

## The Electrical Conductivities of Liquid Alkali-Metal Amalgams.

By D. BOOHARIWALLA, G. R. PARANJPE, AND MATA PRASAD  
(*Royal Institute of Science, Bombay*)

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### ABSTRACT

The electrical conductivities of liquid sodium, potassium and lithium amalgams have been measured by the potentiometer method. The conductivity-concentration curves show breaks at points pointed out by Hine and by Bhatnagar, Prasad and Mukerji.

The conduction of current in the amalgams has been shown to be metallic and not electrolytic by

- (1) Resistance-temperature curves and
- (2) By measuring the electrical conductivities of the same amalgam with direct and alternating current.

The electrical conductivities of sodium, potassium and lithium amalgams have been measured by Hine (*Journ. Amer. Chem. Soc.*, 1917, 39, 882) who has found in the case of sodium amalgams that a discontinuity occurs in the conductivity concentration curve at one point only, while no breaks appear in similar curves in the case of potassium and lithium amalgams. Also the conductivities of sodium and potassium amalgams decrease with the increase in the concentration of the amalgam, while in the case of lithium amalgam, the conductivity increases with the increase of lithium in the amalgam.

Bhatnagar, Prasad and Mukerji (*Journ. Ind. Chem. Soc.*, 1924, 1, 81-89) have measured the surface tension of liquid

amalgams of sodium and potassium at the benzene amalgam interface and have found two discontinuities in the interfacial tension-concentration curves in each case. These discontinuities according to them, indicate the formation of complexes of alkali-metals with mercury. That abrupt changes in the constitution of amalgams take place with regular increase of the percentage of the alkali metal in the amalgam has been further shown by these authors (*Journ. Ind. Chem. Soc.*, 1925, 263-272) from the results obtained on the interaction of water with alkali-metal amalgams in the presence of light

The electrical conductivities of the liquid alkali-metals amalgams have, therefore, been measured with a view to examine their behaviour on changes of alkali-metal contents, when they are present in very small amounts in the amalgams.

### *Experimental.*

The amalgams studied in this investigation were those of sodium, potassium and lithium. They were prepared by the electrolytic method of T. W. Richards (*Journ. Amer. Chem. Soc.*, 1922, 44, 601) by passing an electric current of about 4 to 5 amperes through solutions of Merck's pure sodium, potassium and lithium carbonates for varying intervals of time. In the preparation of lithium amalgams a large amount of heat was developed when the current was passed through lithium carbonate solution and hence the vessel in which the electrolysis was carried out was placed in a freezing mixture.

The amalgams thus prepared were cleaned and dried and stored in an atmosphere of nitrogen out of contact with air (*cf.* Bhatnagar, Prasad and Mukerji *loc. cit.*). The quantity of alkali-metal was determined in each case by adding excess of standard hydrochloric acid to a weighed amount of the amalgam and titrating the excess of the acid back against a standard solution of sodium hydroxide. Thus sodium amalgams containing from 0.0183 to 0.3174 gm. of sodium,

potassium amalgams containing from 0.0100 gm. to 0.2659 gm. of potassium, and lithium amalgams containing from 0.0040 gm. to 0.0252 gm. of lithium in 100 gms. of amalgams respectively, were obtained.

*Measurement of the electrical conductivity.*

The electrical conductivity of amalgams has been measured by Bornemann and Muller (*Metallurgie*, 1910, 7, 396-402.), Hine (*Journ. Amer. Chem. Soc.*, 1917, 39, 882.), Williams (*Phil. Mag.*, 1925, 50, 589-599.), Edwards (*Phil. Mag.*, 1926, 2, 1-21.) Johns and Evans (*Phil. Mag.*, Feb. 1928.) by potentiometer method. The same method of measuring the conductivities was used in this investigation. The potentiometer used was a direct reading potentiometer and with the help of a delicate galvanometer, possessing high sensitivity, resistances accurate up to 104 ohm could be measured. This order of resistance is quite satisfactory for the conductivity measurements as suggested by Williams (*loc. cit.*).

