88°. This 1-ethyl derivative is very soluble in cold water, alcohol, and chloroform and slightly soluble in ether; it does not give a Wheeler–Johnson color test.

Anal. Calcd. for $C_8H_{12}O_2N_2$: C, 57.10; H, 7.20; N, 16.67. Found: C, 57.21; H, 7.13; N, 16.58.

1-Ethyluracil.—This was obtained by dissolving the above compound (1.00 g.) in concentrated hydrochloric acid (10 cc.) and concentrating to dryness on a steam-bath. The residue was crystallized from a solution of alcohol and ether and separated as clusters of prisms; m. p. 147.5°; yield 0.53 g. 1-Ethyluracil is very soluble in cold water, alcohol and acetone, slightly soluble in ether and sparingly soluble in hot carbon tetrachloride; it did not give a Wheeler–Johnson color test.

Anal. Calcd. for $C_6H_8O_2N_2$: C, 51.40; H, 5.76; N, 20.00. Found: C, 51.61; H, 5.75; N, 20.14.

1,2 - Dihydro - 2 - keto - 4 - ethoxypyrimidine was isolated from the products formed in the interaction of either acetobromo-*d*-mannose or acetobromo-*d*-galactose with 2,4-diethoxypyrimidine. As the methods of isolating the material in the two cases was quite similar only the details of the procedure, in which the former sugar was used, will be described. A solution of 7 g. of acetobromo-*d*-mannose and 7 g. of 2,4-diethoxypyrimidine was heated at 65° for seventy hours; after cooling a small amount of uracil deposited and this was removed. From the filtrate, 1,2-dihydro-2-keto-1-ethyl-4-ethoxypyrimidine (2 g.) slowly crystallized and after a week it was collected. The sirupy filtrate over a period of a year slowly deposited a crystalline product. The solid was removed by filtration and washed with a small amount of ether. Trituration with chloroform separated the ethoxy derivative from uracil. The chloroformic extract was concentrated and the residue recrystallized from a solution containing 90% benzene and 10% absolute ethyl alcohol; massive aggregates of colorless plates were thus obtained; yield 0.36 g.; m. p. 168°; a mixed melting point with 1,2-dihydro-2-keto-4-ethoxypyrimidine[17] was unchanged. The properties as well as the response to the Wheeler–Johnson color test are identical with those described previously for this compound.

Anal. Calcd. for $C_6H_8O_2N_2$: C, 51.40; H, 5.76; N, 20.00. Found: C, 51.75; H, 5.76; N, 19.95.

Uracil was isolated in traces in all experiments except when acetobromo-*d*-glucose was used. This pyrimidine was easily obtained in the pure state by triturating the crude material with chloroform and then recrystallizing from water; it was identified by its properties, Wheeler–Johnson color test and analysis.

Summary

Acetobromoglycosides, in general, interact with 2,4-diethoxypyrimidine to give 1,2-dihydro-2-keto - 1 - acetylglycosido - 4 - ethoxypyrimidines. Appreciable amounts of the secondary product, 1,2 - dihydro - 2 - keto - 1 - ethyl - 4 - ethoxypyrimidine are also formed. Presumptive evidence indicates that by-products, structurally related to the 4-ethoxy-2-triacetyl-*d*-ribosidopyrimidine which is formed in the interaction of acetobromo-*d*-ribose and 2,4-diethoxypyrimidine, are present in the products of the reaction of 2,4-diethoxypyrimidine with acetobromo-*d*-mannose and with acetobromo-*d*-galactose: however, attempts to isolate these analogs in the crystalline condition have thus far been unsuccessful. Hydrolysis of 1-acetylglycosidopyrimidine derivatives with alcoholic hydrochloric acid produces the 1-glycosidouracils. 1-*d*-Xylosido-, 1-*l*-arabinosido- and 1-*d*-galactosidouracil were prepared in this manner and their chemical properties found to be similar to those of uridine.

