

CCCXXXIII.—*Conductivities of Some Organic Salts of Beryllium.*

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RECENTLY (this vol., p. 1287) we showed that the molecular conductivity of beryllium oxalate solution was practically constant at concentrations from 0.16 to 0.8*N*, and that the product of conductivity and viscosity actually passed through a minimum at

about 0.1*N*. We have now examined the behaviour of the acetate and malonate.

Beryllium Acetate.—The solution was made by adding the equivalent of barium acetate to a solution of pure beryllium sulphate in conductivity water, and filtering. It was free from barium and sulphate ions. The conductivities and viscosities were measured as described in our previous paper; they are given in Table I. The conductivities are low compared with those of the chloride (*loc. cit.*, p. 1296), being about $\frac{2}{3}$ at 0.01*N*, $\frac{1}{2}$ at 0.13*N*, and $\frac{1}{3}$ at 0.5*N*, which indicates the presence of much non-polar form; but unlike those of the oxalate they decrease regularly with rise of concentration.

Beryllium Malonate.—There seems to be no convenient method for preparing solutions of the malonate or succinate by double decomposition. The reaction of the oxalate with magnesium malonate or succinate cannot be used, since magnesium oxalate, although only slightly soluble in water (0.4 g. per litre at 25°), readily forms supersaturated solutions containing up to 200 times as much salt (Kohlrausch and Mylius, *Ber.*, 1904, 37, 1223). Precipitated beryllium hydroxide could not be washed sufficiently free from salts to be suitable for making the solutions. Solutions of the malonate were ultimately prepared by dissolving the basic carbonate in the required quantity of acid and filtering. They were slightly turbid and apparently supersaturated, since on standing they slowly deposited a white precipitate of basic salt; but if they were not heated this precipitation was very slow, and with the strongest solution used the conductivity only fell 3% in 20 hours; with the more dilute solutions, the fall was much less, so that no serious error was to be expected from this cause in an experiment lasting 4 hours.

With the succinate the precipitation is considerably greater: the deposit was shown to be basic, containing after drying at 100° 9.70% Be [$\text{BeC}_4\text{H}_4\text{O}_4$ requires Be, 7.21; $\text{BeC}_4\text{H}_4\text{O}_4, \text{Be}(\text{OH})_2$ requires Be, 10.74%]. The succinate was therefore not examined further. The results for the malonate are given in Table II.

In the tables, the four columns in each case show the equivalent normality (*N*), the relative viscosity (η), the equivalent conductivity (λ), and the product ($\lambda\eta$) for beryllium acetate and malonate solutions at 25°.

Discussion of Results.

It will be seen that whilst the acetate behaves normally, the molecular conductivity falling continuously as the concentration increases, the malonate resembles the oxalate in that its conductivity is constant over a large range. The only parallel case known is

TABLE I.

Beryllium acetate.			
<i>N.</i>	η .	λ .	$\lambda\eta$.
0.00433	(1.001)	50.92	50.9
0.01390	(1.004)	41.62	41.8
0.02187	(1.006)	37.60	37.8
0.03273	(1.009)	34.17	34.5
0.05310	(1.015)	29.82	30.2
0.07896	(1.022)	26.71	27.3
0.1314	(1.037)	22.41	23.3
0.2173	(1.061)	18.38	19.5
0.2610	(1.073)	16.98	18.2
0.3155	1.088	15.45	16.8
0.6410	1.181	11.16	13.2

TABLE II.

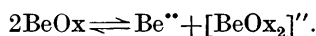
Beryllium malonate.			
<i>N.</i>	η .	λ .	$\lambda\eta$.
0.00309	(1.000)	8.31	8.31
0.00651	(1.001)	7.85	7.86
0.01421	(1.003)	7.56	7.58
0.02696	(1.005)	7.54	7.58
0.04155	(1.008)	7.51	7.57
0.06546	(1.013)	7.49	7.58
0.09225	(1.018)	7.47	7.60
0.1212	(1.024)	7.46	7.64
0.1584	(1.031)	7.46	7.69
0.2108	(1.041)	7.45	7.75
0.2981	(1.058)	7.39	7.81
0.4563	(1.089)	7.30	7.94
0.6244	1.123	7.19	8.07
1.245	1.274	6.60	8.41

that of the alkaline salts of the highest fatty acids (McBain and co-workers, *Z. physikal. Chem.*, 1911, **76**, 179; J., 1911, **99**, 191; 1912, **101**, 2042; 1914, **105**, 967), but McBain's explanation of the phenomenon by micelle formation cannot apply to these beryllium salt solutions, of which the viscosities are quite small (less than those of the beryllium salts of strong acids); moreover, the conductivities, unlike those of the soap solutions, are abnormally low.

The low conductivity of the malonate is no doubt due (like that of the oxalate) to the presence of a non-polar cyclic form

$\text{Be} \left\langle \begin{array}{c} \text{O} - \text{CO} \\ \text{O} - \text{CO} \end{array} \right\rangle \text{CH}_2$. The abnormal constancy of the conductivity

on dilution can be explained by assuming that the Ox'' ion ($\text{Ox}'' = \text{C}_2\text{O}_4$ or $\text{CH}_2:\text{C}_2\text{O}_4$) combines with undissociated BeOx to form a stable complex ion $[\text{BeOx}_2]''$. Evidence of the existence of these complexes (containing the stable 4-covalent beryllium) is given by the ready formation of double oxalates, $\text{R}_2\text{Be}(\text{C}_2\text{O}_4)_2 \cdot n\text{H}_2\text{O}$ (Rosenheim and Woge, *Z. anorg. Chem.*, 1897, **15**, 283), and double malonates, $\text{R}_2\text{Be}(\text{CH}_2:\text{C}_2\text{O}_4)_2 \cdot n\text{H}_2\text{O}$ (Meyer and Mantel, *ibid.*, 1922, **123**, 43), with ammonium and the alkali metals. The main reaction of ionisation in all but very dilute solutions will then be



Since in this reaction the number of molecules on each side is the same, the equilibrium (and hence the molecular conductivity) will be independent of the dilution. In very dilute solution, the further dissociation of the complex into $\text{Be}'' + \text{Ox}''$ will be increasingly important, and the molecular conductivity will rise, as it is found to do. If this hypothesis is sound, the van 't Hoff factor i should be very little greater than 1: the values found for the oxalate (Sidgwick and Lewis, *loc. cit.*) are 1.13 at 0.2*N*, and 1.05 at 0.7*N*. The

minimum conductivity is reached by the oxalate at about 0.1*N*, and by the malonate at about 0.03*N*, indicating that the latter gives the more stable complex; the minimum for the malonate is also about 25% less than for the oxalate.

It was pointed out in our previous paper that the presence of 3 mols. of water (and not 4) in the oxalate can be explained by supposing that in the non-polar beryllium oxalate 2 mols. are attached to the beryllium (giving it a covalency of 4) and 1 mol. (as is usual) to the oxalato-group. The proof now advanced of the existence of complex $[\text{BeOx}_2]$ ions suggests an alternative explanation. The solid may consist of the complex salt with the double formula $\text{Be}[\text{BeOx}_2]_2 \cdot 6\text{H}_2\text{O}$. Of these water molecules, four would be attached to the ionised beryllium, and one of the other two to each of the two oxalato-groups. Only an *X*-ray examination of the structure of the crystals could be expected to decide between these two alternatives.

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