another as the melting points of these derivatives lay closely together. In certain cases the compounds contained a colored impurity which was removed only after numerous crystallizations.

These 2-alkylbenzimidazoles form salts with acids (picric, sulfuric, etc.) which might be used in distinguishing the higher members of the series. This possibility has not yet been investigated.

Summary

1. A procedure for the preparation of 2-alkylbenzimidazoles from aliphatic acids and *o*-phenylenediamine has been described.

2. A series of 2-alkylbenzimidazoles has been prepared using normal aliphatic acids containing from one to eighteen carbon atoms.

CHICAGO, ILL. RECEIVED OCTOBER 28, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE OF THE COLLEGE OF THE CITY OF NEW YORK]

The Liquidus Curve and Surface of the Systems Lithium and Calcium Nitrates and Calcium, Lithium and Potassium Nitrates

BY ALEXANDER LEHRMAN, EDWARD ADLER, JACOB FREIDUS AND MAX NEIMAND

This paper reports an investigation of the liquidus curve and surface of the systems lithium and calcium nitrates and calcium, lithium and potassium nitrates. The work was undertaken in order to be able ultimately to define the liquidus surfaces of the quaternary system composed of the nitrates of lithium, sodium, potassium and calcium. It is hoped that the quaternary system in mind will yield a salt-bath melting below 100°. Such a salt-bath would have distinct advantages.

Of the six binary and four ternary systems that should be known before the quaternary system is investigated, five binary and two ternary are described in the literature.[1]

The completion of the present work leaves uninvestigated only the ternary system lithium, sodium and calcium nitrates (although it seems necessary in the light of the work of Rostkovsky,[1f] of Laybourn and Magdin[1g] and the data presented here, that the ternary system composed of the nitrates of sodium, potassium and calcium as presented by Menzies and Dutt[1b] should be checked).

Experimental

The salts used were prepared from C. P. products by recrystallization followed by drying except the calcium nitrate which was the C. P. salt dissolved, treated with pure lime, filtered, neutralized with nitric acid, evaporated and dried.

Temperature Measurements.—Temperatures were measured with a copper–constantan thermocouple of No. 28 wire in conjunction with a Leeds and Northrup potentiometer indicator, the cold junction being cracked ice. The couple was protected from the molten nitrates by a narrow guard tube made by drawing out Pyrex tubing and sealing at one end. It was standardized by determining the e. m. fs. at the boiling point of water and melting points of U. S. Bureau of Standards tin (231.9°), C. P. cadmium (320.9°), and purified potassium dichromate (397.5°), and plotting the deviations from the standard table of Adams.[2] While the melting point of potassium dichromate is about 10° higher than the upper end of the standard table, it was considered justifiable to extrapolate through this short range.

Method.—Mixtures of the two salts (approximately 20 g.) were made in the 2.5 × 20-cm. Pyrex tubes used in the determinations. The couple in its guard tube was inserted into the salt mixture and held in place by a two-holed stopper. A stirrer made of Pyrex rod passed through a piece of Pyrex tubing in the second hole of the stopper. It was necessary to use Pyrex glassware throughout, as molten lithium nitrate attacks soft glass.

The tube holding the salts was suspended in a small resistance furnace and heated while stirring until the salts were completely molten, care being taken to avoid excessive temperatures. It was then transferred to a double-walled test-tube and held suspended there by an asbestos ring, and constantly stirred.

As the crystallization temperature was approached, crystals formed on the test-tube wall at the surface of the molten salt and were pushed into the liquid by the stirrer. The initial crystallization temperature was seen easily, as clouds of fine crystals suddenly appeared, while above this temperature the crystals when pushed into the melt by the stirrer rapidly dissolved. No supercooling was observed in any of the stirred melts, except in the calcium nitrate region of the ternary system, where it was necessary in some cases to inoculate with very fine crystals in order to prevent the formation of supercooled glasses which when formed did not crystallize on long standing. Crystallization temperature determinations were repeated until they agreed to within 1.0°. The reported values represent at least three determinations.

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[1] (a) Carveth, *J. Phys. Chem.*, **2**, 209 (1898); (b) Menzies and Dutt, THIS JOURNAL, **33**, 1366 (1911); (c) Amadori, *Atti inst. Veneto*, **72**, 451 (1912); (d) Harkins and Clark, THIS JOURNAL, **37**, 1816 (1915); (e) Briscoe and Magdin, *J. Chem. Soc.*, **123**, 1608, 2914 (1923); (f) Rostkovsky, *J. Russ. Phys.-Chem. Soc.*, **42**, 2055 (1930); (g) Laybourn and Magdin, *J. Chem. Soc.*, 2582 (1932), 236 (1933); (h) Laybourn, Magdin and Freeman, *ibid.*, 139 (1934).

[2] "Pyrometric Practice," Bureau of Standards Technological Paper No. 170, p. 309.

