TABLE I

Hydroxamic acid	Formula	M.p., °C.	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found
Picolino-	$C_6H_6O_2N_2 \cdot HCl$	190–191	46	16.1	16.3
Nicotino-[a]	$C_6H_6O_2N_2 \cdot HCl$	186–187	49	16.1	15.9
Isonicotino-	$C_6H_6O_2N_2 \cdot HCl$	206–207	70	16.1	15.8
3-Pyridineaceto-[b]	$C_7H_8O_2N_2$	177–178	73	18.4	18.5
5-Cyano-6-hydroxy-2-methyl-isonicotino-	$C_8H_7O_3N_3$	>250	65	[c]	
5-Methyl-3-isoxazolecarbo-	$C_5H_6O_3N_2$	143–145	56	19.7	19.2

[a] The free base has been reported without being characterized. E. Frommel, A. Bischler, I. T. Beck, F. Vallette and M. Favre, *Inter. Z. Vitaminforsch.*, 19, 193 (1947). [b] The free base was crystallized from ethanol. [c] The product was obtained as a yellow powder by triturating with hot water and then with hot glacial acetic acid. *Anal.* Calcd.: C, 49.8; H, 3.6. Found: C, 50.0; H, 4.1.

ing ethanol (500 ml.). The filtered ethanolic extracts were treated with hydrogen chloride gas, and the product which separated was dissolved in a minimum quantity of hot water; on addition of ethanol and cooling, crystallization of the acid salt occurred; yield 26 g. (59%), m.p. 237°.

Anal. Calcd. for $C_7H_8O_3N_2 \cdot HCl$: N, 13.7. Found: N, 13.2.

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The Diffusion Coefficients of Sodium and Potassium Iodides in Aqueous Solution at 25°[1]

BY P. J. DUNLOP[2] AND R. H. STOKES

In earlier papers[3] are reported measurements of the diffusion coefficients of eight uni-univalent chlorides and bromides. The present note deals with similar studies of sodium and potassium iodides.

Experimental.—The general technique of the measurements, which employ magnetically-stirred porous-diaphragm cells, has already been described.[3] Potassium iodide was the British Drug Houses "Analar" product, used without further purification. Sodium iodide was the same maker's laboratory reagent grade; gravimetric analysis of the thoroughly dried salt for iodide indicated a purity of 99.5%. As the most probable impurities are other sodium salts of very similar diffusion coefficients, no further purification was considered necessary. The cells were calibrated at frequent intervals by diffusing 0.1 N KCl into water, using the measurements of Harned and Nuttall as standards, as previously explained.[3]

Table I presents the integral diffusion coefficients $\bar{D}^0$ (after correction to refer to runs of zero duration) for various values of the average concentration c_m' on the lower (more concentrated) side of the diaphragm. In Table II the integral and differential diffusion coefficients are listed at round concentrations obtained by the methods listed.[3]

In connection with a theoretical interpretation of the results for the ten uni-univalent electrolytes so far studied, values of the relative viscosities of the solutions are required. Since the available data for sodium iodide[4] are somewhat sparse and are not given at 25°, they were supplemented by the measurements given in Table III. These were made with an Ostwald viscometer of standard pattern having a flow-time of 623 sec. for air-free water at 25°. Its accuracy was checked by meas-

TABLE I

INTEGRAL DIFFUSION COEFFICIENTS AT 25°

$\bar{D}^\circ(c_m')$ = integral diffusion coefficient corrected to zero duration of run (cm.^{2} sec.$^{-1}$ × 10^{-5}). c_m' = mean of initial and final concentrations on lower side of diaphragm (moles/liter).

Sodium iodide c_m'	Sodium iodide $\bar{D}^0(c_m')$	Potassium iodide c_m'	Potassium iodide $\bar{D}^0(c_m')$
0.04193	1.554	0.04263	1.932
.04396	1.549	.04383	1.927
.08608	1.535	.08339	1.907
.08811	1.539	.08401	1.906
.08916	1.535	.09213	1.904
.09011	1.538	.09340	1.904
.09073	1.535	.1673	1.883
.09181	1.537	.1748	1.882
.1729	1.529	.1783	1.883
.1759	1.533	.2624	1.879
.2697	1.534	.2753	1.874
.2740	1.534	.3670	1.881
.3743	1.534	.4404	1.890
.3874	1.539	.6090	1.909
.4434	1.541	.6157	1.910
.6142	1.560	.8856	1.940
.6237	1.559	.9079	1.940
.9235	1.579	1.485	2.010
.9324	1.571	1.487	2.006
1.412	1.614	1.936	2.050
1.425	1.612	1.970	2.052
1.675	1.641	2.471	2.101
1.982	1.668	2.494	2.104
1.998	1.667	2.561	2.112
2.341	1.701	3.072	2.161
2.364	1.701	3.100	2.167
2.801	1.742	3.899	2.225
2.835	1.739		
3.439	1.785		

