351. *The Dissociation Constants of Some Chlorides and Perchlorates in Aqueous Acetone from Conductance Measurements.*

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The dissociation constants of HCl, LiCl, NaCl, $HClO_4$, and $NaClO_4$ in 80% and 90% aqueous acetone (by vol.) at 25° have been estimated from their conductances by various treatments. According to these, perchloric acid and sodium perchlorate are completely dissociated. Some spectrophotometric measurements support this view concerning perchloric acid in 80% acetone but not for the 90% solvent.

IN a recent report [1] on some conductances in aqueous dioxan, it was concluded that hydrogen, sodium, and potassium chlorides are weak electrolytes when the dioxan content exceeds about 60%. The values of the derived dissociation constants were shown to be slightly dependent upon the treatments used to analyse the data and this is further illustrated by the results reported here where the solvent is aqueous acetone. The methods of (a) Davies,[2] (b) Fuoss and Kraus (1933),[3] (c) Robinson and Stokes,[4] and (d) Fuoss (1959) [5] have been used; the first two of these treat ions as point charges and the second two incorporate an ion-size parameter. To be consistent, the limiting and the extended form of the Debye–Hückel activity coefficient expression were taken for (a,b) and (c,d) respectively, while the Λ_0 values were selected on the basis that the dissociation constants K should be sensibly constant over the concentration ranges investigated. For these reasons individual values of $K(b)$ and $K(d)$ were calculated for each concentration in preference to the usual plotting procedures.

The conductances of both sodium perchlorate and perchloric acid in 80% and 90% acetone proved to be markedly higher than those calculated by the limiting Onsager equation if dissociation is complete, but by choosing appropriate values of Λ_0 and the ion-size parameter a, both Robinson and Stokes's equation [4] and Fuoss's J equation [5] can reproduce the experimental values within close limits. On the other hand, while there is evidence [6] that perchlorates are stronger electrolytes than the corresponding chlorides, it is doubtful if perchloric acid and sodium perchlorate ionise completely in 90% acetone. To obtain some independent information, solutions of hydrochloric and of perchloric acid were matched spectrophotometrically by means of *m*-Cresol Purple. These measurements confirmed that perchloric acid is very strongly dissociated in 80% acetone but if the value of K_{HCl} from Table 1 is accepted, then perchloric acid does associate in the 90% solvent. Some figures for K_{HClO_4} are given in Table 2; the value of $[H^+]$ in each HCl solution was obtained by approximations, being taken as 4·0 Å when calculating activity coefficients.

The main conclusions which can be drawn from these comparative sets of calculations are that there are only minor differences between the derived dissociation constants by the different treatments, and that the interpretation of the conductances of perchloric acid and sodium perchlorate in the selected solvents is not completely acceptable. The dissociation constants of the chlorides as obtained by the method of Robinson and Stokes,[4] *i.e.*, $K(c)$, are slightly lower than the other sets of figures in Table 1, and this agrees with what was found when the solvent is aqueous dioxan.[1] It is noteworthy that the limiting conductance equation seems to function for the chlorides but not for the perchlorates unless the ion-size parameter is introduced, but a very large value of this would be needed to obtain a value for K_{HClO_4} from the conductances in 90% acetone to match that shown by Table 2. On the other hand, since $\Lambda_0(HClO_4) > \Lambda_0(HCl)$ in the present solvents and

[1] Nash and Monk, *Trans. Faraday Soc.*, 1958, **54**, 1650.
[2] Davies, *Trans. Faraday Soc.*, 1927, **23**, 351.
[3] Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 476; Fuoss, *ibid.*, 1935, **57**, 488.
[4] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 2nd edn., 1959.
[5] Fuoss, *J. Amer. Chem. Soc.*, 1959, **81**, 2659.
[6] " Stability Constants," Part II, *Chem. Soc. Special Publn.* No. 7, 1957.

$\Lambda_0(NaClO_4) > \Lambda_0(NaCl)$ in 80% acetone, these suggest that the radius of the Cl^- ion is greater than that of ClO_4^-. This is contradicted, not only by crystallographic data, but also by a comparison of the conductances of these two anions in water.[4] The answers to these puzzles may emerge from further similar studies and analyses.

TABLE 1. *Conductances and dissociation constants of* HCl, LiCl, NaCl, $HClO_4$, *and* $NaClO_4$ *in aqueous acetone at* 25°.

