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Physical Properties of Isotopic Forms of Some Inorganic Acid-Water Azeotropes

KARL ERIK HOLMBERG

Division of Chemistry, Section for Nuclear Chemistry, AB Atomenergi, Stockholm, Sweden

The azeotropes of DCl, DBr or DNO_3 with D_2O are more volatile than the corresponding azeotropes containing H. In the HCl-H_2O and HBr–H_2O azeotropes, the difference in volatility of ^{16}O and ^{18}O is larger than in water. Other isotope enrichment effects are small or imperceptible. Differences in other physical properties, such as density, viscosity and refractive index, are similar to those between H_2O and D_2O though less pronounced.

In the maximum boiling point azeotropes formed by various inorganic acids and water, there is a considerable interaction between the components in the liquid phase but not in the vapour phase. Different isotopic forms of the azeotropes may therefore differ with respect to volatility and composition (mole ratio acid : water).

The azeotropes of HCl, HBr or HNO_3 with H_2O and the corresponding fully deuterated azeotropes have been prepared and compared with each other with respect to composition, boiling point and some other physical properties. Separation factors for the various isotopes have been determined by Rayleigh distillation at atmospheric pressure and, in some cases, at reduced pressure. The results are summarized in Tables 1—5. For convenience, the following abbreviations will be used for the azeotropes:
$HClH_2O$, $DClD_2O$, $HBrH_2O$, $DBrD_2O$, HNO_3H_2O and DNO_3D_2O although, of course, they are not composed of equimolecular amounts of acid and water.

Physical properties. The H and D forms of the azeotropes do not differ much in composition and the difference with respect to physical properties between them is a reflection of the difference between the two forms of water. Thus, the D azeotropes have a higher density and viscosity and a lower refractive index and the relative differences are approximately proportional to the water content of the azeotrope.

Volatilities. The D forms of the azeotropes are the more volatile while, for pure water, the opposite holds true. This phenomenon is no doubt the same as what was found by Combs and Smith [1] who investigated the volatility of light and heavy water from salt solutions. They found that the relative vola-

Table 1. Composition and physical properties of the H and D forms of the azeotropes of some inorganic acids and water.

	$HClH_2O$	$DClD_2O$	$HBrH_2O$	$DBrD_2O$	HNO_3H_2O	DNO_3D_2O
Weight % of acid	20.22	17.55	47.9	45.0	67.87	66.22
Mole % of acid	11.14	10.33	16.9	16.6	37.66	38.00
Formula	HCl $7.98\ H_2O$	DCl $8.68\ D_2O$	HBr $4.92\ H_2O$	DBr $5.02\ D_2O$	HNO_3 $1.655\ H_2O$	DNO_3 $1.631\ D_2O$
Boiling point at 760 mm Hg, °C	108.58	108.45	124.84	124.38	121.0	118.2
Boiling point difference, °C	0.13		0.46		2.8	
$(\mathrm{d}p/\mathrm{d}t)_{760}$, mm Hg/°C	27.7		27.8		27.2	
d_4^{25}, g/ml	1.10295	1.18915	1.48015	1.56201	1.39815	1.44873
η_{25}, centipoise	1.29	1.49	1.46	1.67	1.85	2.00
n_D^{25}	1.3800	1.3715	1.4370	1.4310		

Table 2. Ratio of the vapour pressures of H and D forms of azeotropes, and separation factors for isotopes upon distillation. Water is included for comparison.

