Physical Properties of Isotopic Forms of Azeotropic Systems Formed from Acetic Acid and Some Tertiary Amines

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Azeotropes of CH_3COOH and CH_3COOD with pyridine, trimethylamine and triethylamine have been prepared. The boiling point differences between the H and D forms of the azeotropes are larger than those between the isotopic forms of pure acetic acid. The composition and some physical properties of the azeotropes have been determined. Upon distillation of the azeotropes, there is some separation of the nitrogen isotopes and, possibly, also of the carbon and oxygen isotopes of the carboxyl group in the acetic acid.

Acetic acid gives, with suitable tertiary amines, maximum boiling point azeotropes. In these azeotropes, the strength of the chemical bond or hydrogen bond between the components will depend on the isotopic constitution of the atoms forming the bond. Different isotopic forms of the azeotropes may therefore have different compositions (*i. e.* ratios amine:acid) and different physical properties.

The azeotropes with acetic acid or acetic acid deuterated in the carboxyl group as one component and pyridine, trimethylamine or triethylamine as the other component have been prepared and investigated with respect to composition and physical properties. After Rayleigh distillation, the isotopic composition has been determined for other elements which may be involved in the compound formation, *viz.* the nitrogen of the amine and the carbon and oxygen of the carboxyl group.

The results are collected in Tables 1 and 2. For convenience, the following abbreviations are used for the azeotropes: PyHAc, PyDAc, Me_3NHAc , Me_3NDAc , Et_3NHAc , Et_3NDAc , in spite of the fact that they are not composed of equimolecular amounts of acid and amine.

The H and D forms of the azeotropes differ rather little in composition. Except for the case with pyridine, the azeotropes seem to contain a compound consisting of one mole amine and four moles acetic acid. Measurements, not

Table 1. Composition and physical properties of the H and D forms of azetropes of acetic acid and tertiary amines.

	PyHAc	PyDAc	Me ₃ NHAc	Me ₃ NDAc	Et ₃ NHAc	Et ₃ NDAc
Weight% of HAc or DAc	52.2	51.6	81.2	81.8	69.9	70.7
Mole% of HAc or DAc	59.0	58.0	80.95	81.3	79.7	80.0
Formula	C ₆ H ₄ N. 1.44 CH ₃ COOH	C ₆ H ₄ N. 1.38 CH ₃ COOD	(CH ₃) ₃ N. 4.25 CH ₃ COOH	(CH ₃) ₃ N. 4.35 CH ₃ COOD	(C ₂ H ₅) ₃ N. 3.92 CH ₃ COOH	(C ₂ H ₅) ₃ N. 4.00 CH ₃ COOD
Boiling point at 760 mm Hg, °C	138.00	136.66	152.9	151.8	161.85	161.01
Boiling point difference, °C	1.34		1.1		0.84	
(dp/dt) ₇₆₀ , mm Hg/°C	21.3		24.1		27.0	
Melting point, °C	-51		glass		glass	
d ₄ ²⁵ , g/ml	1.03678	1.04114	1.03887	1.05365	1.01638	1.02834
η ₂₅ , centipoise	2.21	2.06	11.35	11.47	14.47	14.59
n _D ²⁵	1.4520	1.4510	1.4087	1.4080	1.4218	1.4212

Table 2. Ratio of the vapour pressures of H and D forms of azeotropes and separation factors for other isotopes upon distillation. The errors given refer to the mass spectrometric measurements.

	PyHAc at 138°C	Me ₃ NHAc at 153°C	Et ₃ NHAc at 162°C
$p(D)/p(H)$	1.038	1.032	1.030
$\frac{(^{14}\text{N}/^{15}\text{N})_{\text{vap}}}{(^{14}\text{N}/^{15}\text{N})_{\text{liq}}}$	1.0034 ± 0.0012	1.0097 ± 0.0012	1.0075 ± 0.0012
$\frac{(^{18}\text{O}/^{16}\text{O})_{\text{vap}}}{(^{18}\text{O}/^{16}\text{O})_{\text{liq}}}$	1.0007 ± 0.0009	1.0010 ± 0.0009	1.0018 ± 0.0009
$\frac{(^{13}\text{C}/^{12}\text{C})_{\text{vap}}}{(^{13}\text{C}/^{12}\text{C})_{\text{liq}}}$	1.0017 ± 0.0006	1.0005 ± 0.0006	1.0012 ± 0.0006

reproduced here, of the density and viscosity of mixtures of Py and HAc have shown a maximum deviation from linear relationship at about the composition Py.4HAc. It is therefore possible that the liquid pyridine-acetic acid azeotrope is a mixture of a compound Py.4HAc together with free, or less strongly bound, pyridine.

The ratio of the vapour pressures of the H and D forms of an azeotrope at the boiling point (b.p.) of the H form is larger than the corresponding ratio for acetic acid at its normal b.p. Rabinowitsch *et al.*¹ have investigated the vapour pressures of CH₃COOH and CH₃COOD at different temperatures. From their results, $p(\text{CH}_3\text{COOD})/p(\text{CH}_3\text{COOH})$ is 1.017 at 118°C and passes through a maximum of 1.032 at about 50°C. They give a qualitative explanation of their results.

Similar points of view may perhaps apply for the azeotropes but it is felt that a discussion is of no avail so long as we do not know the composition and amounts of the various possible associates occurring in the liquid and the vapour. An investigation to clarify this situation was beyond the scope of the present work.

