Influence of pH and Ionic Strength upon Solubility of NO in Aqueous Solution

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The solubility of NO(g) in aqueous salt solutions is determined as a function of pH (0–13). Although slight differences in solubility exist for different salt solutions, one can account for the results by comparing the activity coefficients of the salts involved. In general, the solubility of NO decreases with increasing ionic strength. At a particular ionic strength, the solubility of NO is constant in the pH region 2–13. Variations in the solubility are obtained at low pH (<2) by use of HCl and $HClO_4$.

Interest in chemistry of nitric oxide has increased over the last few years, driven by the current excitement in air pollution and in biochemistry. Research into metal nitrosyls and the modes of nitrosyl bonding in metal and organometallic systems has also grown with the increased use of NO as a direct agent for nitrosylating metal centers (*1, 2, 5, 8, 12*). We became concerned with the solubility of NO as a function of electrolyte concentration in connection with our recent studies involving NO reactions with metal-ammines to produce dinitrogen complexes (*13*).

Although several reports on the solubility of NO in water (*6, 15*) and in H_2SO_4 (*15a*) solutions appear, only an occasional reference to its solubility as a function of electrolyte in more convenient concentration ranges appears in the literature (*8*). In addition, incomplete studies appear regarding its solubility over day-to-day variations in atmospheric pressure and over a broad pH region (*3, 14*). The latter question is of significant chemical interest, since one might expect the solubility of NO to vary with pH if NO takes on any acidic or basic character (e.g., H_2NO_2, HNO_2^-, or HNO^+). We wish to report the solubility of NO as a function of the ionic strength, the character and concentration of the electrolyte, pH (0–13), and the day-to-day variation in atmospheric pressure.

Experimental

Nitric oxide (Matheson Gas Products) was vigorously scrubbed to remove NO_2. The all-glass system was previously purged with Cr^{2+} scrubbed argon. The gas flow could be switched rapidly to NO, by rotation of a three-way stopcock. The NO had been previously scrubbed through towers of molecular sieve (at −78°C), solid KOH, and 5*M* NaOH. All gases were passed through a final, common scrubber of 0.1*M* NaCl (*14*). In general, the desired buffer solution was degassed in a 25-ml flask (fitted with a serum cap) by use of a gas-dispersion tube.

Reproducible solubility results were obtained after at least 30 min of NO saturation. The reaction flask and the last scrubbing tower were immersed in a constant temperature bath maintained at 25.0° ± 0.1°. An all-glass syringe, fitted with a platinum needle, was flushed with argon and inserted through the serum cup. After flushing the needle several times first with NO(g) and then with the buffer solution, 5.0 ml of the buffer solution was withdrawn and injected into ~80 ml of oxygen-saturated water, with vigorous stirring. Similar results were obtained with smaller aliquots of the buffer solution or larger volumes of oxygen saturated water. In addition, the results remain unchanged when the initial pH of the oxygen-saturated water was varied from pH = 12 to 1.

The product solution was quantitatively transferred to a 100-ml volumetric flask and analyzed spectrophotometrically for NO_2^-. Nitric oxide is oxidized rapidly and quantitatively (*14*) to HNO_2 in solutions containing excess dissolved oxygen. The NO_2^- arises from the following reactions (*7, 17*):

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2$$

$$NO_2 + NO \rightarrow N_2O_3$$

$$N_2O_3 + H_2O \rightarrow 2HNO_2$$

The method of analysis involved the reaction of the NO_2^- produced with sulfanilamide and *N*-(1-naphtyl)-ethylenediamine hydrochloride (*16*). The absorbance at 540 nm (λ max) was recorded on a Cary 16 spectrophotometer ($\epsilon = 5.32 \times 10^4\ M^{-1}\ cm^{-1}$) (*3, 16*). An additional method of analysis was used to serve as a check on the above method. A solution of $10^{-3}M$ $HClO_4$ was degassed directly in a 5-cm cell with argon and then NO (by means of a Pt-needle). A slight excess of Cr^{2+} ($\sim 2 \times 10^{-3}M$) was injected into the cell and the absorbance at 450 nm recorded. One mole of Cr^{2+} reacts per mole of NO to produce $CrNO^{2+}$ (λ max 450, $\epsilon = 121\ M^{-1}\ cm^{-1}$) quantitatively (*1*). The result obtained was identical to that anticipated from the solubility measurements obtained according to the NO_2^- method of analysis.

