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Solubility of ammonia in rainwater

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ABSTRACT

Partitioning of ammonia between the gaseous and rainwater phases has been investigated at the Australian Baseline Air Pollution Station during in-situ experiments in which rainwater and ammonia gas were sampled concurrently. The relationship between ammonia concentrations in the gaseous and aqueous phases did not follow either traditional solubility theory based on Henry's Law, or a recent modified theory that includes secondary equilibria between dissolved ammonia and carbon dioxide.

1. Introduction

A knowledge of the relevant solubility and acid-base equilibria has been used on a number of occasions to predict the equilibrium relationship between the concentration of atmospheric ammonia gas and the concentration of aqueous ammonia in soils (Dawson, 1977), deliquesced aerosols (Tang, 1980), oceanic surface water (Georgii and Gravenhorst, 1977) and rainwater (Bowersox and De Pena, 1980). Unfortunately, a lack of experimental data in each case has prevented quantitative testing of the predictions. However in the case of rainwater, Junge (1963) and Lau and Charlson (1977) reached the general conclusion that observed concentrations of ammonia in rainwater are as much as 3 orders of magnitude lower than would be predicted on the basis of Henry's Law and atmospheric ammonia gas concentrations of order 1 ppbv.

This point was taken up by Hales and Drewes (1979) who carefully measured the solubility of ammonia in aqueous solutions at atmospheric gas concentrations, the previous solubility studies having been performed at much higher concentrations. Their conclusions were that the traditional value of the Henry's Law constant for ammonia was not significantly in error, but that the partitioning of ammonia between the gaseous and aqueous phases was perturbed by a secondary equilibrium involving carbon dioxide. For typical atmospheric conditions and ~1 ppbv of gaseous ammonia, the modified solubility equilibria proposed by Hales and Drewes (1979) predicts the solubility of ammonia to be about an order of magnitude lower than that predicted by the traditional application of Henry's Law.

While the work of Hales and Drewes (1979) goes some way towards explaining the discrepancies inferred by Junge (1963) and Lau and Charlson (1977), it does not fully account for the apparent discrepancies of as much as 3 orders of magnitude. For this reason, we have carried out in-situ measurements in which we attempted to repeat the laboratory studies of Hales and Drewes (1979), but using the natural atmosphere as the laboratory. Our aim was to attempt concurrent gas and rainwater collections, which at worst would provide a check on the validity of the inferences made by Junge (1963) and Lau and Charlson (1970) on the basis of gaseous and rainwater ammonia concentrations measured at different times. At best it was hoped that the solubility of ammonia in rainwater would be specified under atmospheric conditions, conditions in which the work of Hales and Drewes (1979) suggested that ammonia solubility did not follow Henry's Law.

The experiments were carried out in June 1981 at the Australian Baseline Air Pollution Station located at Cape Grim (40°42′S, 144°41′E) on the northwestern tip of the island of Tasmania. This station frequently experiences the west to south-

westerly winds of the "roaring forties" that often have had no contact with land for several thousands of km of travel.

Each experiment involved concurrent collection of rainwater in a large polyethylene beaker and collection of ammonia gas essentially following the method of Ferm (1979), modified to allow for blank correction as described by Gras (1984). Sampling times for ammonia gas were usually 10–12 h, while rainfall occurred for periods of from one to several hours during each of these gas collection periods. The concentration of ammonia in the rainwater and the mass of ammonia collected in the gas sampling tubes were determined immediately upon completion of sampling, using the indophenol-blue method (Dal Pont et al., 1974). Estimated uncertainty in the determinations was ±20%. A combination glass electrode was used to measure rainwater pH to an accuracy of ±0.02 pH units. A total of 16 concurrent collections were performed, as detailed in Table 1.

2. Discussion

A possible criticism of this work and that of Junge (1963) and Lau and Charlson (1977) stems from the assumption that the data actually represent gas/aqueous-phase equilibrium of ammonia under atmospheric conditions. In none of these cases has there been an independent means of demonstrating that such was the case. The assumption has usually been justified by physical arguments, but it remains the major uncertainty in all work to date. For this reason two pertinant questions can be asked of our data.