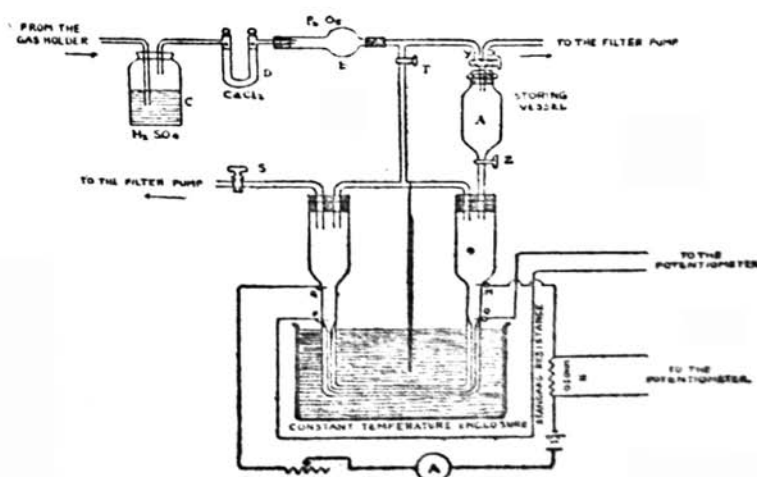


Fig. 1.

The conductivity was measured in a cell which consisted of uniform capillary-tube of about 35 cms. in length and a bore of about 1 mm. in diameter, bent in the shape of an U-tube with its ends joined to broad glass tubings. Four platinum electrodes P, Q, R and M were fused into glass tubings, two at each end of the U-tube as shown in Fig. 1. The two upper-electrodes R and M served the purpose of conducting the current, and the two lower ones, P and Q, acted as leads between which the potential drop was measured. By the use of two sets of electrodes in this fashion, the resistance of the platinum does not enter into the actual measurement of the resistance of the amalgam.

The cell was well cleaned and dried in an air-oven; the capillary tube of the cell took about four to five hours to get completely dried. It was then fitted by means of two air-tight rubber corks as shown in the figure. The long narrow stem of the storing vessel was fixed in one of the two corks for the amalgam to run down from the storing vessel into the cell. The stop-cock "T" was closed and "S" was opened and connected to the filter-pump. The amalgam cell as well as the narrow stem of the storing vessel were thus completely evacuated. The stop-cock "S" was closed and "T" was opened until the whole system was completely filled with nitrogen. Now the stop-cock "Z" was opened and the amalgam from the storing vessel was allowed to run down into the cell. The amalgam was thus kept out of contact with air throughout the whole process.

The cell was placed in a water-bath, the temperature of which was kept constant at 30°C. M and R were then connected to a storage cell, giving constant voltage. Current from the same source was taken for maintaining a difference of potential at the ends of the potentiometer wire.

The potential drops  $L_1$ , between the points P and Q of the circuit and  $L_2$ , at the ends of the known standard resistance N (0.1 ohm.) were then measured by the potentiometer

and from the ratio of these two measurements, the resistance of the amalgam was calculated as follows :—

$$\frac{R_a}{R_k} = \frac{L_1}{L_2}$$

$$\therefore R_a = \frac{L_1}{L_2} \cdot R_k$$

where  $R_a$  = Resistance of the amalgam.

$R_k$  = Known resistance (0.1 ohm.).

The constant of the cell was determined by measuring the resistance of pure dry mercury in the cell as described above and dividing this value by the specific resistance of mercury ( $96.69 \times 10^{-6}$  ohm.) at  $30^\circ\text{C}$ . The specific resistances and the specific conductivities of the amalgams were then calculated and the results obtained are given in Tables I, II and III. The conductivities of the amalgams were plotted against their concentrations and curves obtained are shown in figures, 2, 3, and 4.

*Results.*

TABLE I.

*Electrical Conductivity of Sodium Amalgam at 30°C.*

Quantity of Na in 100 gms. of Amalgam.	Resistivity of Mercury $\times 10^{-6}$ .	Conductivity of Mercury $\times 10^4$	Resistivity of Amalgam $\times 10^{-6}$ .	Specific conducti- vity of Amal- gam $\times 10^4$ .
0.0000 gms.	96.69	1.0342	...	...
0.0183 "	"	"	97.38	1.0269
0.0314 "	"	"	97.70	1.0235
0.0524 "	"	"	98.33	1.0176
0.0702 "	"	"	98.86	1.0115
0.0790 "	"	"	96.20	1.0395
0.1068 "	"	"	96.90	1.0330
0.1226 "	"	"	97.34	1.0273
0.1313 "	"	"	97.70	1.0235
0.1696 "	"	"	98.54	1.0148
0.1776 "	"	"	98.83	1.0118
0.2026 "	"	"	99.49	1.0051
0.2254 "	"	"	100.10	0.9990
0.2364 "	"	"	100.70	0.9990
0.2680 "	"	"	101.50	0.9852
0.2714 "	"	"	95.48	1.0473
0.2899 "	"	"	96.99	1.0310
0.2987 "	"	"	97.68	1.0237
0.3174 "	"	"	98.40	1.0102

TABLE II.

