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Solubility of ammonia in water in the presence of atmospheric CO_2

By G. P. AYERS, R. W. GILLETT and E. R. CAESER, *CSIRO Division of Atmospheric Research, Private Bag No. 1, Mordialloc, Victoria, 3195, Australia*

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ABSTRACT

The equilibrium solubility of ammonia in water, in the presence of atmospheric CO_2, has been determined at room temperature over the aqueous phase concentration range 75–1200 micromolar. In contrast to a previous study, we find no evidence of a deviation from Henry's Law occasioned by the presence of atmospheric CO_2. We therefore conclude that the solubility of ammonia in cloud and rainwater should be adequately described by traditional solubility theory.

1. Introduction

The suggestion by Hales and Drewes (1979) that the presence of CO_2 in the system causes the solubility of ammonia to decrease from that predicted by Henry's Law has important implications for atmospheric processes that involve the dissolution of ammonia in aqueous solution. Examples are the scavenging of atmospheric ammonia by clouds and rain, and the reaction of ammonia with deliquesced aerosols. If the solubility of ammonia is as much as an order of magnitude less than expected on the basis of traditional Henry's Law theory, then attempts to model atmospheric processes using the traditional Henry's Law constant as an input parameter will be subject to significant error. For this reason we have carried out an independent determination of the solubility of ammonia in the presence of atmospheric CO_2

2. Experimental

The apparatus used is depicted schematically in Fig. 1. It consisted of a 200 litre polyethylene chamber and lid, the latter clamped in place on a 40 mm diameter neoprene O-ring to give a gas-tight seal. The chamber was partially filled with approximately 80 litres of aqueous solution for each series of experiments, leaving an air space of about 120 litres. A valve at the bottom of the chamber allowed air to be bubbled through the aqueous solution, to exit ultimately through a teflon swagelok fitting in the centre of the lid. Gas flow into the chamber was controlled by a precision flow controller (Brooks Instrument model 5841-1A2BQ) that was periodically checked against a laboratory "soap bubble" standard. As an added precaution a Brooks model 5810B1J2E5B flow transducer was connected periodically to the chamber outlet port to ensure that the inlet and outlet gas flows were equal. Room temperature and temperature of the solution-gas interface in the chamber were measured using IC temperature sensors (Bird, 1983) calibrated at ice point and the boiling point of water. To ensure homogeneity the aqueous phase was stirred continuously by means of a 75 mm magnetic spinbar. Analog signals from the temperature and flow transducers were recorded by a minicomputer via a 16 channel 12 bit A/D converter (Interactive Structures model AI13).

The aim of the experiment was to produce a close approximation to a sealed chamber in which ammonia added to the aqueous phase as ammonium chloride crystals would outgas into the gas phase until equilibrium was achieved. The equi-

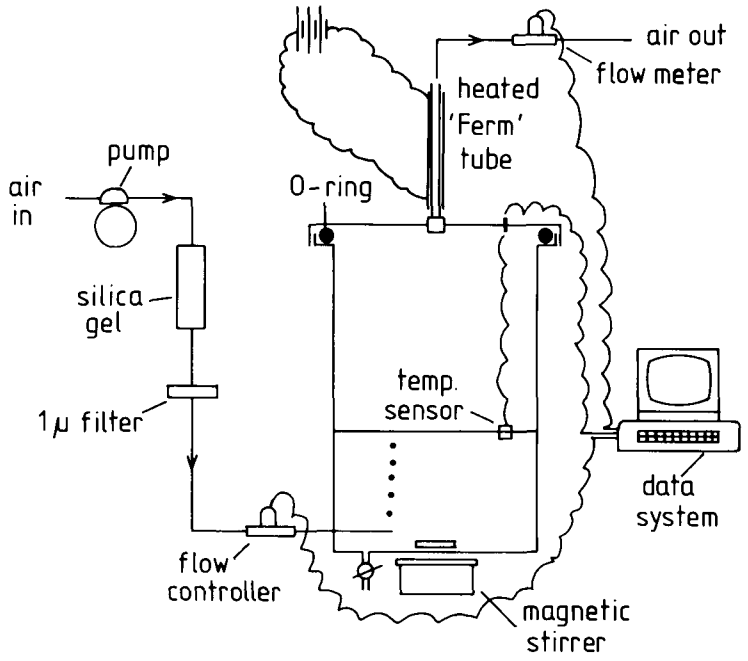

Fig. 1. Schematic representation of the apparatus used.

