glass bulbs, this operation being carried out in an inert atmosphere.

Department of Chemistry
Massachusetts Institute of Technology
Cambridge 39, Mass.

The Conductance and Viscosity of Highly Concentrated Aqueous Solutions of Hydrazinium Chloride and Hydrazinium Nitrate

By Ralph P. Seward

Received October 25, 1954

Since the properties of salt solutions at concentrations higher than those corresponding to saturation at room temperature have been but little investigated, it seemed worthwhile to measure some of the properties of solutions of salts having sufficiently low melting points that the observations could be made up to 100% salt at moderately elevated temperatures. In an earlier publication,(1) measurements of the viscosity and electrical conductance of solutions of tetrabutylammonium picrate in butyl alcohol over the complete concentration range, 0–100% salt, were reported. It was shown that the salt behaved as if incompletely dissociated in dilute solution but, judging from the behavior of the conductance–viscosity product, became fully dissociated at very high salt concentrations. As the extent to which the conductance–viscosity product may be relied on as a measure of the degree of dissociation is questionable, it appeared desirable to have measurements on aqueous solutions of uni-univalent salts in which little or no ion pair formation is expected. Hydrazinium chloride, N_2H_5Cl, and hydrazinium nitrate $N_2H_5NO_3$, were found to be suitable salts for this purpose. Measurements of the density, viscosity and conductance were made on solutions up to 100% salt for hydrazinium chloride at 95° and for hydrazinium nitrate at 75°. Since it was thought that the temperature coefficients of conductance and viscosity might be of interest, measurements were made at 25° with both salts up to approximate saturation, and with the chloride at several other temperatures.

C. A. Kraus(2) has recently reviewed previous measurements of conductance and viscosity in concentrated aqueous solutions of uni-univalent salts. The salt concentration, however, did not exceed 60 mole % in any of these solutions. The four salts, silver nitrate, ammonium nitrate, cesium formate and potassium formate discussed by Kraus showed, with increasing salt concentration, an initial sharp drop in the conductance–viscosity product followed by a leveling off or flat minimum. The measurements reported here confirm the existence of the minimum and show that at still higher concentrations the conductance–viscosity product increases smoothly to its limiting value at 100% salt.

Experimental

The hydrazinium salts were prepared by adding a slight excess of hydrazine hydrate to a mixture of five volumes of methanol to one of concentrated acid. The salts precipitated on cooling and were recrystallized from methanol and dried in vacuum at room temperature. $N_2H_5 \cdot NO_3$ melted at 70.5°, N_2H_5Cl at 92.0°.

The conductance bridge and viscometers were those previously described.(1) Densities were measured with a 5-ml. pycnometer, except for that of the pure chloride which, because the salt crystallized in the pycnometer so rapidly, was obtained by dropping a calibrated bulb with a capillary outlet into the fused salt, drawing out air in a vacuum, and then letting in air to force the liquid into the bulb.