	$HClH_2O$ at 108°C	$HBrH_2O$ at 124°C	HNO_3H_2O at 121°C	H_2O at 100°C
$p(\mathrm{D})/p(\mathrm{H})$	1.0047 ± 0.0007	1.017 ± 0.001	1.100 ± 0.004	0.950
$\frac{(\mathrm{D/H})_{\mathrm{vap}}}{(\mathrm{D/H})_{\mathrm{liq}}}$	1.0043 ± 0.0014		1.044 ± 0.008	0.978 ± 0.001
$\frac{(^{16}\mathrm{O}/^{18}\mathrm{O})_{\mathrm{vap}}}{(^{16}\mathrm{O}/^{18}\mathrm{O})_{\mathrm{liq}}}$	1.0074 ± 0.0009	1.0086 ± 0.0009	1.0009 ± 0.0009	1.0039 ± 0.0009
$\frac{(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})_{\mathrm{vap}}}{(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})_{\mathrm{liq}}}$	> 0.995			
$\frac{(^{81}\mathrm{Br}/^{79}\mathrm{Br})_{\mathrm{vap}}}{^{81}\mathrm{Br}/^{79}\mathrm{Br})_{\mathrm{liq}}}$		1.000 ± 0.002		
$\frac{(^{14}\mathrm{N}/^{15}\mathrm{N})_{\mathrm{vap}}}{(^{14}\mathrm{N}/^{15}\mathrm{N})_{\mathrm{liq}}}$			1.0003 ± 0.0012	

Table 3. Separation factors by Rayleigh distillation of azeotropes at reduced pressure. Water included for comparison.

	$HClH_2O$ about 10°C	$HBrH_2O$ about 10°C	H_2O about 10°C
$\frac{(^{16}O/^{18}O)_{vap}}{(^{16}O/^{18}O)_{liq}}$	1.0143 ± 0.0009	1.0167 ± 0.0009	1.0076 ± 0.0009
$\frac{(^{37}Cl/^{35}Cl)_{vap}}{(^{37}Cl/^{35}Cl)_{liq}}$	1.0008 ± 0.002		
$\frac{(^{81}Br/^{79}Br)_{vap}}{(^{81}Br/^{79}Br)_{liq}}$		1.000 ± 0.002	

Table 4. Boiling points of HNO_3H_2O and DNO_3D_2O azeotropes at various pressures; p and b.p. are not corrected. The values at low pressures are uncertain because of bumping.

p mm Hg	HNO_3H_2O b.p. °C	DNO_3D_2O b.p. °C	difference °C
50.5	57.95	55.87	2.08
105.5	72.12	70.17	1.95
310	96.35	93.93	2.42
776	120.67	117.83	2.84

Table 5. Comparison of separation factors by column distillation of $HClH_2O$ azeotrope containing about 10 % D. The figure in bold type is assumed to be correct and is used for calculating the number of theoretical plates.

Isotope pair	Q	Elementary separation factor α			error in α from error in Q
D/H	1.054	1.0058	**1.0047**	**1.0043**	± 0.0002
$^{16}O/^{18}O$	1.0685	**1.0074**	1.0059	1.0054	± 0.0003
$^{37}Cl/^{35}Cl$	1.003_8	1.0003_6	1.0002_8	1.0002_6	± 0.0002
Number of theoretical plates		9	11.5	12.5	

tility of D_2O increases with the salt concentration and that the effect is more pronounced at higher temperatures.

The ratios of the vapour pressures of the H and D forms of the azeotropes have been calculated from the boiling point differences. The separation factors for H/D have been determined by Rayleigh distillation using $HClH_2O$ and HNO_3H_2O containing a fair amount of D.

Distillation of $HClH_2O$, containing 18.5 % D, gave a separation factor $\alpha = 1.0043$ with an estimated error of ± 0.0014 in close agreement with the

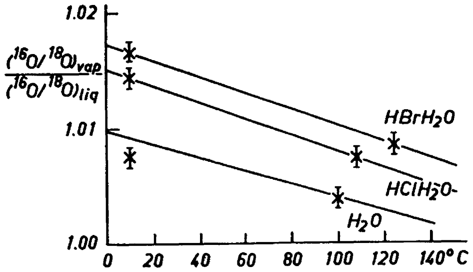

Fig. 1. Separation factors for $^{16}O/^{18}O$ from Rayleigh distillations. The line for H_2O is drawn according to a compilation by Dostrovsky[6].

ratio of the vapour pressures of the D and H systems. In fact, the separation factor α would be expected to be the square root of the vapour pressure ratio (or even smaller) just as the separation factor upon distillation of water is the square root of $p(H_2O)/p(D_2O)$. The reason for the different behaviour may be that the H and D forms of the azeotrope have somewhat different compositions, or it may be partly due to experimental errors.

