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Isotopic Effects in Systems Containing an Amine and Carbon Dioxide

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Dedicated to Professor *Ole Lamm* on his 60th birthday

On distillation of compounds of lower amines with carbon dioxide, which compounds are dissociated in the gas phase, there is an enrichment of several isotopes generally with the following elementary factors: $\alpha(^{14}N/^{15}N) = 1.013$, $\alpha(^{18}O/^{16}O) = 1.006-1.010$ and $\alpha(^{12}C/^{13}C) = 1.0025$. The isotope mentioned first enriches in the vapour during distillation. The vapour pressure of a secondary amine, deuterated at the nitrogen, by distillation with carbon dioxide becomes 7–9 % higher than that of the undeuterated compound at the temperature corresponding to the normal boiling point of the latter.

Carbon dioxide forms, with sufficiently low-boiling primary and secondary amines, distillable compounds, or azeotropes with a maximum boiling point. Melting and boiling points of such compounds, according to approximate determinations, are given in Table 1, which also includes some ternary azeotropes, containing ethanol or water as the third component. In this table, as in the following Me, Et, Pr and Bu represents methyl, ethyl, propyl and butyl groups, respectively.

When these compounds are distilled, there is a dissociation in the gas phase, and there is an isotopic effect for all elements whose binding conditions are changed by this dissociation. These elements are: carbon and oxygen of the carbon dioxide, and nitrogen and nitrogen-bonded hydrogen of the amine. The structure of these compounds is not known, but it is evident that these elements are involved.

Isotopic effects for carbon, oxygen and nitrogen in some of these systems have been determined by Rayleigh distillation. A similar determination of the hydrogen isotopic effects would probably meet considerable analytical difficulties. Instead, compounds deuterated at the nitrogen were prepared, and their boiling points were compared with those of the non-deuterated compounds. At the same time, other physical properties of the deuterated and non-deuterated compounds were compared.

Table 1. Melting and boiling points of compounds and azeotropes containing carbon dioxide and an amine.

	Melting point °C	Boiling point °C	B.p. of the amine °C
$MeNH_2 + CO_2$	109	83	−6.5
$EtNH_2 + CO_2$	116	81	16.6
$PrNH_2 + CO_2$	74	84	48.7
sec-$PrNH_2 + CO_2$	99	72	34
$BuNH_2 + CO_2$	75	93	78
iso-$BuNH_2 + CO_2$	77	86	68
sec-$BuNH_2 + CO_2$	44	77	63
$Me_2NH + CO_2$	35	61	7.4
$MeEtNH + CO_2$	−17	61	35
$Et_2NH + CO_2$	28	62	55.5
$MePrNH + CO_2$	< 0	72	63

	Complete solution °C	Boiling point °C
$MeNH_2 + CO_2 + EtOH$	—	72
$EtNH_2 + CO_2 + EtOH$	~ 36	74
$PrNH_2 + CO_2 + EtOH$	<10	77
$BuNH_2 + CO_2 + H_2O$	~ -20	91

Table 2. Composition and properties of compounds between carbon dioxide and secondary amines.

Formula	Me_2NH 0.528 CO_2	Me_2ND 0.503 CO_2	$MeEtNH$ 0.487 CO_2	$MeEtND$ 0.498 CO_2	Et_2NH 0.353 CO_2	Et_2ND 0.356 CO_2
Weight % amine	66.0	67.55	73.4	73.25	82.5	82.45
Boiling point at 760 mm Hg, °C	60.2	58.5	61.12	59.51	62.03	60.62
Boiling point difference, °C	1.73		1.61		1.41	
$(dp/dt)_{760}$ mm Hg/°C	41.2		40.1		38.6	
Melting point, °C	34.5	36.2	−17	−13	28.3	29.9
d_4^{25}, g/ml	1.02299	1.04187	0.96429	0.97373	0.87654	0.88218
η_{25}, centipoise	64.9	78.2	45.9		4.45	4.12
n_D^{25}	1.4520	1.4521		1.4479	1.4333	1.4350

Table 3. Vapour pressure ratios of H and D forms of amine-CO_2 compounds and separation factors for other isotopes on distillation. The errors refer to the mass spectrometric measurements.