TABLE II

INTEGRAL AND DIFFERENTIAL DIFFUSION COEFFICIENTS AT ROUND CONCENTRATIONS

D = differential diffusion coefficient (cm.^{2} sec.$^{-1}$ × 10^{-5}). $\bar{D}^\circ = \frac{1}{c}\int_0^c D\,dc$ = integral diffusion coefficient for experiments of vanishingly short duration between concentration c and pure water. c = moles solute/liter.

c	$\bar{D}^0$ (NaI)	$\bar{D}^0$ (KI)	D (NaI)	D (KI)
0.0[a]	1.616	2.001	1.616	2.001
.05	1.549	1.923	1.527	1.891
.1	1.536	1.900	1.520	1.865
.2	1.530	1.879	1.532	1.859
.3	1.534	1.876	1.547	1.884
.5	1.546	1.896	1.580	1.955
.7	1.559	1.919	1.612	2.001
1.0	1.582	1.953	1.662	2.065
1.5	1.623	2.008	1.751	2.166
2.0	1.667	2.058	1.846	2.254
2.5	1.711	2.107	1.925	2.347
3.0	1.753	2.154	1.992	2.440
3.5		2.203		2.533

[a] Nernst limiting values.

TABLE III

RELATIVE VISCOSITIES OF SODIUM IODIDE SOLUTIONS AT 25°

η = viscosity of solution. η° = viscosity of water. c = moles NaI/liter.

c	0.290	0.607	1.050	2.059	2.947
η/η^0	1.008	1.015	1.032	1.094	1.201

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[1] This note summarizes a thesis submitted by P. J. Dunlop in partial fulfillment of the requirements of the degree of Bachelor of Science with Honors in the University of Western Australia.

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[3] R. H. Stokes, THIS JOURNAL, 72, 763, 2243 (1950).

[4] "International Critical Tables," Vol. V, p. 15.

uring the viscosity of a 3.6% sucrose solution at 25°, taking the figures given by Gosting and Morris[5] as standard. Kinetic energy corrections were found to be negligible.

The junior author is indebted to the University of Western Australia for a Hackett Scholarship during the tenure of which this work was done.

[5] L. J. Gosting and M. W. Morris, This Journal, 71, 1998 (1949).

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Purification of Tetraethylenepentamine

By E. H. Gause, T. B. Crumpler and H. B. Jonassen

Tetraethylenepentamine, $NH_2C_2H_4NHC_2H_4NHC_2H_4NHC_2H_4NH_2$, has recently become of importance as a colorimetric reagent[1] and as an activator in low temperature copolymerization.[2] However, in both these instances relatively impure pentamine was used. The peculiar form of the graph obtained by Crumpler[1] depicting the effect of excess pentamine on color development with Cu^{++} ion suggested the need for a study of the complexes existing in solution. The purified sample is being used for a continuous variations study. Spolsky and Williams[3] noted the presence of iron in their pentamine samples and suggested the desirability of a study to differentiate the functions of iron and pentamine in the activator effect.

Previous attempts in this Laboratory to isolate this amine by fractional distillation and by the selective precipitation of normal as well as acid salts of various anions were unsuccessful. We have now succeeded by an ion exchange method in separating pure pentamine from the commercially available material which contains lower and higher molecular weight polyamines as well as an appreciable amount of iron.