All solutions were made from reagent-grade materials. Distilled water was redistilled from alkaline-permanganante. $LiClO_4$ and $NaClO_4$ were prepared by addition of $HClO_4$ to the corresponding carbonates. The solution was then concentrated by boiling, and the respective solids were obtained upon cooling the solution in an ice bath (*1*). LiCl was recrystallized by dissolution of the reagent-grade material in a minimum of hot water, followed by filtration and cooling of the product solution.

Buffers were prepared from $HClO_4$ or HCl (pH 0–2), HOAc/NaOAc (pH 4), $H_2PO_4^-/OH^-$ (pH 6–8), borax/HCl (pH 8–9.2), borax/OH^- (pH 9.2–10.5), HPO_4^{2-}/OH^- (pH 10.5–12), NaOH (pH 12–14). Efforts were made to overlap certain pH regions (8, 10.5, 11.5) to insure against specific base effects. The pH (at 25°) was recorded on a Beckman expandomatic pH meter and adjusted for Na^+ effects.

The values represented in the following tables have been corrected for slight variations in the day-to-day atmospheric pressure by first correcting the solubility to 760 mm Hg (at 0°) (*10*). A further correction then involved a determination of the day-to-day solubility of NO in a buffer of $H_2PO_4^-/OH^-$ (no Cl^-, $\mu = 0.10$) at a pH = 7.16. Between 770 and 740, the atmospheric pressure depended somewhat linearly upon the observed solubility of NO. On the average, the solubility was observed to increase by $0.10 \times 10^{-3}/1.80 \times 10^{-3}$ between 750 and 770 mm. This slight increase is partially obscured by the error associated with the determination itself (e.g., at 760 mm, solubility of NO is $1.80 \pm 0.06 \times 10^{-3}M$, 25.0°).

Results and Discussion

The chief method of analysis for NO employed in this investigation has been used in the past (*14*). It has the advantage that it is convenient and sufficiently sensitive enough to detect the limited amounts of NO_2^- resulting from the low solubility of NO.

The solubility of NO as a function of pH is described in Table I. In the pH region between 13 and 2, the solubility varies within the error associated with the method of analysis (±4%). One might have expected to detect increasing amounts of NO_2^- in strongly alkaline solutions (*3*). However, within the saturation times used in this study (average of 40 min), no unusual differences were observed. In alkaline solutions, NO is expected to disproportionate (*9*) into NO_2^- and N_2O; however, the rate of the reaction might be quite slow and of no significance in this study. The same arguments (*9*) and conclusions can be applied regarding the stability of NO in strongly acidic solutions. It is interesting to note that the solubility of NO in 1*M* $HClO_4$ did not change if saturation was maintained for 30 or 180 min.

Table II describes the solubility of NO as a function of ionic strength and the particular salt used to maintain ionic strength. As expected (*8*), the solubility does decrease with increasing ionic strength. The values reported for LiCl at both 0.10 and 1.0*M* are within error of those assigned for the corresponding NaCl concentrations. By way of comparison, the solubility of NO in water at 25.0° has been reported as 1.9×10^{-3} (*14*), 1.98×10^{-3} (*6*), and $1.88 \times 10^{-3}M$ (*15a*). The solubility of NO at $\mu = 0.50$, which is based upon extrapolated data and lower ionic strengths (*8*), has been previously reported as $1.4 \times 10^{-3}M$. The difference between the latter result and the one now being reported is outside the margin of error. However, the latter value is not consistent with the values obtained at 0.1 and 1.0*M* NaCl or LiCl. Additional comparisons can be made with other gases. The solubility of oxygen decreases by approximately the same amount as NO in 1*M* NaCl (relative to water) (*15b*). However, the solubility of the polar SO_2 molecule increases with increasing salt concentrations (*15c*).