(Methods *a*, *b*, *c*, and *d* are as noted on p. 1817, the last using the extended Fuoss–Onsager conductance theory.)

HCl; aq. acetone, 90% by vol. = 87.6% by wt.; ε = 25.3; η = 0.00457.

a (Å)	Λ_0	$10^4c =$	2.016	2.467	4.446	5.408	6.324	7.172	8.874	11.779	
		$\Lambda =$	97.52	96.26	91.31	89.13	87.48	85.88	83.19	79.33	
0	107.60	$10^3K(a) =$	2.94	2.99	3.04	2.96	2.98	2.96	2.93	2.92	Av. = 2.97 ± 0.05
0	107.60	$10^3K(b) =$	2.91	2.99	3.02	2.95	2.98	2.93	2.92	2.92	Av. = 2.95 ± 0.05
4.0	107.60	$10^3K(c) =$	2.88	2.94	2.96	2.89	2.89	2.88	2.89	2.86	Av. = 2.90 ± 0.03
4.0	107.70	$10^3K(d) =$	3.02	3.10	3.11	3.04	3.08	3.03	3.01	3.00	Av. = 3.05 ± 0.03

LiCl (90%).

a (Å)	Λ_0	$10^4c =$	2.631	3.784	5.764	8.503	12.067	17.178	18.778	21.532	
		$\Lambda =$	87.52	85.16	82.27	78.79	75.25	71.01	70.08	68.22	
0	96.25	$10^3K(a) =$	5.17	4.93	5.14	5.09	5.09	4.99	5.11	5.00	Av. = 5.07 ± 0.07
0	96.25	$10^3K(b) =$	5.17	4.93	5.11	5.09	5.09	4.99	5.06	4.97	Av. = 5.05 ± 0.07
4.0	96.25	$10^3K(c) =$	4.89	4.70	4.88	4.84	4.82	4.73	4.81	4.73	Av. = 4.80 ± 0.06
3.5	96.40	$10^3K(d) =$	5.20	4.97	5.16	5.10	5.05	4.90	4.96	4.85	Av. = 5.02 ± 0.10

NaCl; aq. acetone, 80% by vol. = 75.9% by wt.; ε = 32.0; η = 0.00700.

a (Å)	Λ_0	$10^4c =$	2.636	5.331	6.003	8.564	12.119	13.481	16.356	18.385	
		$\Lambda =$	75.00	73.31	72.92	71.66	70.21	69.81	68.72	68.25	
0	78.60	$10^2K(a) =$	3.3	3.4	3.3	3.3	3.2	3.5	3.2	3.5	Av. = 3.3 ± 0.1
0	78.60	$10^2K(b) =$	3.3	3.4	3.3	3.3	3.3	3.4	3.3	3.4	Av. = 3.3 ± 0.05
4.0	78.60	$10^2K(c) =$	2.7	2.8	2.7	2.7	2.7	2.8	2.7	2.8	Av. = 2.7 ± 0.05
4.0	78.70	$10^2K(d) =$	2.7	2.8	2.7	2.65	2.6	2.7	2.5	2.65	Av. = 2.7 ± 0.06

HCl; aq. acetone, 80%.

a (Å)	Λ_0	$10^4c =$	4.624	5.558	6.386	7.704	9.116	
		$\Lambda =$	103.2	102.6	102.2	101.5	100.9	
0	108.50	$10^2K(a) =$	5.8	5.5	6.0	5.8	6.1	Av. = 5.5 ± 0.35
0	108.50	$10^2K(b) =$	5.6	5.3	5.7	5.7	6.0	Av. = 5.6 ± 0.2
4.0	108.50	$10^2K(c) =$	4.4	4.3	4.7	4.5	4.5	Av. = 4.5 ± 0.1
4.0	108.55	$10^2K(d) =$	5.6	5.3	5.6	5.3	5.4	Av. = 5.4 ± 0.1

$HClO_4$; aq. acetone, 90%.

a (Å)	Λ_0	$10^4c =$	2.304	3.452	4.503	5.676	6.319	8.735	10.612	11.929
		$\Lambda =$	131.95	130.75	130.0	129.05	128.7	127.3	126.2	125.65
4.0	137.70	calc. (c) =	132.1	130.9	130.0	129.1	128.7	127.2	126.2	125.65
5.0	137.80	calc. (d) =	132.0	130.7	129.8	128.9	128.5	127.2	126.3	125.8