Table I

Mole % salt	Density	c	Λ	$\eta \times 10^3$	$\Lambda\eta$
		$N_2H_5 \cdot Cl$ at 25°			
0.35	1.001	0.1896	107.2	8.99	0.962
2.85	1.035	1.516	87.3	9.24	.811
8.07	1.092	3.990	69.8	10.74	.740
11.29	1.120	5.338	60.2	11.96	.720
15.03	1.149	6.743	50.5	13.90	.702
20.50	1.182	8.542	37.6	19.20	.722
28.20	1.224	10.70	26.3	29.00	.764
		$N_2H_5 \cdot Cl$ at 95°			
0.35	0.968	0.183	284.0	3.04	0.863
2.85	0.998	1.463	208.4	3.40	.710
8.07	1.052	3.845	155.6	4.15	.662
11.29	1.082	5.151	131.8	4.90	.646
15.03	1.110	6.613	111.5	5.60	.625
20.50	1.149	8.282	88.30	7.03	.621
28.20	1.186	10.39	64.07	9.89	.634
38.40	1.227	12.60	43.90	15.50	.685
50.65	1.266	14.63	28.00	26.83	.742
59.97	1.293	16.02	19.50	40.08	.782
69.80	1.313	17.20	13.37	62.5	.837
81.30	1.334	18.35	8.65	103.8	.899
91.50	1.352	19.25	5.78	162.2	.940
100.00	1.363	19.89	4.10	234.4	.960
		$N_2H_5 \cdot NO_3$ at 25°			
0.23	1.002	0.125	103.6	8.95	0.927
0.98	1.018	0.529	88.1	8.92	.786
2.10	1.040	1.058	79.8	9.08	.724
4.25	1.083	2.167	67.3	9.51	.640
9.23	1.163	4.226	50.4	11.57	.583
15.8	1.242	6.51	36.34	15.80	.574
27.2	1.340	9.36	22.10	27.54	.609
38.7	1.403	11.25	14.55	44.37	.646
		$N_2H_5 \cdot NO_3$ at 75°			
2.1	1.017	1.070	160.4	4.04	0.648
4.8	1.063	2.239	130.9	4.47	.585
7.5	1.113	3.511	108.3	5.12	.554
11.2	1.160	4.882	88.83	6.06	.538
15.9	1.215	6.390	71.05	7.63	542
22.9	1.277	8.194	53.78	10.43	.562
30.7	1.334	9.863	40.40	14.15	.572
43.3	1.402	11.83	27.02	22.8	.616
63.5	1.472	13.96	15.39	43.0	.662
78.2	1.510	15.08	10.42	65.0	.678
100.0	1.549	16.29	6.12	115.1	.705

As the conductances were much greater than those encountered in the butanol solutions, a new cell was constructed. The cell consisted of two 1.5-cm. electrode chambers, equipped with 1-cm. platinum electrodes, connected by about 7 cm. of 1-mm. capillary tubing. The cell constant, determined with the "one demal" potassium chloride solution of Jones and Bradshaw(3) was 276.4. Bright platinum electrodes were employed because platinum black catalyzes decomposition of the hydrazinium salts. The solutions appeared to be perfectly stable with the bright elec-

---

(1) R. P. Seward, This Journal, **73**, 515 (1951).

(2) C. A. Kraus, *J. Phys. Chem.*, **58**, 673 (1954).

(3) G. Jones and B. C. Bradshaw, This Journal, **55**, 1780 (1933).

trodes. A change in frequency of 1000 to 2000 cycles caused a change of 0.1 to 0.2% in the balancing resistance. No correction was made for this effect as it was quite constant in all solutions including that of the calibrating solution. The measurements reported were obtained at a frequency of 2000 cycles. Considering possible errors in determining concentration, density, viscosity and conductance, the values of the conductance–viscosity product should be accurate to about ±1%.

Results and Discussion

Values of concentration (c) in moles per liter, density in g. per ml., the equivalent conductance (Λ), the viscosity (η) in poises, and the $\Lambda\eta$ product for solutions of varying composition are presented in Table I.

Plots of the logarithms of the equivalent conductances and of the logarithms of viscosities against the reciprocals of absolute temperatures were made for hydrazinium chloride solutions. Nearly, but not quite, linear relations were found. From the estimated slopes of these curves at 95°, values for the activation energy of the conduction process and for the activation energy of viscous flow were calculated, these quantities being respectively defined by the equations $\Lambda = ae^{-A/RT}$ and $\eta = be^{B/RT}$.

The conductance–viscosity products from the table have been plotted against the mole % of salt in Fig. 1. The decrease in the conductance–viscosity product, with increasing salt concentration, to a minimum and continuous increase beyond the minimum to the value for 100% salt is what was previously found for tetrabutylammonium picrate in butanol.[1] Quantitatively, however, there is considerable difference. With the aqueous hydrazinium salt solutions the minimum appears at much higher salt concentration, 5–8 mole per liter compared to less than 0.1 mole salt per liter in the butanol system. Also, the conductance–viscosity product for hydrazinium chloride at the minimum is 65% of the value for the fused salt and for hydrazinium nitrate 77%, compared to only 20% for tetrabutylammonium picrate in butanol.