The effect of ClO_4^- in place of Cl^- was tested at pH's of 8.98, 7, and 2.00. The observed solubility was consistent with that recorded in Cl^- media. However, the solubility of NO in ClO_4^- media did not vary below a pH of 2, whereas the values obtained in Cl^- media at pH = 0 and 1 did vary from those obtained at higher pH.

The latter result suggests that there may be a particular effect of HCl upon the solubility of NO at very low pH. However, one cannot rule out the possibility that the 1*M* $HClO_4$ result is unusually high. The latter possibility would suggest two effects: a specific interaction of NO in strongly acidic ClO_4^- solutions, which serves to increase the apparent solubility of NO; and an association of NO with H_3O^+, which leads to a general decrease in solubility below a pH of 2. The first effect has been observed in aqueous H_2SO_4 solutions at much higher concentrations of H_2SO_4. [The solubility of NO decreases from 0 to 7*M* H_2SO_4 and then increases again (*15, 11*).] This has been explained by the formation of nitrosyl sulfonates (*11*).

Some additional insight into the above result and into the solubility of NO in aqueous salt solutions in general can be gained by looking at the activity coefficients of the solutions involved. The activity coefficients (*4*) of 1.0*M* LiCl and 1.0*M* NaCl are 0.775 and 0.657, respectively, and the solubilities of NO are quite comparable. Further, the activity coefficients of 1*M* $LiClO_4$ and 1*M* $HClO_4$ are comparable (0.887 and 0.826, respectively) (*4*), and the solubility of NO in both solutions is similar. The activity coefficient for 1.0*M* $NaClO_4$ (0.630) (*4*) is less than that for $LiClO_4$, and the solubility of NO is less in $NaClO_4$. Comparison of the activity coefficient of 1.0*M* HCl (0.811) (*4*) with 1.0*M* $HClO_4$ and 1.0*M* NaCl seems to indicate that the results obtained for the solubility of NO in 0.1*M* and 1.0*M* HCl are unusual. (Other sources of standardized HCl solutions gave the same results. Further, when the analysis of NO_2^- solutions was performed in the presence and absence of high concentrations of HCl, while determining the solubility of NO in ClO_4^- media, similar results were obtained.) These differences in solubility only serve to point out the importance for knowing the solubility of NO under the conditions used in this study.

In conclusion, except for 0.1*M* and 1.0*M* HCl, the solubility of NO is independent of pH from 2 to 13 (0–13 with ClO_4^-). Within the 30–60 min permitted to achieve saturation, the results suggest that there is no general association of NO with H^+ or OH^- which serves to alter the solubility of NO. Upon association of NO with H_3O^+ or OH^-, one might have expected the apparent solubility of NO to vary with a dramatic alteration in the ionic character of the medium. The solubility was observed to decrease in a regular manner ($\mu = 0.01$ to 1.2) (above a pH of 2) independent of any large effects by Na^+ or Li^+ and by ClO_4^- or Cl^-.

Table I. Solubility ($\times 10^3 M$) of NO at 25.0° (Corrected to 760 mm Hg at 0°)

Med buffer[a,b,c]	Buffer +0.10*M* NaCl[d]	Buffer +1.0*M* NaCl[e]
1.70 (13.0)[f]	1.52 (12.9)	1.35 (12.7)
1.78 (12.12)	1.77 (11.92)	1.32 (11.51)
...	1.73 (10.8)	1.34 (10.3)
1.78 (9.87)	1.71 (9.88)	1.29 (9.56)
1.76 (9.34)	1.68 (9.27)	1.23 (9.00)
		1.37 (8.95)[g]
1.85 (8.15)	1.74 (8.09)	1.31 (7.82)
1.80 (7.18)	1.69 (7.06)	1.22 (6.69)
1.73 (4.24)	1.78 (4.09)	1.36 (3.91)
1.69 (2.0)[h]	1.47 (1.0)[i]	1.02 (0)[j]
1.71 (2.0)[k]		1.37 (0)[l]