librium solubility of ammonia would then be specified by measurement of the aqueous dissolved ammonia concentration and the gas phase ammonia concentration. In practice, working with total ammonia plus ammonium concentrations in solution of as little as 75 micromolar meant that gas volumes exceeding 1000 litres were required to provide sufficient ammonia for detection by the only method available to us, the indophenol blue method (Dal-Pont et al., 1974). Thus the system was actually used dynamically, in the sense that a continual slow air bleed into the aqueous phase and exit of air through the lid enabled large volumes of air at equilibrium with the aqueous phase to be sampled. The bleed air in all cases was laboratory air filtered through a 1 micron Fluoropore filter and introduced to the chamber at 2 litres/minute. At this flow rate an average residence time of 60 minutes in the chamber resulted. Results from preliminary experiments carried out at 1 and 2 litres/minute indicated that this time was adequate for the gaseous and solution phases to reach equilibrium with respect to ammonia.

Ammonia was removed at the exit of the chamber during passage of the exhaust gas through a glass tube of 3 mm inside diameter and 50 cm length. The inside of the tube had been coated previously with a thin layer of oxalic acid, according to the method of Ferm (1979). To avoid condensation of water in the glass tube, a resistively-heated outer tube of aluminium was used to maintain the glass tube at 10 °C above ambient. At the end of each sampling period the glass "Ferm" tube was washed out in two halves, each with 5 ml of de-ionized water. In this way the first half of the tube gave a sample-plus-blank reading, the second half a blank-only reading, as suggested by Gras (1984). Periodically throughout each sampling run samples of the aqueous phase were taken and stored at 2 °C in polyethylene bottles. Subsequently these samples were analysed for pH and total dissolved ammonia content at the same time that the "Ferm" tube samples were analysed. For the latter analyses 1 cm cells and a wavelength of 630 nm were employed (Dal Pont et al., 1974).

Two series of experiments were performed. The first series commenced with an aqueous ammonium chloride concentration of approximately 600 μM. After 4 runs at this concentration the concentration of ammonium chloride was doubled and a further 5 runs made. The second series of experiments consisted of 4 runs at an aqueous

ammonium chloride concentration of approximately 75 μM followled by 4 runs at a concentration of about 180 μM and 6 runs at 415 μM.

To reduce the number of variables in the system the aqueous phase in all experiments was buffered to a pH of 7 by a weak Na_2HPO_4/NaH_2PO_4 buffer of 0.005 M/0.005 M concentration. This concentration provided ample buffer capacity to maintain the set pH over the complete range of dissolved ammonium concentrations but was sufficiently dilute that ionic strength effects did not have to be introduced into the equilibrium calculations.

Since the aim of these experiments was specifically to include atmospheric CO_2 in the system the aqueous phase was equilibrated with the atmosphere for two weeks prior to the commencement of each series of experiments. During this period the lid was raised from the chamber and the aqueous phase was continuously stirred. The initial quantity of ammonium chloride was then added to the solution and the lid was sealed onto the chamber 24 h prior to the commencement of the first run in each series. For this final 24 h period air was also bubbled through the aqueous phase at 2 litres/min.

3. Theory

A complete description of the appropriate solubility theory and values for all the necessary constants are given by Hales and Drewes (1979). The aim here is simply to compare the observed equilibrium gas phase concentrations of ammonia at each given aqueous phase concentration with those predicted by what Hales and Drewes call the "traditional theory" and their CO_2-modified theory. The easiest way of doing this is to do so in terms of the two quantities that are directly measured, the gas phase ammonia concentration and the total aqueous phase concentration of ammonia plus ammonium, $[NH_3 + NH_4^+)_{(aq)}$.