*Electrical Conductivity of Potassium Amalgam at 30°C.*

Quantity of K in 100 gms. of Amalgam.	Resistivity of Mercury $\times 10^{-6}$ .	Conductivity of Mercury $\times 10^4$ .	Resistivity of Amalgam $\times 10^{-6}$ .	Specific conducti- vity of Amal- gam $\times 10^4$ .
0.0000 gms.	96.69	1.0342	...	...
0.0100 "	"	"	97.18	1.0290
0.0211 "	"	"	97.77	1.0228
0.0407 "	"	"	98.68	1.0139
0.0413 "	"	"	98.79	1.0122
0.0434 "	"	"	98.33	1.0179
0.0513 "	"	"	98.49	1.0153
0.0551 "	"	"	98.79	1.0122
0.0612 "	"	"	99.31	1.0068
0.0776 "	"	"	99.59	1.0041
0.0907 "	"	"	100.40	0.9960
0.0938 "	"	"	99.10	1.0091
0.1006 "	"	"	99.49	1.0052
0.1069 "	"	"	99.59	1.0041
0.1140 "	"	"	100.10	0.9990
0.1223 "	"	"	100.20	0.9980
0.1429 "	"	"	100.80	0.9920
0.1624 "	"	"	101.20	0.9881
0.1693 "	"	"	101.70	0.9825
0.1783 "	"	"	100.20	0.9980
0.2080 "	"	"	101.00	0.9901
0.2092 "	"	"	100.90	0.9911
0.2118 "	"	"	101.40	0.9862
0.2156 "	"	"	101.60	0.9843
0.2271 "	"	"	102.00	0.9804
0.2462 "	"	"	102.77	0.9730
0.2659 "	"	"	103.57	0.9655

TABLE III.  
Electrical Conductivity of Lithium Amalgam at 30°C.

Quantity of Li in 100 gms. of Amalgam.	Resistivity of Mercury $\times 10^{-6}$	Conductivity of Mercury $\times 10^4$	Resistivity of Amalgam $\times 10^{-6}$	Specific Conductivity of Amalgam $\times 10^4$
0.0000 gms.	96.69	1.0342	.....	.....
0.0040 "	"	"	100.60	0.9940
0.0041 "	"	"	100.90	0.9911
0.0055 "	"	"	100.70	0.9930
0.0072 "	"	"	98.79	1.0122
0.0082 "	"	"	97.81	1.0224
0.0083 "	"	"	98.68	1.0134
0.0087 "	"	"	98.04	1.0200
0.0104 "	"	"	97.77	1.0228
0.0140 "	"	"	103.00	0.9709
0.0154 "	"	"	102.80	0.9728
0.0172 "	"	"	101.50	0.9851
0.0197 "	"	"	101.40	0.9852
0.0221 "	"	"	99.20	1.0099
0.0252 "	"	"	97.77	1.0228

Discussion of Results.