The first is: to what extent were the 10–12 h gas samples representative of the gas concentrations during rainfall events that lasted for only 10–50% of the gas sampling period? Cape Grim was chosen as the site for this work largely on the basis that previous work showed ammonia gas concentrations and air temperature to be stable for lengthy periods. Maritime air masses in particular yielded a mean ammonia gas concentration of ~0.07 ppbv which, to the accuracy available for such low-level measurements (±40% for an individual measurement), was stable from the shortest time scales used (3 h), up to seasonal time scales (Ayers and Gras, 1979; 1983). On this basis, it seemed reasonable to assume that during these maritime, or baseline, air mass conditions, the concentration of ammonia deduced from 10–12 h samples would to an accept-

Table 1. *Summary of results; T = 11 °C*

Date	Time (GMT)	Air mass[a] category	pH	Ammonia concentration			
				Gas phase (ppbv)	Rainwater (μmol dm^{-3})	Predicted[b] (μmol dm^{-3})	Predicted[c] (μmol dm^{-3})
8	1100	C	6.64	0.58	2.5	91	4.0
9	1100	C	6.72	0.77	7.9	100	4.6
10	0000	C	5.89	0.092	7.7	81	3.0
12	1000	B	6.88	0.059	2.8	6.5	0.31
13	0100	B	7.08	0.11	2.1	6.1	0.35
13	1200	MB	5.60	0.16	4.3	277	10
14	0100	MB	5.83	0.11	3.6	116	4.3
14	1000	MB	5.89	0.067	2.1	59	2.2
15	0200	B	6.61	0.055	1.1	9.2	0.40
15	1200	MB	6.56	0.030	4.8	5.8	0.25
16	1200	C	6.38	0.039	17	11	0.45
17	0100	C	6.55	0.11	11	21	0.90
18	1200	MB	6.11	0.17	11	88	3.4
19	1100	MB	6.35	0.073	0.77	25	0.90
19	2300	MB	5.83	0.14	1.4	144	5.3
21	2300	C	5.99	0.49	16	346	13

[a] Continental, baseline or modified baseline. For definitions see text.
[b] Based on traditional solubility theory (Henry's Law).
[c] Based on the modified solubility theory of Hales and Drewes (1979).

able degree, be representative of the gas concentration over shorter time scales.

It may seem surprising that gaseous ammonia concentrations do not show wide variability in response to precipitation scavenging. However at Cape Grim, rainfall is frequent, but consists mostly of light rain and drizzle so that sub-cloud scavenging of ammonia should generally be slight and not cause substantial, sharp reductions in ammonia concentration. Furthermore, the pH of rain at Cape Grim is reasonably high, in the range 5.5 to 7.0, so presumably relatively little ammonia actually need be scavenged to produce equilibrium. Indeed an idealized calculation by Ayers (1982) for cloudwater at Cape Grim suggests that a significant fraction of the aqueous-phase ammonia required for equilibrium can sometimes be provided by the aerosol on which the cloud droplets form. Thus the absence of wide variability in ammonia gas concentrations at Cape Grim seems quite plausible even when aqueous-phase scavenging is considered.

There is some objective evidence to support these comments. It comes from a tipping-bucket rain gauge (Rimco, 0.2 mm resolution) that has been in operation at Cape Grim for some years. Despite intermittent gaps in the records due to malfunctions of the data logger, it was possible to obtain some rainfall data for all but the first of the periods described by Ayers and Gras (1983) in which ammonia was measured at Cape Grim. About 80 individual ammonia gas determinations, made during baseline conditions, are covered by this data. The ammonia data were stratified in two ways, first according to the total amount of precipitation recorded during each ammonia measurement, and second according to the fraction of each ammonia sampling period during which rain fell. The latter was based on the fraction of total 10 min data logger integration periods per ammonia sample in which at least 0.2 mm of rain was recorded. Mean ammonia concentrations for each category are shown in Table 2. There is no convincing evidence that scavenging of ammonia increases either with increase in total precipitation or with increase in fraction of ammonia sampling time during which rain fell.

The second question to be asked of our data is whether raindrops falling at Cape Grim would have sufficient fall-time to achieve equilibrium with sub-cloud ammonia. During the experimental period in June 1981, daily aircraft ascents showed cloud base to be at an altitude of $\sim$ 1000 m. For drizzle droplets and light rain droplets, fall speeds of order 1–5 m s^{-1} imply fall times of order 1000–200 s. For the droplet sizes concerned, radius $\leqslant$ 0.5 mm, these times should be adequate for a close approach to gas-liquid equilibrium with respect to ammonia (Hales, 1972).