The Binary System Lithium and Calcium Nitrates.—In order not to overlook any break in the liquidus curve, time–temperature and time–differential temperature cooling curves were made on a number of melts. No halt due to a transition or reaction was observed. These curves showed the eutectic temperature of the system to be at 235.2°. The apparatus used for the time–temperature and time–differential temperature cooling curves has been described previously.[3] It should be mentioned that when stirring is omitted as was the case in obtaining the cooling curves, supercooling takes place at the initial crystallization temperature and slight supercooling at the eutectic point.

Decomposition was not apparent in any of the melts until the concentration of calcium nitrate reached 60%. By slow and careful heating of this mixture decomposition was reduced to a negligible amount. The observed melting points are recorded in Table I and plotted in Fig. 1.

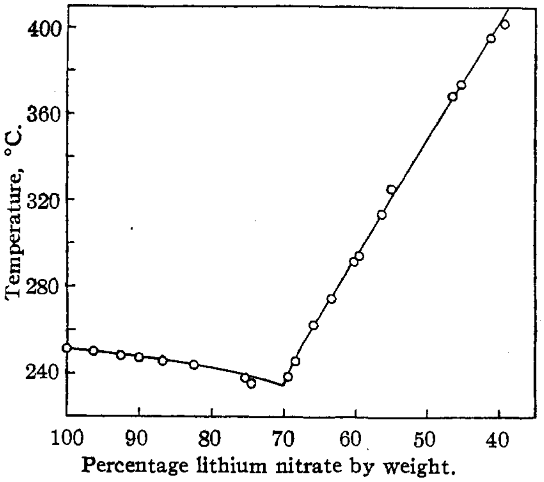

Fig. 1.—Liquidus of the lithium nitrate–calcium nitrate system.

The melting point of lithium nitrate found (251.4°) agrees well with that determined by Briscoe, Evans and Robinson (252°).[4]

TABLE I

CRYSTALLIZATION TEMPERATURES. LITHIUM NITRATE–CALCIUM NITRATE

$LiNO_3$ wt. %	Temp., °C.	$LiNO_3$ wt. %	Temp., °C.
100.0	251.4	66.0	263
96.2	250	63.5	274
92.4	248	60.3	292
90.0	247	59.5	294
86.7	246	56.3	314
82.2	244	55.0	326
75.3	237	46.5	369
74.6	235	45.3	374
69.4	238	41.2	396
68.4	246	39.4	403

The Ternary System Lithium, Potassium and Calcium Nitrates.—The region near the 100% calcium nitrate point was not investigated as calcium nitrate decomposes before it melts. In all cases care was taken not to heat the mixtures above 400° to avoid decomposition. Furthermore, no effort was made to find the boundaries of the region in which the compound $4KNO_3 \cdot Ca(NO_3)_2$ is formed from the melt. The determination of a few points in the binary system potassium and calcium nitrate showed that Rostkovsky's results[1f] are more reliable than those of Menzies and Dutt.[1b] In the region of high concentration of

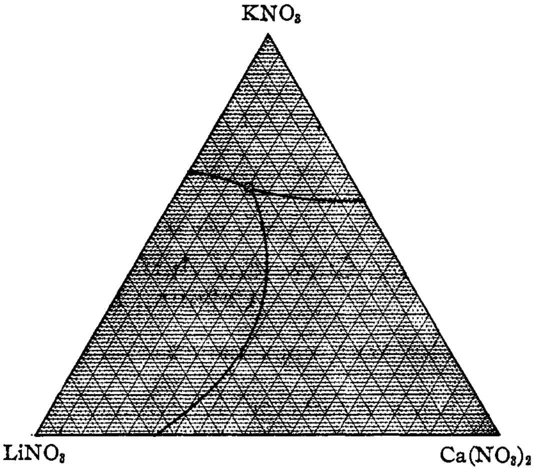

Fig. 2.—Liquidus surface of the system lithium, potassium and calcium nitrates.

TABLE II

CRYSTALLIZATION TEMPERATURES: LITHIUM, POTASSIUM AND CALCIUM NITRATES

$LiNO_3$ wt. %	KNO_3 wt. %	Temp., °C.	$LiNO_3$ wt. %	KNO_3 wt. %	Temp., °C.
36.3	29.5	211	70.0	9.9	236
27.8	23.9	304	50.1	19.9	217
23.2	39.2	229	60.0	20.0	226
13.0	40.6	215	40.1	30.0	199
27.8	20.3	322	50.1	30.0	210
16.5	64.0	142	39.9	40.0	184
19.3	49.4	149	50.2	40.0	195
40.7	10.7	331	30.0	50.1	153
35.6	17.9	301	40.9	50.0	170
19.0	54.3	141	30.0	60.0	131
31.0	10.7	371	20.0	70.0	168
9.8	79.0	247	60.0	30.0	217
9.3	71.7	210	70.0	20.0	230
27.2	33.8	219	80.0	10.0	241
18.8	19.8	373	40.0	20.0	266
22.1	48.7	146	30.0	40.0	163
2.9	70.2	215	20.0	60.0	127
16.2	50.9	142	10.0	80.0	248
3.5	56.6	149	25.1	50.0	147
25.4	30.9	267	25.0	62.0	120
11.4	26.1	362	24.0	60.4	125
11.4	31.2	338	20.0	62.0	124
8.4	49.2	146	22.4	60.1	128
50.0	9.8	283	20.0	65.0	139
60.0	10.0	230	22.8	62.9	124
26.4	61.8	124	27.0	61.0	126

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(3) Lehrman, Selditch and Skell, THIS JOURNAL, **58**, 1612 (1963).