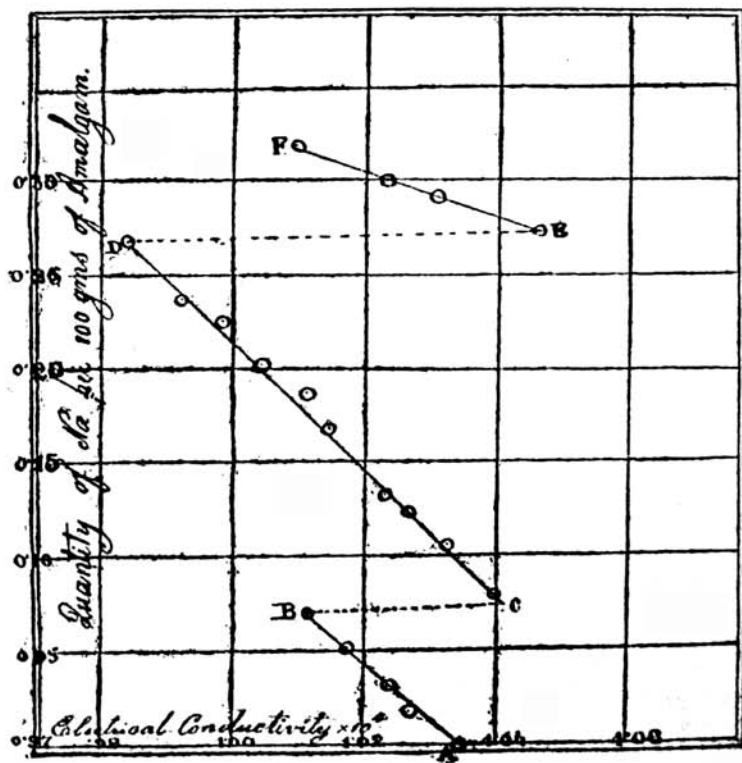


Fig. 2.



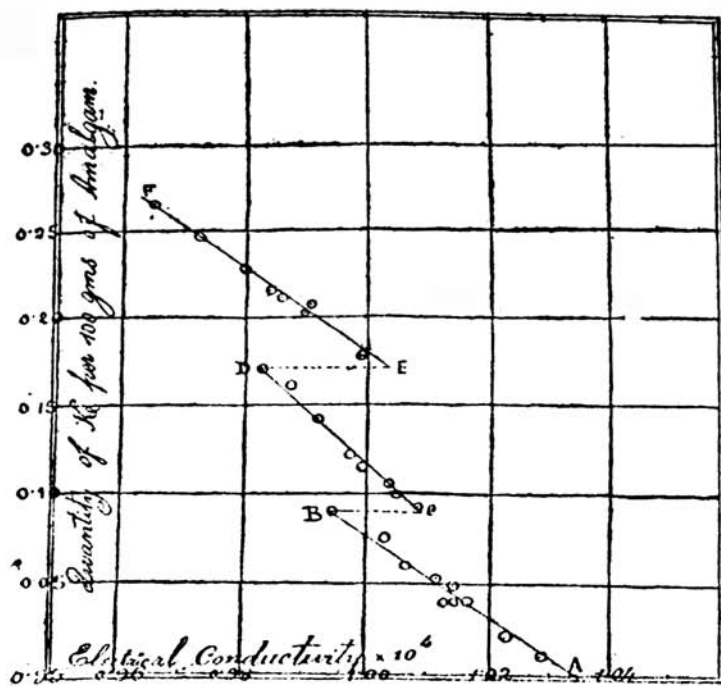


Fig. 3.

It is clear from Tables I, II and III that the conductivity of amalgams varies with the increase of alkali-metals in mercury. Starting with pure mercury at A (*vide* Fig. 2) the electrical conductivity decreases with an increase in the concentration of sodium until it reaches a minimum value about the point B corresponding to the concentration of 0.07 per cent. of sodium where a discontinuity occurs in the curve.

Again from the point C the electrical conductivity decreases with the increasing concentration and a second discontinuity is observed at D, at the concentration 0.265 per cent. of sodium.

Similarly in the case of potassium amalgams, two discontinuities occur at the points B and D corresponding to the concentration 0.09 and 0.17 per cent. of potassium (*vide* Fig. 3).

The curve (*vide* Fig. 4) in the case of lithium amalgam has a tendency to rise, *i. e.*, starting from the point A, the

conductivity of mercury increases with the increase of lithium in mercury. There is a break at the point B corresponding to the concentration 0.01 per cent. of lithium. The curves between the points A and B, C and D, and E and F are linear in each case.

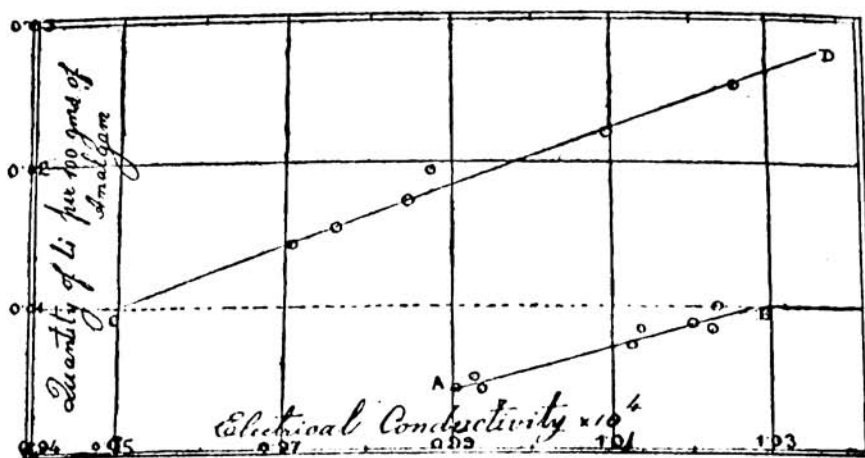


Fig. 4.