The ratio of the vapour pressures of the H and D forms of HNO_3H_2O was found to be 1.100. The separation factor upon distillation of a mixture may be predicted tentatively. If differences in the forces between the water molecules are chiefly responsible it may be expected to be $1.100^{1.65/(1+2\times1.65)} = 1.037$ while, if it is due to the differences in the forces between HNO_3 and H_2O, we would get $1.100^{1/(1+2\times1.65)} = 1.022$.

From a Rayleigh distillation of a HNO_3H_2O azeotrope with about 4.5 % D abundance, the separation factor α was found to be 1.052 calculated on the first distillate and 1.037 calculated on the residue. A weighted average was 1.044. This is probably not too large considering the tendency of the Rayleigh distillations to give low values [2].

From boiling point measurements at various pressures (Table 4), it is evident that the separation factor will not be much better at other pressures than atmospheric. In this connection, it may be observed that Dawber and Wyatt [3] have found that at 0°C the vapour pressure of pure DNO_3 is more than 7 % larger than that of HNO_3.

The behaviour of the oxygen isotopes is very interesting. In the $HClH_2O$ and $HBrH_2O$ azeotropes, ^{16}O is enriched in the vapour, just as for water, but with a considerably larger factor, *cf.* Fig. 1. Further, the enrichment increases when the temperature decreases. This is quite in contrast to the H isotopes which are enriched in different directions in water and in the azeotropes.

In the HNO_3H_2O system, there is almost no enrichment of oxygen isotopes possibly because there is an exchange of O between H_2O and HNO_3 [4,5] and because the tendency of ^{18}O enrichment in the H_2O and HNO_3 vapours from the azeotrope may be in opposite directions.

Heavy isotopes of oxygen have been enriched, *e.g.* by Dostrovsky [6], on a rather large scale by the distillation of water. From the point of view of column volume and heat consumption, the $HClH_2O$ and $HBrH_2O$ azeotropes should be more favourable but the corrosion problems will probably be so serious as to offset the advantages.

The possibility of an enrichment of Cl isotopes by distillation of azeotropic hydrochloric acid has been pointed out by London [7]. The actual separation is, however, very small and therefore difficult to ascertain. By Rayleigh distillation, it has now been found that the separation factor is probably less than 1.001, ^{37}Cl enriching in the vapour. According to a column distillation experiment, described below, it is probably about 1.0003. This is a little surprising. It has been found by Johnston and Hutchison [8] that, upon electrolysis of a NaCl solution, ^{37}Cl enriches in the liquid by a factor of 1.0060. If this is an equilibrium process, the separation factor for the exchange between Cl^-(aq) and Cl_2(gas) will be the same ($\alpha = 1.0060$). It has been calculated by Urey [9] that, upon exchange between gaseous HCl and Cl_2, ^{37}Cl will enrich in the Cl_2 by the factor 1.003. From this, it is expected that, on exchange between Cl^-(aq) and HCl (gas), which must occur between the liquid and gaseous $HClH_2O$ azeotrope, ^{37}Cl should be enriched in the liquid by a factor of 1.009 (at 25°C).

The present experimental results, however, agree with those of Urey *et al.*[10] who found a rather small enrichment of ^{37}Cl in the gas upon exchange between HCl (gas) and HCl (aq) at ambient temperature.

Similarly, for $HBrH_2O$, no separation of Br isotopes could be observed.

Considerable difficulties are met with when very small separation factors are to be determined. Ordinary mass spectrometric measurements seldom give the isotope ratio with a better accuracy than 0.1 %. To obtain a better accuracy, the elementary factor must be multiplied. By means of Rayleigh distillation, it is possible to have conveniently an enrichment corresponding to four single steps.

Column distillation would be an excellent multiplication method if the actual number of theoretical plates at equilibrium were known. A given column operates with a different number of theoretical plates for different systems. Therefore, it is not possible to evaluate a column with a known system and then use it to investigate unknown systems (if any accuracy is desired).