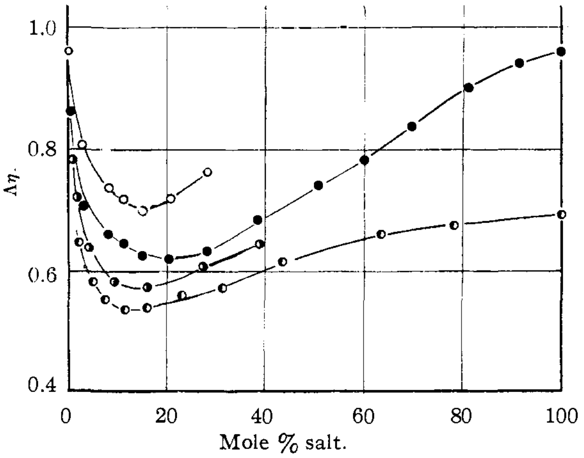

Fig. 1.—The conductance–viscosity product as a function of composition: O, $N_2H_5{\cdot}Cl$ at 25°; ●, $N_2H_5{\cdot}Cl$ at 95°; ◑, $N_2H_5{\cdot}NO_3$ at 25°; ◐, $N_2H_5{\cdot}NO_3$ at 75°.

Campbell and Kartzmark,[4] who measured the conductance and viscosity of ammonium nitrate solutions at 95°, found no upturn in the conductance viscosity product although their concentrations ran up to 57 mole % salt. No reason for the difference between the hydrazinium nitrate and ammonium nitrate systems can be suggested.

It was not thought profitable to attempt to evaluate the limiting equivalent conductance of the hydrazinium salts since, at elevated temperatures, considerable hydrolysis may be expected in very dilute solutions. Based on Gilbert's[5] value of 59 for the limiting equivalent conductance of the hydrazinium ion at 25° and the difference between the conductance–viscosity products for hydrazinium chloride at 25 and 95°, a value of 1.17 for the conductance–viscosity product at infinite dilution at 95° is estimated. This value is definitely larger than the 0.96 for the fused hydrazinium chloride at this temperature, in contrast to the substantial equality of the limiting product in butanol at 91° and the product for fused tetrabutylammonium picrate at 91°.

The activation energies have been plotted against the mole % of salt in Fig. 2. No great accuracy can be presumed for these values but they appear sufficiently self consistent to lead to the conclusions that the temperature coefficient of viscosity is always greater than that of conductance except for the pure fused salt and that both coefficients pass through a flat minimum with increasing salt concentration. Since even the limiting conductance–viscosity product for aqueous solutions in general decreases with rising temperature, this phenomenon is probably related to the structure of water rather than to the ionic atmosphere.

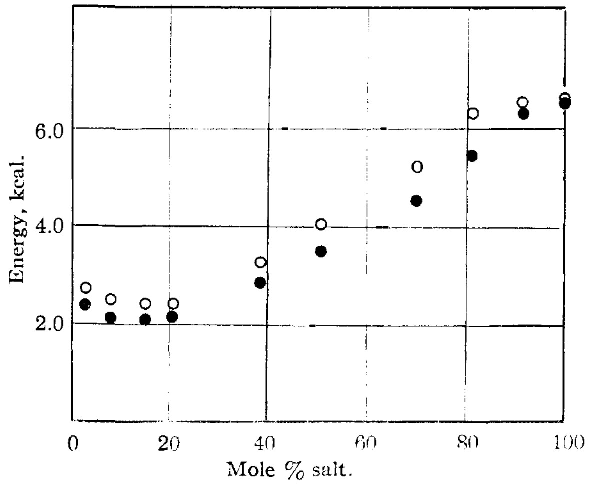

Fig. 2.—Activation energy for conductance ● and for viscous flow O in aqueous N_2H_5Cl at 95°.