WASHINGTON, D. C. RECEIVED NOVEMBER 16, 1936

[17] Hilbert and Jansen, THIS JOURNAL, **57**, 552 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Conductivities of One-Molal Mixtures of Alkali Halides and Nitrates

BY PIERRE VAN RYSSELBERGHE AND LEE NUTTING

Introduction

As pointed out by Smith and Gortner,[1] few systematic studies of the conductivity of mixed electrolytes are available for theoretical investigation. Moreover, the available data have not as yet received an entirely satisfactory interpretation. The small but definite departures from the mixture rule observed by Stearn and by Ruby and Kawai[2] in the case of mixed alkali halides have recently been discussed by Van Rysselberghe and Nutting.[3] They showed that these departures could be reduced appreciably if the mixture rule is corrected by means of simple but plausible assumptions concerning the adjustment of mobilities which takes place upon mixing. The modified form of the mixture rule obtained by them involves the transport numbers of the ions in solutions of the pure salts. As these transport numbers are not always known with great accuracy calculations of real significance cannot be carried

---

[1] Smith and Gortner, *J. Phys. Chem.*, **37**, 79 (1933).

[2] Stearn, THIS JOURNAL, **44**, 670 (1922); Ruby and Kawai, *ibid.*, **48**, 1119 (1926).

[3] Van Rysselberghe and Nutting, *ibid.*, **56**, 1435 (1934).