In Table 2, the observed concentrations of dissolved ammonia are compared with the concentrations calculated on the basis of the traditional Henry's Law theory, and the modified theory of Hales and Drewes (1979). A detailed description of the calculations and values for the necessary equilibrium constants can be found in Hales and Drewes (1979). Input to the calculations were the observed rainwater pH, gas phase ammonia concentration and air temperature. The latter was taken as 11 °C, since the range during measurements was only 11 $\pm$ 3 °C: in the absence of any direct knowledge, we assume that ambient air temperature is a reasonable approximation to droplet temperature. The modified theory also required as input the ambient CO_2 gas concentration: a value of 338 ppm, accurate to better than

Table 2. *Mean ammonia concentration and standard deviation during baseline conditions*

Rainfall (mm)	Number in category	Mean NH_3 (ppbv)	σ (ppbv)	Time fraction (%)	Number in category	Mean NH_3 (ppbv)	σ (ppbv)
0	43	0.07	0.04	0	43	0.07	0.04
0.2–0.8	14	0.07	0.03	0.1–10.0	18	0.06	0.02
1.0–2.8	10	0.06	0.01	10.1–20.0	7	0.08	0.05
3.0–4.8	7	0.09	0.03	20.1–50.0	7	0.1	0.03
5.0–19.8	5	0.09	0.03				

Data stratified according to total rainfall during gas measurement, and according to fraction of gas sampling time during which rain fell.

1%, was obtained from Baseline Station records (Pearman, 1983). The ratio of calculated to observed rainwater ammonia concentration is given the symbol R and is plotted against observed rainwater pH in Figs. 1 and 2.

In the tables and figures, each set of data is classified according to wind direction, θ, and Aitken particle concentration, N, as either baseline ($180° < \theta < 280°$, $N \leqslant 300$ cm^{-3}), modified baseline ($180° < \theta < 310°$, $N \leqslant 600$ cm^{-3}) or continental ($310° < \theta < 180°$, $N > 600$ cm^{-3}). The first category corresponds to the criteria for purely maritime air at Cape Grim discussed by Ayers and Gras (1983). The second category uses slightly less stringent criteria, but still excludes air masses that have traversed directly over Tasmania or have

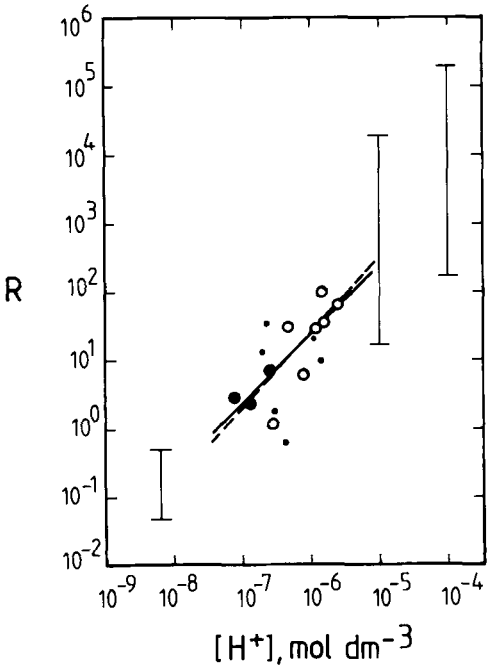

Fig. 1. Ratio of calculated to observed aqueous ammonia concentration as a function of hydrogen ion concentration, derived using traditional theory. Cape Grim in-situ data are represented by individual points: the large closed circles, large open circles and small dots represent data obtained in baseline, modified baseline and continental air masses, respectively. Rainwater data from Sydney are represented by the ranges shown at pH 4 and 5; that at pH 8.2 is derived from Cape Grim seawater data. The solid and broken lines drawn through the in-situ data points correspond respectively to eqs. (10) and (11).

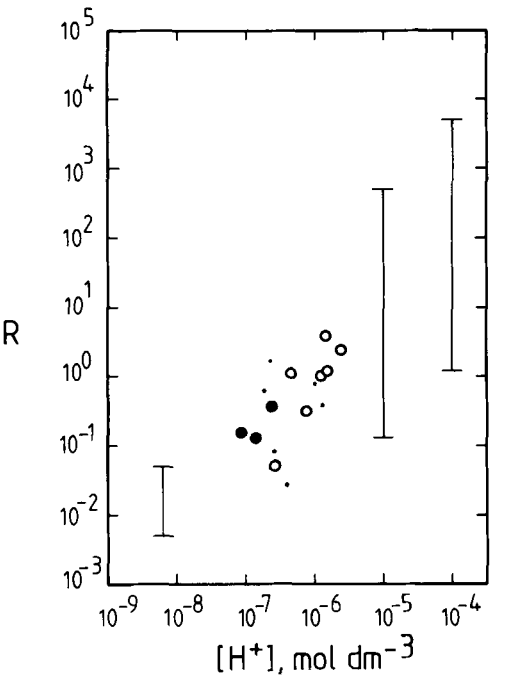

Fig. 2. As for Fig. 1, except that the calculations were performed using the modified solubility theory of Hales and Drewes (1979).