Wishau and Stokes[6] have shown recently that extension of the Onsager treatment of conductance, with the addition of a correction for changes in bulk viscosity of the solutions, can account satisfactorily for the measured conductances of ammonium chloride to 5 molar without assumption of any ion-pairing. If one assumes ion-pairing to be absent in hydrazinium chloride solution, it is obvious that

---

(4) A. N. Campbell and E. M. Kartzmark, *Can. J. Chem.*, **30**, 128 (1952).

(5) E. C. Gilbert, THIS JOURNAL, **53**, 3956 (1931).

(6) B. F. Wishau and R. R. Stokes, *ibid.*, **76**, 2065 (1954).

changes in the conductance–viscosity product alone are not reliable as indicating changes in the degree of dissociation of a salt. The equations of Wishau and Stokes cannot account for an increase in the conductance–viscosity product and some significant change in the theory must be introduced before the behavior of salts at extremely high concentrations is understood.

College of Chemistry and Physics
The Pennsylvania State University
State College, Penna.

The Preparation of Chloromethyl Derivatives of Germanium and Silicon by the Diazomethane Method

By Dietmar Seyferth[1] and Eugene G. Rochow

Received August 19, 1954

This paper reports the application of the reaction of diazomethane with germanium and silicon halides (or their organic derivatives) to the preparation of chloromethyl compounds of these two elements. It is shown that the reaction proceeds more readily with the halides of germanium than with those of silicon, permitting yields as high as 94% of theoretical for germanium (in the preparation of chloromethylgermanium trichloride) and 73% for silicon (in the preparation of chloromethyldichlorosilane). Other methods for the same purpose are available. Side-chain chlorination of tetramethylsilane,[2] of methylchlorosilanes[3-6] and of methylsiloxanes[7] can be accomplished by treatment with chlorine under the influence of ultraviolet light or by reaction with sulfuryl chloride in the presence of a peroxide catalyst. However, similar reactions have not been reported for any methylgermanium compounds. These methods cannot be applied to the preparation of chloromethyl derivatives of silanes containing an Si–H bond, since either reagent would cause chlorination of that bond as well. Even when they do apply, chlorinations give only moderate yields of mono-(chloromethyl) derivatives, and so it seemed desirable also to prepare our chloromethyl derivatives of germanium by a more efficient method.

Hellerman and Newman[8] first described a novel method for the preparation of halomethyl derivatives of mercury: the reaction of diazomethane with a mercuric halide in ether solution

$$\mathrm{HgCl_2 + CH_2N_2 \longrightarrow ClHgCH_2Cl + N_2}$$

More recently Yakubovich and his co-workers have extended this "methylenation"[9] reaction to the preparation of α-haloalkyl derivatives of thallium,[10] silicon,[11] tin,[11a,12] lead,[11a,13] phosphorus,[14,15] arsenic,[14,16,17] antimony[14,16] and bismuth.[14,16]

We found that treatment of germanium tetrachloride with one equivalent of diazomethane in ether solution at −60 to −70° in the presence of copper powder gave a 93.7% yield of chloromethylgermanium trichloride. Higher boiling residues from three preparations of approximately 0.1 mole each were combined and fractionated to give 5.5 g. of bis-(chloromethyl)-germanium dichloride. Similarly, the reaction of diazomethane with methylgermanium trichloride gave chloromethylmethylgermanium dichloride in 78% yield. Treatment of CH_3GeCl_3 with a slight excess of diazomethane over that required for introduction of two methylene groups under the same conditions resulted in a 20.5% yield of methyl-bis-(chloromethyl)-germanium chloride and a 33.5% yield of the mono-(chloromethyl) derivative. However, no methylenated product was obtained from the reaction of dimethylgermanium dichloride with diazomethane at −60 or at 0°.