	$Me_2NH + CO_2$ at 60°C	$MeEtNH + CO_2$ at 61°C	$Et_2NH + CO_2$ at 62°C
$p(D)/p(H)$	1.094	1.085	1.072
$\frac{(^{14}N/^{15}N)_{vpp}}{(^{14}N/^{15}N)_{liq}}$	1.0137 ± 0.0012	—	1.0080 ± 0.0012
$\frac{(^{12}C/^{13}C)_{vap}}{(^{12}C/^{13}C)_{liq}}$	1.0021 ± 0.0006	—	1.0023 ± 0.0006
$\frac{(^{18}O/^{16}O)_{vap}}{(^{18}O/^{16}O)_{liq}}$	1.0065 ± 0.0009	—	1.0081 ± 0.0009

The following systems have been investigated in detail: $Me_2NH + CO_2$, $MeEtNH + CO_2$, $Et_2NH + CO_2$ and the ternary azeotropes $EtNH_2 + CO_2 + EtOH$ and $BuNH_2 + CO_2 + H_2O$. The results are presented in a number of tables. For example, Table 2 gives the physical properties of the compounds of ordinary and deuterated secondary amines. The deuterium content of the deuterated compounds is estimated to be 95 %. No correction has been made for this approximation. The data presented in the table are those actually measured.

It is evident that the compounds contain two moles of amine for one mole of carbon dioxide, except for diethyl amine, in which system there is an excess of amine.

From the boiling point differences, and the rate of change of vapour pressure with temperature, one may calculate the ratio of vapour pressures of deuterated and non-deuterated compounds at a common temperature, *e.g.* the boiling point of the former. These data and the separation factors for the carbon, oxygen and nitrogen isotopes, determined by Rayleigh distillation, are given in Table 3.

Table 4. Distillation of $Me_2NH + CO_2$ with a 4 m column.

	% ^{15}N	% ^{18}O	% ^{13}C
Top	0.169	0.296	0.966
Still pot	0.439	0.174	1.158
	$^{14}N/^{15}N$	$^{18}O/^{16}O$	$^{12}C/^{13}C$
$Q_{top/pot}$	2.60	1.70	1.198
α	1.0137	1.0065	1.0021
n theoretical plates	70	84	86

Table 5. Viscosities of amine + CO_2 compounds and ternary azeotropes at several temperatures, and extrapolated to the boiling point. Unit: centipoise.

$Me_2NH + CO_2$		$Et_2NH + CO_2$		$EtNH_2 + CO_2 + EtOH$		$BuNH_2 + CO_2 + H_2O$	
t°C	η	t°C	η	t°C	η	t°C	η
25.00	64.9	25.00	4.45	25.00	4.71	25.00	18.0
40.5	28.2			45	2.93	40.1	10.4
50.8	18.3			60	2.11	60.0	5.8
56	14.8			70	1.71	79.8	3.65
b.p. 60	11	b.p. 62	1.4	b.p. 74	1.6	b.p. 91	2.9

Table 6. Data for the ternary azeotropes $EtNH_2 + CO_2 + EtOH$ and $BuNH_2 + CO_2 + H_2O$.

Suggested composition	$EtNH_2 + 0.5\,CO_2 + 1.89\,EtOH$	$BuNH_2 + 0.5\,CO_2 + 2.51\,H_2O$
Weight % amine	29.2	57.35
Boiling point, °C	74.1	90.6
$(dp/dt)_{760}$, mm Hg/°C	36.6	31.8
Point of complete melting, °C	~36	~ −20
d_4^{25}, g/ml	0.86694	0.96443
η_{25}, centipoise	4.71	18.0
n_D^{25}	1.3978	1.4282

Table 7. Separation factors on distillation of ternary azeotropes containing an anime and carbon dioxide.

	$EtNH_2 + CO_2 + EtOH$ at 74°C	$BuNH_2 + CO_2 + H_2O$ at 91°C
$\frac{(^{14}N/^{15}N)_{vap}}{(^{14}N/^{15}N)_{liq}}$	1.0144 ± 0.0012	1.0129 ± 0.0012
$\frac{(^{18}O/^{16}O)_{vap}}{(^{18}O/^{16}O)_{liq}}$	1.0104 ± 0.0009	1.0002 ± 0.0009
$\frac{(^{12}C/^{13}C)_{vap}}{(^{12}C/^{13}C)_{liq}}$	1.0000 ± 0.0006	1.0006 ± 0.0006

Some column distillations have been performed. Thus $Me_2NH + CO_2$ was distilled in a column of 4 m length and 13 mm inner diameter, packed with 2.7 × 2.4 × 2 mm glass helices. When approximate equilibrium had been attained, samples were taken from top and still pot. Data are given in Table 4. The small disagreement in calculated numbers of theoretical plates may derive from errors in the α values.

In another experiment, a column of 50 cm length and 6 mm i.d., packed with the same type of glass helices, was used to distil $Me_2ND + CO_2$ with 74 % D at the nitrogen position. From the boiling point, the D content at the top was estimated to be 83 ± 3 % corresponding to separation by a factor 1.7. In this case the isotopic separation factor is probably different from the vapour pressure ratio given in Table 3, and therefore the number of theoretical plates cannot be stated. A direct determination of the isotopic factor has not been undertaken because of anticipated analytical difficulties.