obvious continental influence, as judged by particle concentration. We believe that these categories together reflect maritime air masses to which the earlier comments regarding stability of ammonia concentration and lack of variation due to scavenging are relevant. The third category corresponds to air masses that have had recent passage over Tasmania or the Australian mainland to the north. In these cases, ammonia concentrations can exceed 1 ppbv and particle concentrations 10,000 cm^{-3}.

In Figs. 1 and 2 the data points classified as continental exhibit no clearcut trend. However the data classified into the two baseline categories show a distinct dependence on hydrogen ion concentration for both solubility theories. For each theory, agreement between observation and theory ($R = 1$) appears to exist at only one value of pH: below that value, the calculated ammonia concentration exceeds the observed concentration; above that value the reverse is true. It is apparent that the slopes of the trends in Figs. 1 and 2 are not very different, so the major effect of the modified solubility theory is to shift the pH at which agree-

ment occurs from about 7 for the traditional theory to about 6 for the modified theory.

While the observed pH range of 5.6 to 7 is typical for unpolluted maritime rain at southern mid-latitudes, it is far short of the pH range (3 to 8) that can be found in the atmosphere. Apart from the question as to the generality of the Cape Grim observations over a wide pH range, there is also the question of comparability of the present results with the inferences drawn by otheres, for example Lau and Charlson (1977), based on rainwater and gas observations that were not concurrent. Two sets of observations are available to us that enable these questions to be addressed. These two additional data sets are of lower accuracy than the Cape Grim data, but nevertheless are useful for the present discussion.

The first set of data was obtained from 294 rainwater samples collected in the city of Sydney (33°52′S, 155°12′E) between November 1980 and March 1981. The volume-weighted mean pH was 4.44, range 4.0–5.0, the volume-weighted mean ammonia concentration 18.6 μmol dm^{-3}, range 2.0–40 μmol dm^{-3} and the estimated mean temperature during rainfall was 20 $\pm$ 5 °C (based on meteorological records from Sydney Airport). Although the concentrations of ammonia gas and CO_2 were not determined concurrently with the rainwater collections, gas measurements performed routinely at other times over the past three years suggest that ammonia concentrations generally lie within the range 0.5–10 ppbv. CO_2 concentrations can be expected to lie within the range 335–400 ppmv (G. Pearman, personal communication). Calculations performed using the extreme values for each variable gave the range of R values depicted graphically at pH 4 and 5 in Figs. 1 and 2. In both figures, the additional data at lower pH lends some support to the pH dependence shown by the Cape Grim data and suggests that the inferences drawn from non-current data are consistent with those drawn on the basis of our concurrent ammonia measurements.

The second additional set of data results from the earlier series of ammonia gas measurements made during baseline conditions at Cape Grim (Ayers and Gras, 1980, 1983). Ammonia gas concentrations were found to be relatively stable, averaging 0.073 ppbv in measurements made between February 1978 and May 1980. If this concentration represents a lower bound determined mainly by equilibrium with the oceanic surface, then we can use the mean observed surface water pH of 8.2, CO_2 concentration of 338 ppm and mean surface temperature of 13 °C to predict dissolved ammonia concentrations in the surface waters. Comparison of predicted values with extremes in surface water concentration of 0.5–5 μmol dm^{-3}, observed by us at Cape Grim between February 1978 and May 1980, gives the range of R values shown at pH 8.2 in Figs. 1 and 2. Note that corrections for the ionic strength of seawater were incorporated in these calculations (Millero, 1979, 1981). Once again the additional data give general support for the trend exhibited by the in-situ Cape Grim data, since in both Figs. 1 and Fig. 2, the range of R at pH 8.2 lies well below $R = 1$.