The appropriate equations are:

$$[NH_3]_g = \frac{x.\mathrm{Kw}}{\mathrm{H1}(\mathrm{K1}[H^+] + \mathrm{Kw})} \quad (1)$$

and

$$[NH_3]_g = \frac{x.\mathrm{Kw}(\mathrm{H1}.\mathrm{H2}.[CO_2].Q + 1)}{\mathrm{H1}(\mathrm{H2}.[CO_2].P.\mathrm{Kw} + \mathrm{K1}.[H^+] + \mathrm{Kw})} \quad (2)$$

where eq. (1) results from a combination of eqs. (4), (5) and (7) in Hales and Drewes (1979) and eq. (2) is a rearrangement of their eq. (38). Both equations give gas phase ammonia concentration in terms of x, the sum of aqueous ammonia and ammonium concentrations. H1 and H2 are the Henry's Law constants for ammonia and carbon dioxide, respectively, K1 is the ionization constant for aqueous ammonia, Kw is that for water, $[CO_2]$ in our experiments is the atmospheric CO_2 concentration and P and Q are empirical parameters specified by eqs. (40) and (41) in Hales and Drewes (1979). Note that eq. (2) reduces to eq. (1) if $[CO_2]$ goes to zero. Furthermore with $[CO_2]$ fixed at the atmospheric value (340 ppmv) and $[H^+]$ buffered to 10^{-7} M the ratio of the $[NH_3]_g$ values predicted by the two equations should remain invariant as x is varied.

Although the validity of the revised solubility theory developed by Hales and Drewes for cases involving CO_2 has no bearing on the fact that they experimentally observed an unexpectedly low solubility for ammonia, the existence of a valid theoretical interpretation of the experimental results would lend support to those results. However we are of the opinion that the revised theory is in fact thermodynamically untenable. If this is so, then the experimental results must stand alone. Our query is as follows: the reaction scheme proposed can be written as

$$NH_{3_{(g)}} + CO_{2_{(g)}} \overset{1.}{=} NH_{3_{(aq)}} + CO_{2_{(aq)}} \overset{2.}{=} NH_3.CO_{2_{(aq)}} \overset{3.}{=} NH_{3_{(g)}} + CO_{2_{(g)}} \quad (3)$$

the proposal made by Hales and Drewes being that only step 1 is at disequilibrium (this being the consequence of a fast forward reaction for step 3). Given that the other steps are at equilibrium the chemical potentials on each side of steps 2 and 3 must be equal. That is, with μ_i as chemical potential of species i.

$$(\mu NH_3 + \mu CO_2)_{(aq)} = (\mu NH_3.CO_2)_{aq} = (\mu NH_3 + \mu CO_2)_{(g)} \quad (4)$$

so

$$(\mu NH_3 + \mu CO_2)_{(aq)} = (\mu NH_3 + \mu CO_2)_{(g)} \quad (5)$$

However, the starting assumption was that step 1 is not at thermodynamic equilibrium, which requires that

$$(\mu NH_3 + \mu CO_2)_{(g)} \neq (\mu NH_3 + \mu CO_2)_{(aq)} \quad (6)$$

which contradicts the conclusion just reached (eq. (5)).

There is another aspect of the proposal that is less than satisfactory. If in fact step 1 is at disequilibrium with respect to ammonia, then the 1:1 coupling of the ammonia and carbon dioxide cycles in step 2 implies that CO_2 is also at disequilibrium to some extent in step 1. This possibility is not discussed by Hales and Drewes and is ignored in the development of the theory. Our conclusion is that the theory proposed is not valid.

