Liquid Structure of Aqueous Nitric Acid Solutions

T. G. OWE BERG

Avesta Jernverks AB, Avesta, Sweden

The heat of vaporization E_{HNO_3} of HNO_3 from aqueous nitric acid solutions has been determined from the temperature-dependence of the partial vapor pressure of HNO_3 . A formula for E_{HNO_3} similar to that for E_{HCl} derived previously is found. This formula is discussed and interpreted. The existence of the hydrate $2 \text{HNO}_3 \cdot 3 \text{H}_2\text{O}$ is confirmed. The structures of this and of lower hydrates are discussed. Those contain H_2O bound by a N—O bond. The existence of the ortho-acid $\text{HNO}_3 \cdot \text{H}_2\text{O} = \text{H}_3\text{NO}_3$ is discussed.

1. EMPIRICAL FORMULAE

The heat of vaporization E_{HNO_3} of HNO_3 from aqueous solutions of nitric acid has been determined from plots of $\ln P_{\text{HNO}_3}$ against $\frac{1}{T}$ at various concentrations, the partial vapor pressure P_{HNO_3} of HNO_3 being taken from the compilation by Taylor ^{1,2}. Only pressures P_{HNO_3} less than 100 mm Hg were included in those plots, corresponding to temperature ranges varying from 55—105° C for 20 % HNO_3 to 0—30° C for 100 % HNO_3 . The results are given in Table 1 and plotted in Fig. 1 against mole fraction of HNO_3 .

Table 1.

weight-% HNO_3	m	$\frac{100}{m+1}$	E_{HNO_3} kcal/mole
20	13.99	6.671	16.46
25	10.49	8.703	15.62
30	8.149	10.930	15.29
35	6.495	13.34	15.02
40	5.246	16.01	14.58
45	4.267	18.99	13.63
50	3.498	22.23	13.23
55	2.861	25.90	12.64
60	2.332	30.01	11.94
65	1.883	34.69	11.18
70	1.499	40.02	10.66
80	0.8742	53.36	10.38
90	0.3880	72.05	10.12
100	0	100.00	10.52

When m denotes the number of H_2O molecules per HNO_3 molecule we find from Fig. 1 the empirical formulae

$$E_{\text{HNO}_3} = 16.8 - \frac{16}{m+1} \text{ kcal/mole, } m > 1.5 \quad (1)$$

$$E_{\text{HNO}_3} = 10.4 \text{ kcal/mole, } m \leq 1.5 \quad (2)$$

We will compare the formula (1) with the corresponding formula for E_{HCl} written in the form³

$$E_{\text{HCl}} = E_{v.d.w} + 5 E_{\text{Cl-H-O}} - \frac{10}{m+1} E_{\text{O-H-O}}, m < 10 \quad (3)$$

With a suitable choice of coefficients we may write (1) in a form similar to that of (3), viz.

$$E_{\text{HNO}_3} = E_{v.d.w} + \left(\frac{9}{2} - 1\right) E_{\text{O-H-O}} - \left(\frac{9}{2} - 1\right) \frac{1}{m+1} E_{\text{O-H-O}} \quad (4)$$

For inserting in (4) $E_{v.d.w} = 0.47$ kcal/mole for the van der Waals energy and $E_{\text{O-H-O}} = 4.63$ kcal/mole for the energy of the O—H—O hydrogen bond³ we have, in fact,

$$E_{\text{HNO}_3} = 16.7 - \frac{16.2}{m+1} \text{ kcal/mole} \quad (5)$$

which agrees with (1) within the accuracy of the empirical data.

A comparison of (4) and (3) suggests a common interpretation of the two formulae. In the case of HCl we have five hydrogen bonds between the Cl atom and adjacent H_2O molecules and a total number of ten H_2O molecules in the immediate vicinity of the HCl molecule³. Since the HNO_3 molecule can form nine hydrogen bonds with adjacent molecules we might expect the factors 5 and 10 for HCl to be replaced by 9 for HNO_3 . Such a comparison indicates, however, that of the nine hydrogen bonds only one half minus one contribute to binding the HNO_3 molecule. The factor $\frac{1}{2}$ indicates that each bond is shared by two HNO_3 molecules. We will return to the discussion of (4) in section 3.