Under similar conditions the reaction with silicon tetrachloride gave chloromethyltrichlorosilane in only 45–47% yield, while treatment of methyltrichlorosilane with diazomethane resulted in a 13% yield of chloromethylmethyldichlorosilane.[11b]

We have found that trichlorosilane, $HSiCl_3$, reacts readily with diazomethane in ether solution at −60 to −70° in the presence of copper powder to give a 73.3% yield of chloromethyldichlorosilane, a heavy, colorless liquid that fumes strongly in air. Trimethylchlorosilane, triphenylchlorosilane and tetraethoxysilane do not react with diazomethane at −60° or at 0°. Only the unreacted silanes, together with small amounts of their hydrolysis products, were recovered.

Chloromethyltrimethylgermane, chloromethyldimethylsilane and chloromethyldiethylsilane were prepared by the reaction of the chloromethyl derivatives obtained by the diazomethane method with the appropriate Grignard reagent. The fully alkylated products were obtained from Grignard derivatives in about 90% yield.

The preparation of chloromethyltrimethylgermane is of importance because this compound may serve as an intermediate for the study of the as yet unexplored field of organofunctional germanium chemistry. The preparation of chloromethyltrimethylsilane and other halomethyl derivatives of silicon similarly was instrumental in making the

---

(1) Charles Lathrop Parsons Scholar, 1953–1954.

(2) F. C. Whitmore and L. H. Sommer, This Journal, **68**, 483 (1946).

(3) R. H. Krieble and J. R. Elliott, *ibid.*, **67**, 1810 (1945).

(4) G. F. Roedel, *ibid.*, **71**, 269 (1949).

(5) F. Runge and W. Zimmermann, *Ber.*, **87**, 282 (1954).

(6) J. J. McBride and H. C. Beachell, This Journal, **70**, 2532 (1948).

(7) R. H. Krieble and J. R. Elliott, *ibid.*, **68**, 2291 (1946).

(8) L. Hellerman and M. D. Newman, *ibid.*, **54**, 2859 (1932).

(9) By "methylenation" is meant the introduction of the $-CH_2-$ group, just as methylation indicates the introduction of the $-CH_3$ group.

(10) A. Ya. Yakubovich and V. A. Ginsburg, *Doklady Akad. Nauk S.S.S.R.*, **73**, 957 (1950); *C. A.*, **45**, 2857 (1951).

(11) (a) A. Ya. Yakubovich, S. P. Makarov, V. A. Ginsburg, G. I. Gavrilov and E. N. Merkulova, *ibid.*, **72**, 69 (1950); *C. A.*, **45**, 2856 (1951); (b) A. Ya. Yakubovich and V. A. Ginsburg, *J. Gen. Chem.* (*U.S.S.R.*), **22**, 1783 (1952); *C. A.*, **47**, 9256 (1953).

(12) A. Ya. Yakubovich, S. P. Makarov and G. I. Gavrilov, *ibid.*, **22**, 1788 (1952); *C. A.*, **47**, 9257 (1953).

(13) A. Ya. Yakubovich, E. N. Merkulova, S. P. Makarov and G. I. Gavrilov, *ibid.*, **22**, 2060 (1952); *C. A.*, **47**, 9257 (1953).

(14) A. Ya. Yakubovich, V. A. Ginsburg and S. P. Makarov, *Doklady Akad. Nauk S.S.S.R.*, **71**, 303 (1950); *C. A.*, **44**, 8320 (1950).

(15) A. Ya. Yakubovich and V. A. Ginsburg, *J. Gen. Chem.* (*U.S.S.R.*), **22**, 1534 (1952); *C. A.*, **47**, 9254 (1953).

(16) A. Ya. Yakubovich and S. P. Makarov, *J. Gen. Chem.* (*U.S.S.R.*) **22**, 1528 (1952); *C. A.*, **47**, 8010 (1953).

(17) G. I. Braz and A. Ya. Yakubovich, *J. Gen. Chem.* (*U.S.S.R.*) **11**, 41 (1941); *C. A.*, **35**, 5459 (1941).