4. Results

Results are summarized in Table 1 and Fig. 2. Note that in both the table and the figure the second series of measurements is shown with two experimental results for $[NH_3]_g$, an uncorrected and a corrected value. The correction stems from the fact that after the series of runs with x at 1200 μM the chamber exhibited a small blank when the aqueous phase was added for the second series of measurements. Three blank runs were made prior to the addition of ammonium chloride for the first run at $x = 75$ μM. These three blank runs (each had x measured at <0.1 μM) yielded ammonia gas concentrations of 0.19, 0.016 and 0.017 nM. The data is therefore presented as two extremes, the uncorrected values assume that the blank is zero, the corrected values assume a blank equal to the mean plus one standard deviation of the three measured blanks, or a gas phase ammonia concentration of 0.18 nM. No significant blank was evident in the first series of measurements.

As is evident from the table the overall quality of the data is determined mostly by uncertainty associated with the ammonia determinations. For x the standard deviations calculated for each run and the inter-run variability for any given set of runs suggest that x is uncertain to about 10%. The measured values of $[NH_3]_g$ are more uncertain, both because they were single measurements only and because there is uncertainty associated with analysis of both the sample end and blank end of

Table 1.

Run no.	Run time (min.)	Interface temperature (°C)	Flow rate (l/min.)	pH	x (μM)	$[NH_3]$ gas corr. (nM)	$[NH_3]$ gas uncorr. (nM)	$[NH_3]$ gas trad. (nM)	$[NH_3]$ gas modif. (nM)
3	185	21.8 (0.1)	1.93 (0.03)	6.96 (0.01)	627 (82)		1.43	1.24	19.3
4	185	22.5 (0.3)	1.93 (0.03)	6.95 (0.01)	595 (45)		2.62	1.24	18.8
5	155	20.4 (0.0)	1.93 (0.03)	6.97 (0.01)	648 (13)		1.11	1.12	18.6
6	165	20.6 (0.1)	1.93 (0.02)	6.97 (0.01)	658 (8)		1.32	1.17	19.1
7	60	21.0 (0.0)	1.89 (0.02)	6.96 (0.00)	1186 (42)		1.87	2.12	34.8
8	61	21.0 (0.0)	1.91 (0.08)	6.96 (0.00)	1160 (28)		1.86	2.10	34.2
9	60	21.1 (0.0)	1.89 (0.02)	6.96 (0.00)	1237 (10)		2.21	2.26	36.7
10	78	21.2 (0.1)	1.90 (0.02)	6.96 (0.00)	1173 (4)		2.41	2.20	35.2
11	60	21.5 (0.1)	1.90 (0.03)	6.97 (0.01)	1160 (9)		2.82	2.25	35.2
22	321	23.2 (0.5)	1.92 (0.03)	7.00 (0.00)	77 (30)	0.06	0.24	0.19	2.5
23	301	23.6 (0.3)	1.94 (0.01)	6.96 (0.00)	77 (4)	0.10	0.28	0.18	2.6
24	304	23.6 (0.5)	1.93 (0.02)	6.96 (0.00)	78 (15)	0.14	0.32	0.19	2.6
25	315	23.0 (0.5)	1.94 (0.03)	6.97 (0.01)	90 (2)	0.22	0.40	0.23	3.0
26	136	24.4 (0.1)	1.92 (0.02)	6.96 (0.00)	186 (4)	0.52	0.69	0.49	6.3
27	79	24.9 (0.1)	1.92 (0.01)	6.96 (0.00)	205 (21)	0.63	0.81	0.57	7.1
28	120	25.3 (0.1)	1.94 (0.01)	6.97 (0.01)	168 (25)	0.40	0.58	0.49	5.9
29	143	25.8 (0.1)	1.94 (0.00)	6.97 (0.00)	178 (11)	0.37	0.55	0.56	6.4
30	105	25.4 (0.1)	1.91 (0.01)	6.97 (0.01)	407 (3)	1.66	1.84	1.21	14.4
31	90	25.5 (0.1)	1.93 (0.01)	6.98 (0.01)	417 (56)	1.54	1.72	1.28	14.8
32	91	25.7 (0.1)	1.94 (0.01)	6.98 (0.01)	421 (41)	2.30	2.48	1.32	15.1
33	96	25.8 (0.1)	1.92 (0.01)	6.98 (0.01)	415 (32)	0.44	0.62	1.14	14.9
34	97	25.6 (0.2)	1.92 (0.01)	6.98 (0.01)	415 (32)	0.99	1.17	1.29	14.8
35	98	25.4 (0.1)	1.92 (0.01)	6.98 (0.00)	415 (32)	1.44	1.62	1.25	14.7

