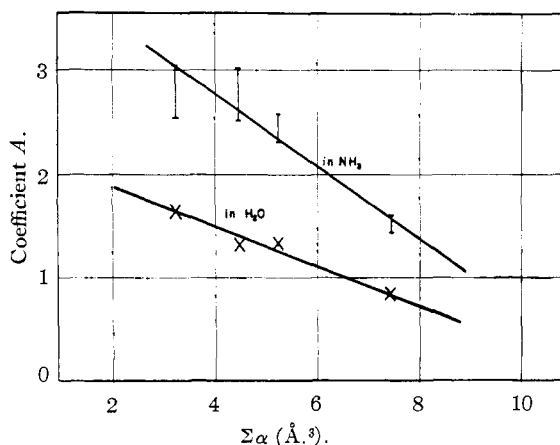

Fig. 2.—Alkali halide solutions: the coefficient A in $\Delta\gamma = Ac + Bc^2$ as a function of the sum of the ionic polarizabilities.

The surface tension values recorded in the "International Critical Tables" for aqueous solutions of these same four salts, when expressions of this type are fitted to them, yield values of B that are all zero within experimental error. Figure 3 shows a plot of the B coefficients in liquid ammonia against the inverse of the polarizability sum. As the vertical bars indicate, the linear relationship appears more nearly exact than the precision of the data would lead one to expect. There is at present no theoretical reason to expect this exact dependence. Following Oka,[1] who wrote

$$\Delta\gamma = Ac\alpha_d$$

where α_d is the degree of dissociation which he did not define precisely, it may be suggested that the B-coefficients are related to the Bjerrum ionic association which occurs with small ions and in media of low dielectric constant. In Bjerrum's the-
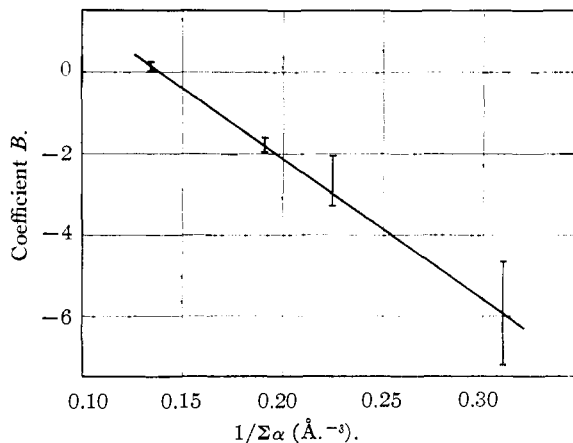

Fig. 3.—Alkali halide solutions in ammonia: the coefficient B in $\Delta\gamma = Ac + Bc^2$ as a function of the reciprocal of the sum of the ionic polarizabilities.

ory, as given by Harned and Owen,[20] one may write an equilibrium constant for dissociation.

$$K = \frac{C\alpha^2_d}{1 - \alpha_d}$$

whence

$$\alpha_d = \frac{-K + \sqrt{K^2 + 4Kc}}{2c}$$

$$= 1 - \frac{c}{K} + \dots$$

so that Oka's formula becomes

$$\Delta\gamma = Ac - \frac{A}{K} c^2 + \dots$$

so $-B$ is proportional to $1/K$. The constant K is determined by the distance of closest approach, a, and Bjerrum's

$$q = \frac{e^2 |Z_1 Z_2|}{2DkT}$$

K is small if $a < q$ and is very large if $a > q$. In water at 18° for a 1-1 electrolyte, $q = 3.52$ Å., while in ammonia at $-40°$, $q = 17.6$ Å. In water K should be large and hence B approximately zero for all the alkali halides except some of the fluorides[19]; in ammonia K should be small and B of appreciable magnitude for all the salts. Rough measurement of the surface tension of aqueous sodium fluoride solutions, subject to uncertainty owing to attack of the fluoride on the glass apparatus, suggests that B may be fairly large in this case. Quantitative evaluation of this suggestion requires independent measurements of K for the various salts in liquid ammonia, but at least qualitatively the facts are in agreement with it.

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(20) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Second edition, Reinhold Pub. Corp., New York, N. Y., 1950, p. 42 ff.