[a] Values in parentheses represent the pH of the solution. [b] Ionic strength of pH 12 buffer is 0.10; pH ~9 buffer, 0.05; pH ~7 buffer, 0.10; and pH ~4 buffer, 0.06. [c] Error on solubilities: $\pm 0.06 \times 10^{-3}M$. [d] Ionic strength (first column + 0.1) ~0.2. [e] Ionic strength (first column + 1.0) ~1.1. [f] 0.1*M* NaOH. [g] 1*M* $NaClO_4$. [h] 0.01*M* $HClO_4$. [i] 0.1*M* HCl. [j] 1*M* HCl. [k] 0.01*M* HCl. [l] 1*M* $HClO_4$.

Table II. Solubility of NO as Function of Ionic Medium at 25.0°

Medium, pH = 7.0[a]	[NO], $\times 10^3 M$[b]
H_2O	1.95[c]
0.05 $H_2PO_4^-/OH^-$ [0.10]	1.80
0.1*M* NaCl	1.62
0.1*M* LiCl	1.74
0.5*M* NaCl	1.61
1.0*M* NaCl	1.38
1.0*M* LiCl	1.52
1.0*M* $LiClO_4$	1.58
1.0*M* $NaClO_4$	1.28

[a] Values in brackets represent ionic strengths. [b] Error on solubilities: $\pm 0.06 \times 10^{-3}M$. [c] Value obtained from our work.

Literature Cited

(1) Armor, J. N., Buckbinder, M., *Inorg. Chem.*, **12**, 1086 (1973).
(2) Armor, J. N., Scheidegger, H., Taube, H., *J. Amer. Chem. Soc.*, **90**, 5928 (1968).
(3) Barr, G., *J. Chem. Soc.*, **1924**, p 961.
(4) Hamer, W. J., Wu, Y.-C., *J. Phys. Chem. Ref. Data*, **1**, 1047 (1972).
(5) Hughes, W. G., Zuech, E. A., *Inorg. Chem.*, **12**, 471 (1973).
(6) "International Critical Tables," E. W. Washburn, Ed., Vol III, p 259, McGraw-Hill, New York, N.Y., 1928.
(7) Jolly, W., "The Chemistry of the Non-Metals," p 82, Prentice-Hall, Englewood Cliffs, N.J., 1966.
(8) Kustin, K., Taub, I. A., Weinstock, E., *Inorg. Chem.*, **5**, 1079 (1966).
(9) Latimer, W., "Oxidation Potentials," 2nd ed., p 104, Prentice-Hall, New York, N.Y., 1952.
(10) Livingston, R., "Physico Chemical Experiments," 2nd ed., p 56, Macmillan, New York, N.Y., 1956.
(11) Marchot, W., König, J., Reimlinger, S., *Ber.*, **59B**, 2672 (1926).
(12) Pell, S., Armor, J. N., *Inorg. Chem.*, **12**, 873 (1973).
(13) Pell, S., Armor, J. N., *J. Amer. Chem. Soc.*, **94**, 686 (1972).
(14) Seddon, W. A., Sutton, H. C., *Trans. Faraday Soc.*, **59**, 2323 (1963).
(15) Seidell, A., Linke, W. F., "Solubilities of Inorganic and Metal-Organic Compounds," Vol II, 4th ed., American Chemical Society, Washington, D.C., 1965: (a) pp 790–91, (b) pp 1228–32, (c) pp 1408–15.
(16) Shinn, M. B., *Ind. Eng. Chem.*, **13**, 33 (1941).
(17) Yost, D., Russel, H., "Synthetic Inorganic Chemistry," p 79, Prentice-Hall, New York, N.Y., 1944.