Values in parentheses are standard deviations: temperature and flow were measured at 5 minute intervals; pH and x were determined from several aliquots of the aqueous phase taken at intervals during each run.

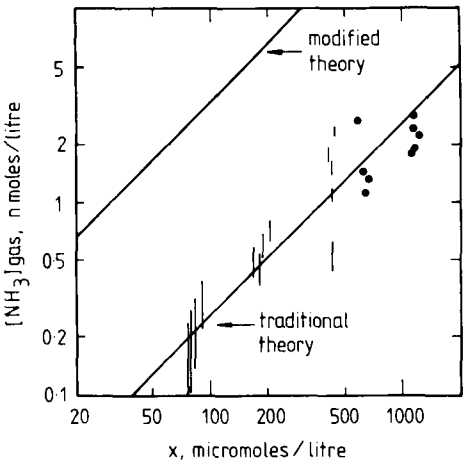

Fig. 2. Plot of measured $[NH_3]_g$ versus measured x, the concentration of aqueous phase ammonia plus ammonium. Results from the second series of measurements are indicated by short vertical lines spanning the range between the corrected and uncorrected values (see text). The two solid lines give the relationship predicted by eq. (1) (traditional theory) and eq. (2) (modified theory according to Hales and Drewes, 1979) for a pH of 7.00 and temperature of 23.4 °C (mean temperature from all runs).

the Ferm tube. Uncertainty in $[NH_3]_g$ is thus probably about 30%. This level of uncertainty in both x and $[NH_3]_g$ is reflected in the scatter shown by the data in Fig. 2 (a small contribution to the scatter also comes from the fact that slight temperature variations occurred between runs: in the context of this paper these were not worth attempting to correct for theoretically).

Nevertheless, even with the added uncertainty allowed in the second series of results the table and figure give no room for doubt that the traditional theory is correct, even though atmospheric CO_2 was present in the system. We therefore conclude that no modification to the traditional theory is necessary, as had been proposed by Hales and Drewes (1979).

5. Further discussion

In view of the importance of unequivocally resolving this whole question it is worth making some final, detailed comments concerning the assumption of complete interphase CO_2 equilibrium that underlies the modified-theory calculations presented here. In the absence of direct experimentsl evidence it could possibly be argued that despite our two week equilibrium procedure CO_2 equilibrium may not have been attained, with the consequence that our results are biased towards the "traditional" line in Fig. 2 because $CO_{2(aq)}$ was at lower than the expected equilibrium concentration. However there are three arguments against such a criticism.

First, we can write the steps involved in CO_2 equilibration as

$$CO_{2(g)} \overset{1.}{\rightleftharpoons} CO_{2(aq)} + H_2O \overset{2.}{\rightleftharpoons} H^+ + HCO_3^- \overset{3.}{\rightleftharpoons} 2H^+ + CO_3^{2-} \quad (7)$$

While it is true that achievement of the overall equilibrium is slow for CO_2, compared for example with NH_3, our understanding is that under our conditions step 2, not step 1, is the rate-limiting step (Bolin, 1960; Hague, 1971). Thus even if steps 2 and 3 had not achieved equilibrium with respect to $CO_{2(g)}$ at 340 ppmv during the two week equilibration procedure we still expect step 1 to have approached equilibrium relatively quickly. In turn this implies that the concentration of $CO_{2(aq)}$ would have adequately reflected equilibrium with the $CO_{2(g)}$ gas concentration of 340 ppmv. Note also that the assumption of a fixed 340 ppmv itself adds negligible uncertainty, since this value is the current background value at Aspendale (Pearman and Beardsmore, 1984), where past experience shows daily deviations from the background value to seldom exceed 10 ppmv (Garratt and Pearman, 1973).