$NaClO_4$; aq. acetone, 90%.

a (Å)	Λ_0	$10^4c =$	1.579	1.821	3.205	4.696	5.157	6.151	7.782	9.423
		$\Lambda =$	127.5	127.7	126.0	124.7	124.1	123.6	122.5	121.5
4.0	132.20	calc. (c) =	127.6	127.3	125.8	124.5	124.2	123.4	121.8	121.5
4.5	132.60	calc. (d) =	127.8	127.4	125.8	124.5	124.2	124.0	122.5	121.6

$HClO_4$; aq. acetone, 80%.

a (Å)	Λ_0	$10^4c =$	5.522	5.727	7.760	7.853	10.040	10.989
		$\Lambda =$	124.8	124.8	124.0	124.2	123.7	123.3
6.0	130.10	calc. (c) =	125.0	124.9	124.1	124.1	123.3	123.0
5.0	130.20	calc. (d) =	125.0	124.9	124.2	124.1	123.5	123.3

$NaClO_4$; aq. acetone, 80%.

a (Å)	Λ_0	$10^4c =$	4.088	5.154	6.609	8.465	9.029	11.949	12.213	15.353
		$\Lambda =$	95.24	94.61	94.23	93.53	93.47	92.65	92.62	91.92
5.0	99.25	calc. (c) =	95.25	94.79	94.24	93.62	93.45	92.65	92.58	91.84
4.5	99.35	calc. (d) =	95.23	94.74	94.18	93.59	93.42	92.68	92.62	91.97

TABLE 2. *Dissociation constant of* $HClO_4$ *in* 90% *acetone from spectrophotometry at* 525 mμ *and* 25° (K_{HCl} *taken as* 0.00305).

$10^2[HCl]$ ...	2.36	2.83	3.37	4.10	4.77	5.48	6.20	6.83	7.52	8.29
$10^2[HClO_4]$	1.78	2.25	2.72	3.24	3.71	4.16	4.61	5.06	5.51	5.85
10^3K	5.5	4.8	4.6	4.7	4.8	4.95	5.1	5.1	5.15	5.5

Average = 5.0 ± 0.25

EXPERIMENTAL

The conductance bridge, cell, and associated apparatus have been described elsewhere [7] together with the method of cell calibration. " AnalaR " sodium chloride was heated to constant weight at 500—600° in a platinum dish before stock solutions were prepared by weight. To make sodium perchlorate solutions, " AnalaR " sodium carbonate was dried at 260—270°, a quantity weighed into a tared flask, 50% " AnalaR " perchloric acid of known concentration added through a reflux condenser to trap spray, the solution brought to the boil, and the flask reweighed after being washed down. To check the concentration, a quantity was reconverted by a H^+ ion resin column and titrated. Ordinary-grade lithium chloride was recrystallised from conductance water, and the crystals were dried at 120—130° before a stock solution was prepared by weight. A check by gravimetric chloride analysis showed the crystals to be $> 99.95\%$ anhydrous. Stock solutions of " AnalaR " hydrochloric acid in conductance water were analysed by gravimetric chloride analysis.

AnalaR acetone was dried by storage over calcium chloride for at least 24 hr., filtered quickly into a distillation apparatus, and the middle fraction of distillate collected. The density of this (100 ml. sample, 25°) was 0.7848 in every case, and interpolation on the data of Dippy and Hughes [8] showed the water content to be 0.46% by wt. (0.36% by vol.); due allowance was made for this. By 80% and 90% acetone is meant 4 : 1 and 9 : 1 acetone : water by vol. The specific conductances of these solvents were in the range 3—10 gemmho. The viscosities (η) and dielectric constants (ε) were obtained by interpolation from published data.[9,10] Each set of results in Table 1 represents two " runs."

A Hilger " Uvispek " spectrophotometer was used, and for this work a stock solution of *m*-Cresol Purple was made by shaking an excess of it with 80% or 90% acetone and filtering.

[7] Davies, *J.*, 1937, 432; Davies and Monk, *J.*, 1949, 413.
[8] Dippy and Hughes, *J.*, 1954, 958.
[9] " International Critical Tables," McGraw-Hill Book Co., New York, 1930; Olson and Konecny, *J. Amer. Chem. Soc.*, 1953, **75**, 5801.
[10] Akerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.