The deviations from the constant value (2) in the range 40—100 mol. % are not greater than the experimental error¹. Further data are available for pure HNO_3 from which the heat of vaporization has been determined. From the vapor pressures of Wilson and Miles⁴ and of Berl and Saenger⁵ we obtain 9.30 and 9.65 kcal/mole, respectively. The vapor pressures given by Taylor are considerably lower than those given by the latter authors and by Klemenc and Rupp⁶ but cover a much wider range of temperature. The calorimetrically determined heat of vaporization is 7.25 kcal/mole at 15°⁷. In view of these discrepancies we will simply take the vapor pressures of Taylor, since those may be supposed to fit better into Taylor's series of vapor pressures of the dilute acid, and, particularly, since their spread is smaller than that of the data of the other authors.

The heat of vaporization of H_2O in pure water and in aqueous nitric acid solutions is $E_{\text{H}_2\text{O}} = 10.54$ kcal/mole at 20° C. Thus, the value (2) of E_{HNO_3} in the range $m \leq 1.5$ does not differ appreciably from $E_{\text{H}_2\text{O}}$.

2. DISCUSSION OF THE FORMULA (2)

There are two interesting features of (2), viz.

1. that $E_{\text{HNO}_3} = E_{\text{H}_2\text{O}}$ in the range $m \leq 1.5$
- b. the limit $m = 1.5$, indicating the existence of the hydrate $2 \text{HNO}_3 \cdot 3 \text{H}_2\text{O}$ which we will now discuss.

Three hydrates have been reported previously in the range $m \leq 1.5$ with $m = \frac{1}{2}$, $m = 1$, and $m = 1 \frac{1}{2}$. Of those the monohydrate is very well known; it has been isolated and studied in the solid as well as in the liquid state.

The hydrate $2 \text{HNO}_3 \cdot 3 \text{H}_2\text{O}$ has been found by a number of investigators. Kolb⁸ found a maximum in the contraction of the solution at this concentration. Veley and Manley⁹ concluded on this hydrate from their curves of electrical conductivity and refraction index. Creighton and Githens¹⁰ pointed out that the vapor pressure has a minimum at this composition. Erdmann claimed to have isolated this hydrate by freezing (-39°)¹¹ and also studied its molecular weight in the vapor¹². Küster and Kremann¹³ ridiculed the results of Erdmann in a paper, the arrogance of which is, fortunately, rare in scientific literature, and claimed that this hydrate is a mixture of the wellknown mono- and tri-hydrates. In view of this criticism Gmelin¹⁴ and Mellor¹⁵ quote both views and consider the existence of this hydrate as still undecided. More recent views on the subject are unknown to the author.

The basic error in the argument of Küster and Kremann is the postulate that a hydrate can not exist in aqueous solution unless it can be isolated from the solution. Thus, the present author has shown in a series of papers¹⁶ that the hydrates $\text{HNO}_3 \cdot 6 \text{H}_2\text{O}$ and $\text{HNO}_3 \cdot 15 \text{H}_2\text{O}$ exist in the solution although they can not be isolated by freezing. Similarly, the hydrate $2 \text{HNO}_3 \cdot \text{H}_2\text{O}$ found by Erdmann¹¹ and equally ridiculed by Küster and Kremann has been shown to exist in aqueous solution by Chédin¹⁷.

The curve in Fig. 1 seems to establish the existence of the hydrate $2 \text{HNO}_3 \cdot 3 \text{H}_2\text{O}$. The fact that no other hydrate shows up in that curve does not prove, of course, that no other hydrates exist.

The existence of hydrates with $m = \frac{1}{2}$ and $m = 1 \frac{1}{2}$ indicates that those hydrates and, may be, the other hydrates as well, form aggregates of an even number, *e. g.* pairs, of HNO_3 molecules or consist of hydrates of the anhydride, $\text{N}_2\text{O}_5 \cdot m \text{H}_2\text{O}$.

In water and in aqueous solutions, the molecules are held together in a structure by hydrogen bonds. The energy of the O—H—O bond is independent of to what kind of molecule the O atoms belong. Thus, O—H—O bonds between H_2O molecules, H_2O and H_2SO_4 molecules, H_2O and HNO_3 molecules, *etc.* all have the same energy. This follows from (4) and from the corresponding formulae for $E_{\text{H}_2\text{O}}$ in HNO_3 and H_2SO_4 solutions³ as well as from the vapor pressure³. Hence, an O—H—O bond between two HNO_3 molecules has the energy $E_{\text{O—H—O}} = 4.6$ kcal/mole, and we must assume that there are two H atoms per evaporating molecule forming bonds with the liquid structure. This means that the HNO_3 molecules either form pairs or dimers, *e. g.* $(\text{HNO}_3)_2 = \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$, or that the H_2O molecules in the hydrates are instru-

Fig. 1.

mental in binding the HNO_3 molecules to the structure, viz. by supplying the lacking number of H atoms for the formation of the bonds. By writing the dimer in the form $N_2O_5 \cdot H_2O$ we see that there is little difference between those two alternatives.