Second, our experimental design was such that within either series of experiments successive runs were carried out on the same aqueous sample. Were CO_2 equilibrium still being achieved slowly during successive runs as more air was bubbled through the aqueous phase then, if the modified theory were valid, we should have seen a consistent trend: each successive point should have moved closer to the modified-theory line in Fig. 2 as successive runs passed more and more CO_2 through the aqueous phase. No such trend is evident in the data.

Third, even if step 1 in eq. (7) were the slow step and steps 2 and 3 were fast common experience tells us that some significant amounts of CO_2

should have entered the aqueous phase during the 2 week equilibration period and the 24 h period of bubbling prior to each series of runs (in the 24 h approximately 3000 litres of air was bubbled through the aqueous phase, while the amount of CO_2 necessary for complete equilibrium is contained in only a few hundred litres of air). Any significant levels of $CO_{2(aq)}$ at all should have placed our experimental points in Fig. 2 between the two theoretical lines, rather than exactly along the traditional line, if CO_2 had any effect. To illustrate this point further we can use equilibria 2 and 3 (eq. (7)) to calculate $CO_{2(aq)}$ at pH 7 for cases when total dissolved carbon is only at some fraction of that expected at equilibrium with $CO_{2(g)}$ of 340 ppmv. Use of these calculated $CO_{2(aq)}$ values in the modified theory leads to the set of curves shown in Fig. 3. Clearly even had our long equilibrium procedure only taken dissolved carbon to 1% of the expected value, a noticeable effect should have been evident on our experimental results if the modified theory were valid. Since this was not the case, and we do not believe that our equilibration procedure was so inefficient as to not even bring dissolved carbon to 1% of the expected value, there is no possibility that the modified theory is correct.

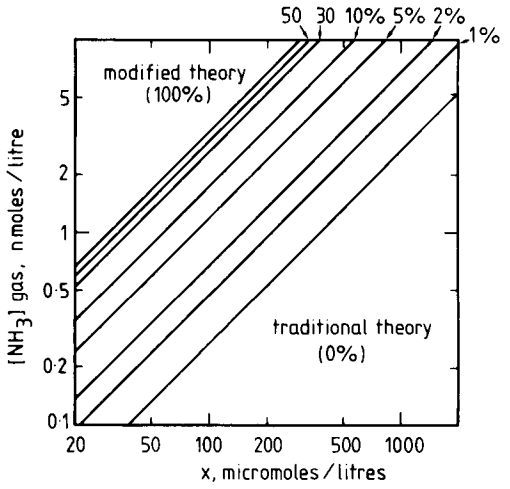

Fig. 3. Predictions according to the modified theory for cases in which the total dissolved carbon ($CO_{2(aq)}$ + bicarbonate + carbonate) is less than the equilibrium value (taken as 100%) for $CO_{2(g)}$ at 340 ppmv. Temperature and pH as for Fig. 2.

6. Conclusion

An experimental reinvestigation of the equilibrium solubility of ammonia in the presence of CO_2 has shown no evidence for a deviation from the traditional Henry's Law equilibrium over a solution concentration range (ammonia plus ammonium) of 75–1200 μM. There also appears to be no valid thermodynamic basis for a theory proposed in support of the existence of a deviation brought about by the presence of CO_2. Therefore the traditional value of Henry's Law constant (which was accurately determined by Hales and Drewes, 1979) is appropriate for use in calculations on the scavenging of atmospheric ammonia by deliquesced aerosols, cloud droplets or rain drops.

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