(4) Briscoe, Evans and Robinson, *J. Chem. Soc.*, 1100 (1932).

calcium nitrate glasses were readily formed, and these showed no signs of further crystallization at room temperature even in the presence of large crystals of calcium nitrate. Cooling curves on melts of composition near that of the ternary eutectic showed a eutectic halt at 117.4°. No halt due to the inversion of potassium nitrate (128° in the pure substance[5]) was observed. This inversion of potassium nitrate should produce a slight break in the liquidus surface near the eutectic point.

The melting points of the ternary mixtures are given in Table II. The regions in which the three solid phases form (neglecting $4KNO_3 \cdot Ca(NO_3)_2$ and the low temperature form of potassium nitrate) and the eutectic points are shown in Fig. 2, the binary eutectics used being those of Rostkovsky[1f] and Carveth.[1a]

Summary

1. The liquidus curve of the binary system lithium nitrate–calcium nitrate has been determined. The eutectic temperature is 235.2°, the eutectic composition is at about 70% lithium nitrate.

2. The liquidus surface of the ternary system calcium, lithium and potassium nitrates has been explored partially. The ternary eutectic temperature is 117.4°, the eutectic composition is 15% calcium, 62% potassium and 23% lithium nitrates.

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(5) F. C. Kracek, *J. Phys. Chem.*, **34**, 225 (1930).

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A Redetermination of the Deuterium–Protium Ratio in Normal Water

BY J. L. GABBARD AND MALCOLM DOLE

In the course of preparing some deuterium-free hydrogen for use in one of the researches on the isotopes of oxygen in progress in this Laboratory, it became possible to redetermine, by means of a method involving a knowledge of the oxygen isotope ratios in water and air, the deuterium–protium ratio in normal water. Limitations of space forbid a detailed discussion of the many previous measurements of this ratio; the reader is referred to the recent papers of Morita and Titani[1] and of Hall and Jones[2] for references and comments on earlier work. At present there seem to be three apparently accurate determinations of the deuterium–protium ratio in which the difficulties due to oxygen isotope fractionation on electrolysis were recognized and avoided, namely, those of Johnston $(-18.3\,\gamma)$,[3] Morita and Titani $(-18.9\,\gamma)$ and Hall and Jones $(-16.5\,\gamma)$. The symbol γ represents in p. p. m. the density of deuterium-free water less the density of normal water; from the γ values the deuterium–protium ratio is calculated easily. The maximum difference in the above results $(2.4\,\gamma)$ is greater than the experimental errors of density measurement and is due, we believe, to the different methods used by the above authors in bringing to normal or correcting for the oxygen isotope ratios in the waters under investigation.

Since the relative atomic weight of oxygen in air and in water has been determined recently[4] it is possible to solve the oxygen isotope problem by combining the deuterium-free hydrogen with oxygen of the air and after measuring the density of resulting water, the proper correction for the difference in the atomic weight of air and water oxygen can be applied, yielding what should be the correct density of water made of isotopically pure protium and the oxygen of normal water. From this latter value the D/H ratio in normal water is calculated readily.

Experimental

The electrolysis apparatus was very kindly constructed for us by Dr. P. W. Selwood who was able to give us frequently valuable advice and suggestions from his great store of electrolytic experience. The lengthy first and second fractionations were carried out by Mr. Stanley Cristol working under an NYA grant from the government. In the case of all electrolyses after the first two, sodium peroxide instead of sodium hydroxide was added to the water to make it conducting; sodium peroxide was used because it contains no deuterium, the excess oxygen was eliminated by boiling. Data for the preparation of deuterium-free water are given in Table I where the letters after the numbers are labels serving to distinguish and identify the various waters in order to clarify the table. All the different waters mentioned in this paper will be marked in this way so that the previous history of the water can be found readily by the reader (N signifies normal, or Lake Michigan, water).

Part of the water obtained from each electrolysis was decomposed electrolytically, the hydrogen passed over hot

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(1) N. Morita and T. Titani, *Bull. Chem. Soc. Japan*, **11**, 403 (1936).

(2) N. F. Hall and T. O. Jones, THIS JOURNAL, **58**, 1915 (1936).

(3) H. L. Johnston, *ibid.*, **57**, 484, 2737 (1935).

(4) M. Dole, *J. Chem. Phys.*, **4**, 268 (1936).