For the rainwater data, two possible reasons for the deviation from Henry's Law are that Henry's Law is not followed under atmospheric conditions, as was suggested by Hales and Drewes (1979) but not completely explained, or that the scavenging of ammonia by cloud and rain was less efficient than expected. Neither possibility can be confirmed or rejected using the present data. However, the slope evident in Fig. 1 is interesting in that it is close to unity. Using the subscript g and aq to refer to the gaseous and aqueous-phase concentrations of ammonia, we can define H_e, the effective Henry's Law constant during our experiments at Cape Grim as

$$H_e = \frac{[NH_{3(aq)}]}{[NH_{3(g)}]}. \tag{1}$$

If scavenging of ammonia were limited in some way so that the ammonia content in rain was restricted to a constant fraction of that in the gas phase, then we could write

$$A[NH_{3(g)}] = [NH_4^+] + [NH_{3(aq)}], \tag{2}$$

where A is the constant of proportionality. For pH less than about 7.5, to a very good approximation $[NH_{3(g)}]$ can be ignored, in (2) so

$$A[NH_{3(g)}] = [NH_4^+]. \tag{3}$$

Using eqs. (4) and (6) from Hales and Drewes (1979), the dissociation constant for ammonia, K_1, can be written as

$$K_1 = \frac{[NH_4^+]\,K_w}{[NH_{3(aq)}]\,[H^+]}, \tag{4}$$

where K_w is the dissociation constant for water. Combining (3) and (4) gives

$$K_1 = \frac{A[NH_{3(g)}]\,K_w}{[NH_{3(aq)}]\,[H^+]}, \quad (5)$$

which, combined with (1) and rearranged yields

$$H_e = \frac{AK_w}{K_1\,[H^+]}. \quad (6)$$

Now the ratio R plotted against $[H^+]$ in Fig. 1 can be written as

$$R = \frac{H_1}{H_e} \quad (7)$$

where H_1 is the traditional Henry's Law constant. Thus from (6) and (7)

$$R = \frac{H_1K_1\,[H^+]}{A\,K_w}, \quad (8)$$

or

$$\log_{10}R = \log_{10}\left(\frac{H_1K_1}{A\,K_w}\right) + \log_{10}[H^+]. \quad (9)$$

Using (3), values of A can be estimated from the data in Table 1. The 10 data sets in the baseline categories give a geometric mean value of 6.9×10^5 (molar units used), which, when combined with values of H_1, K_1 and K_w for 11 °C in (9) gives

$$\log_{10}R = 7.38 + \log_{10}[H^+]. \quad (10)$$

This line is shown in Fig. 1, and can be seen to reproduce the trend in the data very well. Indeed to within the calculated uncertainties, (10) is identical with the equation

$$\log_{10}R = 7.95 + 1.09\log_{10}[H^+], \quad (11)$$

obtained directly from the 10 points in Fig. 1 by linear regression (standard errors for slope and intercept were 0.26 and 1.61; the correlation coefficient was −0.83). Clearly one could speculate that the observed trend in the data need not be due to some perturbation to Henry's Law in the presence of atmospheric CO_2, but could arise if scavenging processes were unable to increase dissolved ammonia concentrations in proportion with increases in rainwater acidity.

3. Conclusions

Perhaps the most important conclusion to be drawn from this work is that the apparent lack of equilibrium between gaseous and rainwater ammonia concentrations inferred from gas and rainwater observations made at different times is no artifact. Although the data presented here are limited, and certainly need to be verified elsewhere, they result from essentially concurrent observations and give a clear indication that the partitioning of atmospheric ammonia between the gas and rainwater phases did not occur simply according to a Henry's Law equilibrium.

This apparent dis-equilibrium could not be explained using the modified solubility theory of Hales and Drewes (1979), except near pH 6. On the other hand, the general hydrogen ion dependence shown by the data could be reproduced if it were arbitrarily assumed that scavenging processes always produced a constant ratio of total dissolved ammonia to gas-phase ammonia, irrespective of rainwater pH.

Therefore, this work emphasises that two areas of uncertainty remain if gaseous and rainwater concentrations of ammonia are to be reconciled. The first is the question mark that still remains over the appropriate value of the Henry's Law constant for ammonia under atmospheric conditions (Hales and Drewes, 1979). The second concerns the fact that there are still no data, including those presented here, for which it can be demonstrated independently rather than by inference, that the scavenging processes, usually assumed to be operative for ammonia, had actually brought the gas and aquesous phases to equilibrium at the observed pH. Both areas of uncertainty will have to be tackled before the question of ammonia solubility in rainwater can be laid to rest.

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