Received for review June 4, 1973. Accepted August 27, 1973.

Excess Enthalpies at 45°C for Ternary System Acetonitrile–Benzene–Carbon Tetrachloride

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Excess enthalpies are measured calorimetrically over the whole range of composition at 45°C for the ternary (single liquid-phase) system acetonitrile(1)–benzene(2)–carbon tetrachloride(3), and for the three constituent binary systems. The excess enthalpy is positive for all these systems (endothermic mixing). For the ternary system the excess enthalpy can be represented simply in terms of binary contributions and reaches its greatest value of 218 cal/g mol in the binary acetonitrile–carbon tetrachloride region at a mole fraction of acetonitrile of about 0.4. Constants are given for the calculation of the excess enthalpies and the excess partial molar enthalpies.

As part of an investigation of three-component behavior in which one component (acetonitrile) is highly polar, excess enthalpies or heats of mixing have been measured at 45°C for the system acetonitrile–benzene–carbon tetrachloride. Although this system is not of commercial importance in itself, acetonitrile is used as a third component in separation processes (*1*), and carbon tetrachloride is a possible cosolvent with it in preventing isopycnics (*5*). The system involving these two components with benzene was chosen for study at 45°C, since information is available on excess enthalpies at this temperature for the three binary systems (*3, 4, 10, 11*) for comparison. All these systems, binary and ternary, form only one liquid phase at 45°C.

Experimental

Purification of the materials used was mainly by fractional distillation in a packed column, with the purified components being removed over a range of less than 0.1°C at a high reflux ratio. Fisher "Spectranalyzed" carbon tetrachloride was first dried over phosphorus pentoxide, and the same grade of benzene was first dried with metallic sodium. BDH "Analar" acetonitrile (methyl cyanide) was first dried over phosphorus pentoxide. Values of the relative densities ($d^{25}{}_4$) and refractive indices ($n^{25}{}_D$) of the purified components are given in Table I. These values all lie within the ranges given by Timmermans (*14*), with the exception of the value of $d^{25}{}_4$ for benzene, for which the range given is 0.8736–0.8739.

Excess enthalpies were measured with the same apparatus used previously (*2, 8*) with only a few minor modifications, as noted below. Measurements were made on the three binary systems at 45°C for comparison with other work and for internal consistency with the measurements on the ternary system at various compositions at the same temperature.

The apparatus used consists essentially of a brass calorimeter divided initially into two compartments by a thin metal disc; a Dewar flask containing a calorimetric fluid, in which the calorimeter is immersed, a thermistor for measuring temperature effects, and a calibrating heater; a thermostat in which the Dewar flask is placed; a recording potentiometer for continuously tracing the temperature changes inside the Dewar flask sensed by the thermistor; and a guarded Wheatstone bridge, one arm of which is the thermistor. The head of the Dewar assembly, which acts as a mounting for the thermistor and heater, was rebuilt, and the calorimetric fluid used was water instead of ethylene glycol. There is a small vapor space in the calorimeter, about 1 or 2% of the total volume.

For the binary systems the procedure involved placing a pure liquid in each compartment, with mixing being effected on continued inversion of the Dewar together with the breaking of the thin metal disc by a steel pellet. For the ternary system, mixtures of benzene and carbon tetrachloride, the binary system with the smallest excess enthalpy, were placed in one compartment and acetonitrile in the other, with allowance being made in each case for the binary system in determining the excess enthalpy for the resulting ternary system.

Results and Discussion

The measured values of excess enthalpies, h_{ij}^E, in cal/g mol for the three binary systems at 45°C and various compositions are given in Table II, in which x is the mole fraction of the component indicated by the subscript used. The data were fitted to equations of the Scatchard (*12*)–Guggenheim (*6*) type:

$$h_{ij}^E = x_i x_j [h_{ij}^{(0)} + h_{ij}^{(1)}(x_i - x_j) + h_{ij}^{(2)}(x_i - x_j)^2 + \dots] \quad (1)$$

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