TABLE I

DENSITIES AND CONDUCTIVITIES OF 1 MOLAL MIXTURES OF ALKALI HALIDES AND NITRATES

Molality	Density	Specific conductivity	Equivalent conductivity Measured	Equivalent conductivity Calculated	ΔΛ
		1. $LiCl + KI$			
1 $LiCl$	1.0202	0.07198	73.54		
$^3/_4$ $LiCl$ + $^1/_4$ KI	1.0433	.08174	84.09	84.80	−0.71
$^1/_2$ $LiCl$ + $^1/_2$ KI	1.0660	.09178	95.08	96.00	− .92
$^1/_4$ $LiCl$ + $^3/_4$ KI	1.0884	.10226	106.66	107.31	− .65
1 KI	1.1106	.11292	118.56		
		2. $NaCl + KI$			
1 $NaCl$	1.0360	0.08439	86.21		
$^3/_4$ $NaCl$ + $^1/_4$ KI	1.0550	.09120	93.83	94.30	−0.47
$^1/_2$ $NaCl$ + $^1/_2$ KI	1.0735	.09810	101.64	102.38	− .74
$^1/_4$ $NaCl$ + $^3/_4$ KI	1.0923	.10542	109.94	110.47	− .53
1 KI	1.1106	.11292	118.56		
		3. $KCl + KI$			
1 KCl	1.0414	0.10861	112.06		
$^3/_4$ KCl + $^1/_4$ KI	1.0589	.10963	113.62	113.68	−0.06
$^1/_2$ KCl + $^1/_2$ KI	1.0762	.11064	115.18	115.31	− .13
$^1/_4$ KCl + $^3/_4$ KI	1.0934	.11179	116.88	116.93	− .05
1 KI	1.1106	.11292	118.56		
		4. $KCl + NaI$			
1 KCl	1.0414	0.10861	112.06		
$^3/_4$ KCl + $^1/_4$ NaI	1.0575	.10346	106.97	106.97	0.00
$^1/_2$ KCl + $^1/_2$ NaI	1.0735	.09826	101.85	101.88	− .03
$^1/_4$ KCl + $^3/_4$ NaI	1.0890	.09295	96.54	96.80	− .26
1 NaI	1.1059	.08820	91.71		
		5. $NaCl + KNO_3$			
1 $NaCl$	1.0360	0.08439	86.21		
$^9/_{10}$ $NaCl$ + $^1/_{10}$ KNO_3	1.0379	.08351	87.35	86.87	+0.48
$^3/_4$ $NaCl$ + $^1/_4$ KNO_3	1.0409	.08674	89.09	87.87	+1.22
$^1/_2$ $NaCl$ + $^1/_2$ KNO_3	1.0455	.08841	91.31	89.52	+1.79
$^1/_4$ $NaCl$ + $^3/_4$ KNO_3	1.0504	.08897	92.36	91.17	+1.19
$^1/_{10}$ $NaCl$ + $^9/_{10}$ KNO_3	1.0530	.08903	92.73	92.17	+0.56
1 KNO_3	1.0551	.08895	92.83		
		6. $KCl + KNO_3$			
1 KCl	1.0414	0.10861	112.06		
$^9/_{10}$ KCl + $^1/_{10}$ KNO_3	1.0425	.10659	110.14	110.13	+0.01
$^3/_4$ KCl + $^1/_4$ KNO_3	1.0446	.10343	107.05	107.25	− .20
$^1/_2$ KCl + $^1/_2$ KNO_3	1.0482	.09843	102.14	102.44	− .30
$^1/_4$ KCl + $^3/_4$ KNO_3	1.0515	.09367	97.50	97.63	− .13
$^1/_{10}$ KCl + $^9/_{10}$ KNO_3	1.0534	.09086	94.74	94.76	− .02
1 KNO_3	1.0551	.08895	92.83		
		7. $NaCl + NaNO_3$			
1 $NaCl$	1.0360	0.08439	86.21		
$^9/_{10}$ $NaCl$ + $^1/_{10}$ $NaNO_3$	1.0373	.08304	84.95	85.23	−0.28
$^3/_4$ $NaCl$ + $^1/_4$ $NaNO_3$	1.0396	.08148	83.48	83.75	− .27
$^1/_2$ $NaCl$ + $^1/_2$ $NaNO_3$	1.0431	.07887	81.04	81.28	− .24
$^1/_4$ $NaCl$ + $^3/_4$ $NaNO_3$	1.0466	.07635	78.67	78.82	− .15
$^1/_{10}$ $NaCl$ + $^9/_{10}$ $NaNO_3$	1.0485	.07480	77.21	77.34	− .13
1 $NaNO_3$	1.0497	.07387	76.36		
		8. $KCl + NaNO_3$			
1 KCl	1.0414	0.10861	112.06		
$^9/_{10}$ KCl + $^1/_{10}$ $NaNO_3$	1.0419	.10415	107.52	108.49	−0.97
$^3/_4$ KCl + $^1/_4$ $NaNO_3$	1.0433	.09761	100.77	103.13	−2.36
$^1/_2$ KCl + $^1/_2$ $NaNO_3$	1.0456	.08841	91.30	94.21	−2.91
$^1/_4$ KCl + $^3/_4$ $NaNO_3$	1.0479	.08038	83.03	85.28	−2.25
$^1/_{10}$ KCl + $^9/_{10}$ $NaNO_3$	1.0493	.07629	78.81	79.93	−1.12
1 $NaNO_3$	1.0497	.07387	76.36		

TABLE I (*Concluded*)

Molality	Density	Specific conductivity	Equivalent conductivity Measured	Equivalent conductivity Calculated	ΔΛ
		9. $KNO_3 + NaNO_3$			
1 KNO_3	1.0551	0.08895	92.83		
$^3/_4$ KNO_3 + $^1/_4$ $NaNO_3$	1.0537	.08491	88.41	88.71	−0.30
$^1/_2$ KNO_3 + $^1/_2$ $NaNO_3$	1.0525	.08108	84.21	84.59	− .38
$^1/_4$ KNO_3 + $^3/_4$ $NaNO_3$	1.0512	.07737	80.15	80.48	− .35
1 $NaNO_3$	1.0497	.07387	76.36		

out in all cases. In this paper we present a series of data obtained with mixtures of alkali halides and alkali nitrates of total molality one. These data are compared with the values derived from the simple, uncorrected mixture rule.