In a third case a 2 m column of 30 mm internal diameter was used, packed with stainless steel Heli-Pak (1.3 × 2.5 × 2.5 mm). The still pot contained water with D_2O, the column proper $Et_2NH + CO_2$, and at the top there was an excess of pure Et_2NH. At equilibrium, the diethyl amine at the top contained 85 % Et_2ND determined from its density, and the water in the pot was calculated to contain 42 % D_2O. This is a total separation by the factor 7.75. The better performance in this case as compared to the next one may be due to the packing but more probably to the lower viscosity of $Et_2NH + CO_2$ (*cf.* Table 5).

The ternary azeotropes $EtNH_2 + CO_2 + EtOH$ and $BuNH_2 + CO_2 + H_2O$ were investigated with respect to boiling point and other properties, but no corresponding deuterated systems were investigated (Table 6). These azeotropes are of a type that may be represented by a saddle surface, and they are perhaps not quite stable upon distillation. For that reason, the composition of the samples investigated may depart somewhat from the correct values. By means of Rayleigh distillation, the separation factors for carbon, oxygen and nitrogen isotopes given in Table 7 were obtained.

The low values of the carbon isotope separation factors in Table 7 are probably due to errors. There is no reason to believe that carbon will behave differently in these systems compared to the simple amine—CO_2 systems and in fact from a column distillation of $BuNH_2 + CO_2 + H_2O$ there was obtained the single stage separation factor 1.0022 for the carbon isotopes.

After this investigation, somewhat similar work was reported by Brown[1] and by Yeatts, Jr.[2] It was found that Pr_2NH (b.p. 110.7°C) with carbon dioxide gives a compound which dissociates to CO_2 and liquid amine on heating. Upon exchange between gas and liquid the separation factor $\alpha(^{12}C/^{13}C)$ varied from 1.0059 to 1.0028 and $\alpha(^{18}O/^{16}O)$ from 1.0081 to 1.0096 when temperature varied from 25 to 60°C. On distillation of a number of compounds from among those given in Table 1, separation factors for oxygen between 1.0040 and 1.0105 were obtained. The agreement with the present work is satisfactory.

EXPERIMENTAL

Preparation of amine + CO_2 compound. This was generally done by saturating the amine with CO_2 and distilling with a column repeatedly until a product with a narrow boiling point range (about 0.1°C) was obtained.

A 25 % solution of Me_2NH in water was saturated with CO_2 and $Me_2NH + CO_2$ was distilled off and refractionated.

A 70 % solution of $EtNH_2$ in water was saturated with CO_2, ethanol was added and the ternary azeotrope was distilled off and redistilled to a constant boiling point.

Butyl amine mixed with water was saturated with CO_2 and distilled to give a ternary azeotrope.

Deuterated compounds were prepared correspondingly by saturating MeEtND and Et_2ND with CO_2 and distilling.

$Me_2ND + CO_2$ was obtained by mixing $Me_2NH + CO_2$ with D_2O, distilling off $Me_2ND + CO_2$, mixing it with a new amount of D_2O, and distilling off again. This operation was repeated until the exchange was sufficiently complete.

The deuterated amines were prepared similarly from ordinary amines and D_2O. The vapour pressure ratios of some such amines at the boiling point of one of them may be interesting and they are therefore given here:
$p\mathrm{MeEtNH}/p\mathrm{MeEtND} = 1.0092$, $p\mathrm{Et_2NH}/p\mathrm{Et_2ND} = 1.0071$ and $p\mathrm{PrNH_2}/p\mathrm{PrND_2} = 1.0125$.

Physical properties were determined and *Rayleigh distillations* were performed as described earlier [3].

Preparation for isotopic analysis. CO_2 was liberated with anhydrous acetic acid and isolated by freezing out with liquid air. The nitrogen of the amines was transformed to NH_3 and H_4NCl by Kjeldahl digestion.

Errors. The only errors given are those derived from the mass spectrometric measurement. It has been observed earlier [3] that the Rayleigh distillation as performed here has a tendency to give too low separation, perhaps by 10—15 %. No corrections for this have been applied here.

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REFERENCES

1. Brown, L. L. ORNL-2983, Chemistry Division. Annual Progress Report for Period Ending June 20, 1960, p. 19.
2. Yeatts, Jr., L. B. *Ibid.*, p. 19.
3. Holmberg, K. E. *Acta Chem. Scand.* **13** (1959) 717.

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