These breaks in the conductivity-concentration curves in the case of sodium and potassium amalgams occur at the same composition as have been found by Hine (*Loc. Cit.*) in the case of sodium amalgam and by Bhatnagar, Prasad and Mukerjee (*Loc. Cit.*) in the case of sodium and potassium amalgams and may correspond to the complexes of alkali-metal with mercury.

The conduction of current in amalgams may be electrolytic or metallic as in the case of alloys and solid solutions. It is known in the case of metallic conduction that the resistance of a conductor increases with the rise of temperature and that the resistance-temperature curve is linear to the first order of approximation. That is, if  $R_t\Omega$  is the resistance of a conductor at the temperature  $T$ , it is given by

$$R_t\Omega = R_0 (1 + \alpha T).$$

The results obtained in the measurement of the resistance of potassium amalgams of varying concentrations at different temperatures are given in Table IV.

TABLE IV.

Nature of Amalgam.	Quantity of K in 100 gms. of Amalgam.	Temperature in degrees Centigrade.	Resistivity of Amalgam $\times 10^{-6}$	Specific conductivity of Amalgam $\times 10^4$	Average Tem.-co-efficient of Amalgam.
POTASSIUM	0.0195	17.85	96.51	1.0862	0.00075
	"	21	96.79	1.0332	
	"	23	96.97	1.0314	
	"	27.20	97.22	1.0286	
	"	30.0	97.40	1.0266	
	"	32.0	97.51	1.0256	
POTASSIUM	0.1531	20.55	99.73	1.0027	0.0010
	"	22.45	100.01	0.9999	
	"	24.50	100.42	0.9959	
	"	27.10	100.69	0.9931	
	"	29.15	100.98	0.9903	
	"	31.00	101.18	0.9883	
POTASSIUM	0.1582	22.62	100.36	0.9964	0.0010
	"	24.95	100.80	0.9920	
	"	27.20	101.01	0.9900	
	"	28.45	101.11	0.9890	
	"	29.95	101.21	0.9880	
	"	31.90	101.36	0.9866	
POTASSIUM	0.1891	18.85	99.10	1.0090	0.0010
	"	21.75	99.50	1.0050	
	"	24.25	99.70	1.0020	
	"	26.58	100.08	0.9992	
	"	30.00	100.20	0.9969	
	"	34.00	100.68	0.9932	
POTASSIUM	0.5591	17.95	101.40	0.9862	0.005
	"	21.00	104.30	0.9588	
	"	22.90	105.00	0.9524	
	"	25.85	106.80	0.9363	
	"	27.00	107.50	0.9302	
	"	29.40	108.60	0.9208	



These results support the view that the conduction in amalgams is not electrolytic in which case a higher value of the conductivity, due to polarisation effects, should have been obtained by the alternating current method.

The amalgams may be either alloys of alkali-metals with mercury or solid solutions of alkali-metals in mercury. The conductivity of an alloy, if it is merely a mechanical mixture, is an additive property of the volume percentages of the components. The conductivities of the amalgams were, therefore, calculated according to the mixture law and in all cases it was found that the calculated results were higher than the observed ones. According to Liebenow (*Zeitsch. F. Electro-chemie*, 4, 201, 1897) the conductivities of some alloys calculated from mixture law are higher than the observed values, because thermo-electric forces arise at the various metallic junctions and they oppose the electric current. But this possibility could not arise in this case (in amalgams) as all the conductivity measurements were taken at constant temperature.

On the other hand the formation of a solid solution is accompanied by a decrease in the conductivity and this further decreases as the concentration of the solution increases. At a particular concentration when the components form a complex, the complex possesses a relatively high conductivity. The similarity of the properties of solid solutions with those of amalgams studied in this investigation, indicates that amalgams behave much like solid solutions of alkali metal in mercury.

Also the temperature co-efficients of alloys differ very little from 0.004—the normal value for pure metals, but they have a much lower value for solid solutions. The temperature co-efficients for the potassium amalgams of various concentrations have been calculated (*vide* Table IV) and have been found to be nearly in all cases less than the above value (0.004).