It may be thought that an internal comparison of different separation factors within the same system by column distillation would be possible with a good accuracy. It is, however, probable that even in this case the theoretical plate height (H.E.T.P.) may be different for different separations. On the other hand, the results could be expected to be much better than for a comparison of quite different systems by means of separate distillations.

A method of distillation where the number of theoretical plates may be predicted has been suggested by Kuhn *et al.*[11] but it requires an accurate regulation of the reflux ratio.

To have a check on the results of the Rayleigh distillations, a column distillation has been performed with the $HClH_2O$ azeotrope containing about 10 % D. In the top reservoir of the column, the various isotopes were enriched by the factors Q given in Table 5. A certain separation factor, determined above, is assumed to be correct and from it the number of theoretical plates is calculated and from this number the separation factors for the other isotopes are found. The discrepancy between the different calculations may be due to errors in the values from the Rayleigh distillations or, perhaps, to a different efficiency of the column towards the different isotope pairs in the system.

EXPERIMENTAL

Preparations. $HClH_2O$ was prepared by dilution of hydrochloric acid to the proper concentration and distillation at atmospheric pressure through a 1 meter column, with glass helices, to obtain an azeotrope with a narrow boiling point range (0.1°C).

SO_2Cl_2 was reacted with an excess of D_2O and distilled. The distillate was fractionated to give the azeotrope $DClD_2O$ with a narrow b.p. range.

$HBrH_2O$ was prepared by distillation from $KBr + H_2O + H_2SO_4$ and fractionation of the product with the 1 meter column [12].

$DBrD_2O$ was prepared in the same way from $KBr + D_2O + D_2SO_4$. D_2SO_4 had been obtained in the reaction above of $SO_2Cl_2 + D_2O$ or by reaction of SO_3 with D_2O.

HNO_3H_2O azeotrope was obtained by fractionation of common nitric acid.

DNO_3D_2O was prepared by distillation from $KNO_3 + D_2O + D_2SO_4$ and fractionation of the product.

Analyses. Analyses were made by titration with standard alkali.

Physical properties. The measurement of boiling points, densities and viscosities has been described earlier [2].

Rayleigh distillations. The apparatus for Rayleigh distillation at atmospheric pressure has been described earlier [2]. Rayleigh distillations at reduced pressure were performed from one flask to another, the first being heated by the surrounding air or a water bath and the second being cooled to 0°C or lower with alcohol and solid CO_2. The distillation temperature was adjusted to be about 10°C.

Test distillations with water followed by oxygen isotope analyses showed that the Rayleigh distillation gave slightly too low values for the separation factors, just as had been found earlier with H_2O-D_2O mixtures [2].

Column distillations. Azeotropic $HClH_2O$ with about 10 % D abundance was distilled in a column of 1.5 meter length packed with glass helices and with a reservoir at the top. It was refluxed for 9 days which was much more than was estimated to be necessary to reach equilibrium. Samples from the top and the still pot were analysed for the abundance of H, O and Cl isotopes.

Preparations for isotopic analyses

D analysis. The acid sample was neutralized with anhydrous Na_2CO_3 and the water was distilled off quantitatively under vacuum. It was purified by redistillation in vacuum and its density was measured.

^{18}O analysis. The acid sample together with a small amount of CO_2 was sealed in a glass tube and equilibrated at room temperature for a few days. The CO_2 was separated from the sample by freezing out. The dilution error was about 1 %.

Cl isotope analysis. Cl was precipitated as AgCl which was reacted with CH_3I in a sealed tube to give CH_3Cl[13].

Br isotope analysis. $HBrH_2O$ and CH_3OH were heated in a sealed tube to give CH_3Br which was separated and analysed [14].

^{15}N analysis. HNO_3 was reduced to NH_3 with Arnd's alloy [15] and then handled as usual for a N isotope analysis.

Errors

The errors in the ratios of the vapour pressures of the H and D forms of the azetropes are calculated from the estimated errors of the b.p. differences. The errors in the H/D separation factors correspond to the scattering of the experimental values. The other errors given correspond to the estimated errors of the mass spectrometric measurements and do not include accidental or systematic experimental errors.

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