Further work is in progress to determine the structure and stabilities of the complexes formed between the various metal ions and pentamine similar to that with the lower amines.[4]

Experimental

An ion exchange column 90 cm. in length and 2.2 cm. in diameter, containing the acid form of 250–500 mesh Ion-X (Dowex-50) resin was prepared. A thick slurry of the resin in distilled water was poured into the column which was partially filled with water and the resin bed was allowed to settle. A liter of solution of commercial tetraethylenepentamine (40 g./l.) was decolorized with Norit and passed through the column under about 300 mm. pressure. The amines were absorbed on approximately $^1/_3$ of the column. The column was then washed with distilled water and eluted with 0.25 *N* NaOH. The flow-rate was 0.7 cc./min. The passage of the amine layer down the column can be followed readily because of the difference in color of the several forms of the resin. The amine solution was collected in 50-cc. fractions. The eluted amine was slightly discolored; therefore, alternate fractions were decolorized with 0.5 g. of Norit and a 25-ml. aliquot diluted with 100 cc. of water, saturated with HNO_3, and titrated potentiometrically with 0.5 *N* HNO_3. Standard HCl and KCl, supporting electrolyte, may also be used. Fractions 5, 7, 9 and 11 were mainly tetraethylenepentamine together with some impurities.

The combined pentamine fractions, together with their even-numbered counterparts (250 cc.) were treated with Norit. They were then passed through a column (29 × 1.7 cm.) operated by an aspirator, at a flow-rate of 0.9 cc./min. and eluted with 0.25 *N* NaOH as described above. Again 50-cc. fractions were collected and 10-ml. aliquots titrated with 0.2 *N* HNO_3 with KNO_3 as supporting electrolyte. The following yield was obtained. (1) Fractions 1 and 2 were pure pentamine solution; (2) fraction 3 was 95% pure pentamine solution; and (3) fraction 4 was a highly impure mixture.

In order to eliminate discoloration which was probably the result of decomposition encountered using the acid form of the resin, attempts were made to adsorb the amine on both the sodium and potassium resins, but in the concentrations used in this work, the aminium ions would not replace the alkali metal ions.

It is important that the resin bed be kept in contact with liquid at all times. If allowed to run dry, channeling will occur, permitting mixing of the NaOH and amine solutions. Should this occur, the Na^+ ions may be removed by passing the solution over a small resin bed, the amount of resin depending on the amount of Na^+ present.

The iron normally present in the commercial tetraethylenepentamine is also removed during the purification. In basic solution the iron–amine complex is strongly adsorbed on the resin, and on reconversion of the resin, is displaced by the acid. Below a *p*H of about 3, the complex is red, and above this *p*H it is yellow. Both basic and acidic solutions of the complex were tested for Fe with $K_4[Fe(CN)_6]$. The acid solution gave a positive test indicating greater stability of the basic yellow form. Some of the complex was oxidized to Fe^{+++} and gave a positive test with KCNS. The eluted amine solution was found to be free of iron by these tests.

The purity of each sample was determined from the titration. The simple titration graph is not satisfactory since only the final inflection point is sharp enough to be accurately located on the curve. The differential plot ($\Delta p\text{H}/\Delta V$ *vs.* *V*) shows that there are breaks corresponding to the neutralization of the fourth and fifth nitrogen atoms of the molecule with indications of breaks for the second and third. The coincidence in the position of the maxima with their theoretical location is taken as the indication of purity (see Fig. 1).

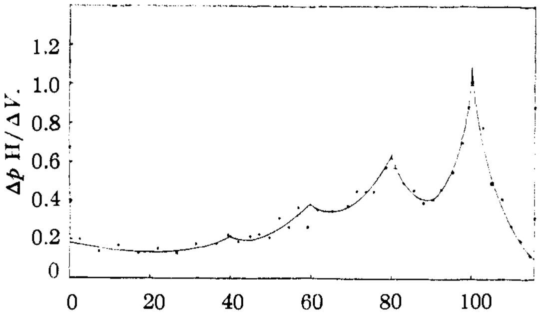

Fig. 1.

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[1] T. B. Crumpler, *Anal. Chem.*, 19, 325 (1947).

[2] R. Spolsky and H. L. Williams, *Ind. Eng. Chem.*, 42, 1847 (1950).

[3] Private communication, H. L. Williams to H. B. Jonassen.

[4] H. B. Jonassen, R. B. LeBlanc and R. M. Rogan, This Journal, 72, 4968 (1950).

The Fluorination of Aqueous Selenious Acid

By John W. George and S. Young Tyree, Jr.

Selenious acid solutions of varying strengths have been fluorinated in an attempt to determine optimum conditions for conversion to selenic acid.

$$H_2SeO_3 + F_2 + H_2O \longrightarrow H_2SeO_4 + 2HF$$