Experimental

A complete description of the circuit used in this work has been given elsewhere by Nutting.[4] One feature of the method is the use of a vacuum tube oscillator as a source of alternating current. A frequency of 1000 ± 5 cycles was obtained by calibrating the oscillator against a 1000 cycle tuning fork. To facilitate the determination of the point at which the bridge was in balance, a two-stage audiofrequency amplifier was used. Comparative tests with a Grinnell Jones bridge used in this Laboratory for other purposes gave satisfactory results. The accuracy of the resistance measurements was estimated at ±0.05%.

The conductivity cell was similar in design to that proposed by McBain, Laing and Titley.[5] A detailed study of the variation of cell constant was made in connection with the present measurements and others to be reported later. Observations in general agreement with those of Jones and Bollinger[6] were made and the true value of the cell constant was obtained for each resistance through an extensive series of measurements involving the various Kohlrausch solutions (prepared according to "I. C. T.," Vol. VI, p. 230) and a number of solutions of single salts for which reliable data are available in the literature. A water thermostat (later replaced by an oil one without any noticeable change in the slight temperature fluctuations nor in the measured resistances) kept the temperature within 25 ± 0.02°.

Salts of the highest purity were used (Kahlbaum, für Analyse; Merck, Reagent, analyzed; Baker, c. p. analyzed). Water of specific conductance consistently lower than 2×10^{-6} was used throughout, but no correction was necessary as all our specific conductances were of the order of 10^{-1} and the accuracy was estimated at ±0.15%. Our results with pure salts compare quite well with those of Stearn and of Ruby and Kawai (for 1 molal KCl, S. finds 111.50; R. and K. find 112.29; we find 112.06; for 1 molal NaCl, S. finds 86.36; R. and K. find 86.07; we find 86.21).

The results are reported in Table I. The densities, specific and equivalent conductivities are given in columns 2 to 4. In column 5 we give the values computed by the ordinary mixture rule and in column 6 the differences ΔΛ between the experimental and theoretical values.

Discussion

The differences between measured and calculated values are in all cases quite definite but regularities are difficult to detect. It can be seen that in most cases the departure from the mixture rule is the larger, the larger the difference between the conductivities of the pure salts. There are, however, conspicuous exceptions (mixtures of sodium chloride and potassium nitrate and mixtures of potassium chloride and sodium nitrate). In Table II we have arranged the various mixtures studied by us and the 1-molal mixtures of NaCl + KCl, NaBr + KBr, NaI + KI studied by Stearn in the order corresponding to decreasing differences between the conductivities of the pure salts. For each pair of salts we give this difference (λ) and the maximum deviation between measured and calculated conductivities (ΔΛ) for the intermediate mixtures. There is a rough parallelism between these two quantities (if the KCl + $NaNO_3$ and the NaCl + KNO_3 mixtures are left out of consideration). A similar parallelism holds at the other total concentrations for which data are available. The mixture rule is thus more nearly correct when the mobilities of the component ions are only slightly different from one another in solutions of the pure salts. The mobilities in the mixtures will then differ but little from their values in solutions of the pure salts. When mobilities are quite different, the adjustment which has to take place upon mixing is less likely

TABLE II

Mixtures	λ	ΔΛ
LiCl + KI	45.02	−0.92
KCl + $NaNO_3$	35.70	−2.91
NaCl + KI	32.35	−0.74
NaBr + KBr	26.60	− .60
NaI + KI	26.05	− .65
NaCl + KCl	25.24	− .63
KCl + NaI	20.35	− .26
KCl + KNO_3	19.23	− .30
KNO_3 + $NaNO_3$	16.47	− .38
NaCl + $NaNO_3$	9.85	− .24
NaCl + KNO_3	6.62	+1.79
KCl + KI	6.50	−0.13

---

[4] Nutting, *J. Chem. Educ.*, **12**, 286 (1935).

[5] McBain, Laing and Titley, *J. Chem. Soc.*, **115**, 1279 (1919).