In order to discuss the structures of and the bonds in the various hydrates we will start out by considering the structural possibilities for the reaction

Concerning the dimer $(HNO_3)_2$, the "nitronium nitrate", reference is made to Gmelin¹⁴. Further reference may be made to Jones and Thorn¹⁸ and to Chédin and coworkers who studied association of HNO_3 molecules^{19,20}, and the complex ions $(HNO_3)NO_3^-$ ²¹ and $(HNO_3)_2NO_3^-$ ²². The structure of gaseous N_2O_5 is

The reaction (6) may be effected by splitting N_2O_5 into NO_2 and NO_3 and by adding OH to NO_2 and H to NO_3 . In both cases, there must be three N—O bonds per HNO_3 molecule. We will therefore assume that the hydrate $N_2O_5 \cdot H_2O$ is the first reaction product in (6) and that the H_2O molecule is

bound to the N_2O_5 molecule by a $\text{N}-\text{O}$ bond. The structure of $\text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$ is then

If a number of such hydrate molecules are bound together with hydrogen bonds as shown schematically by the formula

and the bonds are broken as indicated by the perpendicular lines, HNO_3 molecules will form which may be held together by hydrogen bonds or which may separate after evaporation. Since each $\text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$ molecule according to (8) has two H atoms for forming hydrogen bonds with the liquid structure, the heat of vaporization of one $\text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$ molecule or of the $(\text{HNO}_3)_2$ dimer is equal to $E_{\text{H}_2\text{O}}$.

If, instead of (8), we assume the structure

i. e. that the H_2O molecule is bound in the hydrate $\text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$ by hydrogen bonds, the reaction (6) is not structurally possible.

We will now apply the same arguments to the hydrate $\text{HNO}_3 \cdot \text{H}_2\text{O}$. The structure of this hydrate has been the subject of much controversy¹⁴. According to Chédin and Fénéant^{19,2} its structure should be of the same type as (10), *i. e.*

This hydrate contains only one H atom for the formation of a hydrogen bond with the liquid structure, whereas two are required. We must therefore assume the formation of a dimer $(\text{HNO}_3 \cdot \text{H}_2\text{O})_2 = 2\text{HNO}_3 \cdot 2\text{H}_2\text{O}$ with two H atoms available for the formation of hydrogen bonds with the liquid structure. But then there is no H atom available for internal binding within the dimer and we are led to the conclusion that a N—O bond has to be formed for holding the dimer together.

The same reason as were just given against (10) are valid against (11) and (12) as will be shown presently.

It has seemed natural to compare the hydrate $\text{HNO}_3 \cdot \text{H}_2\text{O}$ to $\text{HPO}_3 \cdot \text{H}_2\text{O} = \text{H}_3\text{PO}_4$ and to $\text{SO}_3 \cdot \text{H}_2\text{O} = \text{H}_2\text{SO}_4$. Adopting this view we will assume that the H_2O molecule is bound in $\text{HNO}_3 \cdot \text{H}_2\text{O}$ by a N—O-bond and write $\text{HNO}_3 \cdot \text{H}_2\text{O}$ in the form

i. e. the same structure as that of H_3PO_4 ²⁴. Salts of the acid H_3NO_4 are known, *viz.* Na_3NO_4 , $\text{Na}_3\text{NO}_4 \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{HNO}_4 \cdot \text{H}_2\text{O}$, and $\text{K}_3\text{NO}_4 \cdot \text{H}_2\text{O}$ ¹⁴. The existence of such salts indicates that the N—O bond may strengthen into a valence bond. The structure (13) contains three H atoms which may form bonds with the liquid structure. However, if those molecules combine in pairs held together by two hydrogen bonds there will be a total of four, *i. e.* two per $\text{HNO}_3 \cdot \text{H}_2\text{O}$ molecule, H atoms available for the formation of external hydrogen bonds. Thus, if the mono-hydrate $\text{HNO}_3 \cdot \text{H}_2\text{O}$ evaporates in the dimer form $(\text{HNO}_3 \cdot \text{H}_2\text{O})_2 = 2\text{HNO}_3 \cdot 2\text{H}_2\text{O}$, we may expect the heat of vaporization per $\text{HNO}_3 \cdot \text{H}_2\text{O}$ molecule to be equal to that of an H_2O molecule. Obviously, the alkali salts quoted can not be formed from (12) but very well from (13).