The ratio of the vapour pressures of the H and D forms of an azeotrope is not to be confused with the separation factor α for H/D on distillation of the azeotrope, $\alpha = (H/D)_{\text{vap}}/(H/D)_{\text{liq}}$. The two quantities may differ since the composition of the H and D forms of the azeotrope differ, since part of the acetic acid distills as double molecules and also since the vapour phase contains a certain amount of amine.

The separation factors for the N isotopes are quite large considering the rather high distillation temperatures. The low value for the PyHAc azeotrope may be explained by the assumption above that only part of the pyridine is strongly bound by the acetic acid as Py.4HAc. If all of the Py had been bound in this way, the separation factor would be expected to be

$$1 + 0.0034 (4/1.44) = 1.0094$$

in fair agreement with the values obtained for the other azeotropes. Of course the different structure of Py compared with the other tertiary amines may offer another explanation.

The separation factors for ^{13}C and ^{18}O are very small — of the same order as the errors of the mass spectrometer measurements. However, since they occur in the same direction in all cases, they may have some real meaning. These factors indicate that the C and O atoms of the carboxyl group are very little influenced by the formation of a compound between HAc and an amine.

EXPERIMENTAL

Preparations

Deuterated acetic acid (CH_3COOD) was prepared from acetic anhydride and D_2O (99.7 %). The acetic anhydride was purified by distillation through a 1 meter column with glass helices and reacted with the calculated amount of D_2O . The product was distilled using the 1 meter column to give a product with a 0.1°C boiling point range. The boiling point was compared with that of ordinary CH_3COOH prepared in the same way. HAc b.p.₇₆₀ = 117.70°C, DAc b.p.₇₆₀ = 116.80°C. In another experiment, however, a b.p. difference of only 0.63°C was found.

The azeotropes. Pyridine was mixed with an equal weight of HAc or DAc and the mixture was then fractionated to give a product with a 0.1–0.2°C b.p. range. Et_3NHAc and Et_3NDAc were prepared in a similar way.

HAc was added to 25 % aqueous Me_3N , water was distilled off and the remaining Me_3NHAc fractionated to a narrow b.p. range.

Me_3N was expelled by heating from its 25 % aqueous solution. The product was dried with solid NaOH and absorbed in anhydrous DAc. The resulting Me_3NDAc was fractionated to a narrow b.p. range.

Analyses

A weighed amount of azeotrope dissolved in water was washed through a cation exchanger in the H^+ form. The HAc in the eluate was titrated with standard alkali.

Physical properties

Boiling points were determined in a special all-glass apparatus with thermometer pocket and reflux cooler. Mercury thermometers were used and the pockets were filled with mercury. The H and D forms of the azeotrope were measured simultaneously. Stem and pressure corrections were applied. There may have been some uncertainty in these corrections and thus the absolute values of the boiling points may not be very exact. The b.p. differences, however, are probably correct to $\pm 0.02^\circ\text{C}$. The rate of change of b.p. with pressure has been determined by a direct comparison with the b.p. of water at three pressures near atmospheric, generally p , $p + 20$, and $p + 40$ mm Hg.

The melting point of PyHAc was determined on a small sample in a test tube and the value is thus rather rough. It was taken as the temperature at which the greater part of the sample had passed into the liquid state. Me_3NHAc and Et_3NHAc could not be made to crystallize. They formed glasses which began to soften at about -100°C .

Densities were determined with a 10 ml pycnometer at 25.00°C .

Viscosities were determined with a probable error of less than 1 % using an Ostwald viscometer.

Rayleigh distillations

A 100–200 ml sample was distilled from a 250 ml flask surrounded by a vapour thermostat at a few (1–4) degrees above the b.p. of the azeotrope. The bottom of the flask rested on an asbestos plate with a hole through which the flask was heated with a small flame. The heating was such that the distillation occurred without the formation of bubbles. The vapour thermostat prevented refluxing from the walls of the flask and from the tube leading to the condenser. 5–10 % of the total amount were taken as a first distillate and about an equal amount was left behind as residue. The first distillate and the residue were analysed for the isotope abundance of ^{15}N , and of ^{13}C and ^{18}O in the carboxyl group of the acetic acid.

The precautions described above were such as to minimize all possibilities for introducing errors giving too high values for the separation factor. Several tests with H_2O – HDO mixtures gave separation factors of 1.0222–1.0235 instead of the accepted value of 1.026 *i. e.* the separation obtained was only 85–90 % of the expected value. Similar errors may occur in the case of the azeotropic systems. No corrections have been introduced, however, since it is not certain that the errors will be of the same magnitude as those in the case of water.

Preparations for isotopic analyses

The N of the amine was transformed by Kjeldahl digestion to NH_3 and then to H_4NCl . Pyridine was digested for several days in the presence of mercury sulphate to insure complete decomposition.

Calculated amounts of $\text{Ba}(\text{OH})_2$ solution and sample were evaporated and dried to form anhydrous Ba acetate. This was pyrolyzed in a slow stream of nitrogen to give BaCO_3 which was reacted in an evacuated tube with concentrated (96 %) sulphuric acid. The CO_2 formed was purified by freezing out with liquid air and analyzed for ^{13}C and ^{18}O .

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