[6] Jones and Bollinger, THIS JOURNAL, **53**, 411 (1931).

to lead to satisfactory agreement with the mixture rule. When large departures are observed, as in the case of solutions containing simultaneously the ions Na^+, K^+, Cl^-, NO_3^-, some specific effect is probably present and its cause may be due to slightly incomplete dissociation of one of the salts present. Outside of these exceptional cases, the regularities which we have just discussed hold whether the salts have a common ion or not.

The application of the mixture rule to solutions of a given molality rather than to solutions of a given molar concentration has been quite customary. We have found that the departures between measured and calculated conductivities are of the same order of magnitude in both scales of concentration.

Summary

1. The densities and the conductivities of nine pairs of alkali halides and nitrates have been measured at a total concentration of one-molal.

2. The mixture rule has been found to be more nearly correct when the component salts have conductivities which differ but slightly.

3. Attention has been called to the wide discrepancies between measured and calculated conductivities in the case of solutions containing simultaneously the ions Na^+, K^+, Cl^- and NO_3^-.

STANFORD UNIVERSITY, CALIF.

RECEIVED NOVEMBER 3, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Conductivities of Concentrated Binary Mixtures of Electrolytes with a Common Anion and at Least One Ion of Charge Two

BY PIERRE VAN RYSSELBERGHE, S. W. GRINNELL AND J. M. CARLSON

Introduction

In the foregoing paper, Van Rysselberghe and Nutting[1] have shown, in general agreement with previous results of Stearn and of Ruby and Kawai,[2] that mixtures of 1-1 salts exhibit but small departures from the mixture rule, with the exception of mixtures containing simultaneously the Na^+, K^+, Cl^- and NO_3^- ions for which the departure is sometimes larger than 2 conductivity units. The results seem to show that there is a rough parallelism between the maximum departure from the mixture rule observed for a series of mixtures of a given total concentration and the difference between the conductivities of the pure salts at this same concentration.

In the case of mixtures containing ions of higher valence Smith and Gortner[3] observed departures as large as 7 conductivity units on a Λ of about 120 at concentrations as low as 0.01 *N*. In the present investigation we have studied mixtures for which extreme departures from the mixture rule were observed (cadmium halides + potassium halides) and others for which large departures were expected but were actually found to be small (magnesium chloride + alkali halides). Other cases are of an intermediate type. Some of these mixtures have been studied previously in a less systematic manner from the point of view of complex ion formation. This older literature is reviewed in various monographs such as that of Walden.[4] The interpretation given by the various authors is based upon the Arrhenius theory and should be carefully revised.

Experimental

The method followed in the present work is essentially the same as that used by Van Rysselberghe and Nutting.[1] Solutions were prepared on a volume concentration basis by means of calibrated glassware. The salts used were of the highest possible purity (Baker C. P. Analyzed, Merck reagent analyzed, Kahlbaum für Analyse). Several of these salts, however, are very hygroscopic, others decompose upon drying at temperatures above 120° and, although all the usual precautions were taken, the accuracy is in several cases less than ±0.5% on the absolute value of the conductivity. Mixtures were prepared by mixing solutions of the pure salts. Conductivities of the pure salts were measured several times, each time with a freshly prepared solution, and were found to be at least as accurate as the data available in "I. C. T." or in the Landolt–Börnstein–Roth Tables. The temperature was in all cases 25 ± 0.02°. In Table I we give the measured specific conductivity, the measured equivalent conductivity, the equivalent conductivity as deduced from the mixture

---

[1] Van Rysselberghe and Nutting, THIS JOURNAL, **59**, 333 (1937).

[2] Stearn, *ibid.*, **44**, 670 (1922); Ruby and Kawai, *ibid.*, **48**, 1119 (1926).

[3] Smith and Gortner, *J. Phys. Chem.*, **37**, 79 (1933).

[4] Walden, "Das Leitvermögen der Lösungen," in "Handbuch der allgemeinen Chemie," Akademische Verlagsgesellschaft, Leipzig, Vol. IV, Part II, 1924, pp. 257–262.