When further H_2O is added to the mono-hydrate dimer, *i. e.* to pairs of the structure (13), we arrive at the hydrate $2\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ with four external and, consequently, four internal hydrogen bonds. The third H_2O molecule is then bound to the $(\text{HNO}_3 \cdot \text{H}_2\text{O})_2$ molecule by hydrogen bonds and not by a N—O bond.

3. DISCUSSION OF THE FORMULA (4)

In the structure of water, each O atom is surrounded by four nearest neighbors forming a tetrahedron with one O atom at each corner and one O atom in the centre. We may assume that the same co-ordination number applies to the O atoms of the HNO_3 molecule²⁵. Hence, each O atom of the HNO_3 molecule will have one N atom and three O atoms, belonging to other HNO_3 molecules or to H_2O molecules, as nearest neighbors. The total number of nearest neighbors per HNO_3 molecule is then 9. Thus, when $m > 9$ the HNO_3 molecule may have its full number of H_2O neighbors without sharing any of those with any other HNO_3 molecule. However, as has been shown by the author in connection with the dissociation of the HNO_3 molecule in aqueous solution^{25,26}, this occurs at low temperatures only. At higher temperatures, above 21°C , the actual number required is $m = 15$ owing to the formation of a hexa-hydrate with whose H_2O molecules the $(m-6)$ further added H_2O molecules may bind.

However, the coordination number 9 may still be valid for $m < 9$, because some of the H_2O molecules may be shared by several HNO_3 molecules or replaced by O atoms of neighbor HNO_3 molecules. This is indicated by the formula (4) to be the fact for $m > 1.5$. As discussed in section 2, for $m \leq 1.5$, the structure is held together by H_2O molecules bound with N—O bonds to the HNO_3 molecules and to the liquid structure by hydrogen bonds, the hydrates forming dimers of two HNO_3 molecules. If this state is preserved at higher values of m , two external hydrogen bonds per HNO_3 molecule will be lost, because one will be engaged in forming the dimer and one is replaced by an internal N—O bond. Hence, the total number of external bonds will not be 9 but $9 - 2 = 7$. Since those are shared by the two HNO_3 molecules in the dimer, the number of bonds per HNO_3 molecule will be $\frac{7}{2}$ as indicated by the empirical formula (4).

When treating the partial vapor pressure of water above nitric acid solutions³ we found the limiting formula

$$p = \frac{m-1}{m+1} \quad (14)$$

instead of Raoult's law

$$p = \frac{m}{m+1} \quad (15)$$

The formula (14) shows that one of the m H_2O molecules does not contribute to the vapor pressure, *i. e.* it is bound in a hydrate. Although this conclusion was actually drawn, no satisfactory explanation could be given, because we assumed at that time as well as previously²⁵ that the mono-hydrate has the structure (11) which is not possible at values of m greater than 1. It should be pointed out in this connection that the N—O bond according to (13) does not affect the derivation of the degree of dissociation²⁵, since we are only concerned with hydrogen bonds in that derivation.

In concluding this section it should be pointed out that the validity of (4) has been established only in the range $14 > m > 1.5$. At lower concentrations we would expect the HNO_3 pairs to separate and the factor $\frac{1}{2}$ in (4) to disappear and, thus, E_{HNO_3} to increase above the value given by (4). Unfortunately, data are lacking in the range $m > 14$.

4. CONCLUSIONS

A. From the following evidence:

1. the existence of the hydrates $\text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$, $\text{HNO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$, and $\text{HNO}_3 \cdot 1\frac{1}{2} \text{H}_2\text{O}$;
2. the existence of the "nitronium nitrate" $(\text{HNO}_3)_2$ and the complex ion $(\text{HNO}_3)\text{NO}_3^-$;
3. the factor $\frac{1}{2}$ in (4);
4. the formula (2);

we conclude upon the existence of dimers or structural units containing two HNO_3 molecules.

B. From the following evidence:

1. the existence of salts of the type Na_2NO_4 ;
 2. the term -1 in the formula (4);
 3. the formula (14);
 4. the structural possibilities for reactions;
 5. a comparison with $\text{HPO}_3 \cdot \text{H}_2\text{O} = \text{H}_3\text{PO}_4$, $\text{SO}_3 \cdot \text{H}_2\text{O} = \text{H}_2\text{SO}_4$,
- we conclude upon the existence of a N—O bond in the mono-hydrate which may strengthen into a valence bond with formation of the ortho-acid, $\text{HNO}_3 \cdot \text{H}_2\text{O} = \text{H}_3\text{NO}_4$.

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