Thermo-magnetic Study of Mercury and Dilute Amalgams of Sodium and Potassium

By S. SRIRAMAN and V. SHANMUGASUNDARAM

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The idea of the probable existence of definite compounds between mercury and an alkali element has been suggested by several investigators from their work on vapor pressure[1], surface tension[2] and electrical conductivity[3] measurements of these amalgams. But similar investigations by different authors[4-8] on these amalgams have failed to show any such compound formation. Rao and Aravamuthachari[9] have studied the magnetic susceptibility of dilute alkali amalgams at room temperature. At very low concentration of amalgams lithium showed an increase of diamagnetic susceptibility while the other alkali metals indicated a decrease. Klemn and Hauschulz[10] made magnetic measurements on alkali amalgams at 20 and $-180°C$. The maximum and minimum in χ-concentration curves have been explained as due to the formation of compounds. The magnetic study of dilute alkali amalgams at higher temperatures may throw more light on the structure of the alkali amalgams. Hence the present investigation has been taken up.

Experimental

Sodium, potassium and mercury used in this investigation were of the highest purity. The amalgams were prepared in vacuum with a specially prepared pyrex apparatus (Fig. 1) by distillation.

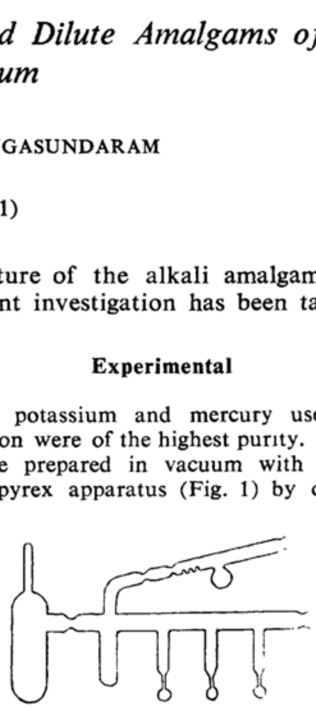

Fig. 1. The pyrex apparatus to prepare the amalgam.

The estimation of alkali content was carried out in accordance with improved procedure for the alkalimetric titration given by Lewis Adams and Lanman and described in detail by Rao and Aravamuthachari[9].

The specific susceptibilities of mercury, the two alkali metals and the amalgams were found by the Curie retorsion method using the vacuum arrangement described by Venkateswarlu and Sriraman[11]. For each specimen χ values were determined for four different field currents. Graphs were drawn between χ and $1/H$ for each specimen and in all cases the points were found to plot themselves in a horizontal straight line showing the complete

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[1] H. E. Bent and J. H. Hilderbrand, *J. Am. Chem. Soc.*, **49**, 3011 (1927).

[2] S. S. Bhatnagar, Mata Prasad and D. M. Mukerji, *J. Ind. Chem. Soc.*, **1**, 81 (1924).

[3] D. Booharıwala, G. R. Paranjapee and Mata Prasad, *Indian. J. Phys.*, **4**, 147 (1929).

[4] R. W. Millar, *J. Am. Chem. Soc.*, **49**, 3003 (1927).

[5] P. P. Pugachevich and O. A. Timsfeevicheva, *Doklady Akad. Nauk SSSR*, **94**, 285 (1954).

[6] P. P. Pugachevich and O. A. Timsfeevicheva, ibid., **104**, 98 (1955).

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[8] W. J. Davis and E. J. Evans., *Phil. Mag.*, **10**, 569 (1930).

[9] S. R. Rao and S. Aravamuthachari, *Proc. Ind. Acad. Sci.*, **9**, 181 (1939).

[10] W. Klemn and B. Hauschulz, *Z. Elektrochem.*, **45**, 346 (1939).

[11] K. Venkateswarlu and S. Sriraman, *Z. Naturforsch.*, **13a**, 451 (1958).

TABLE I. SUSCEPTIBILITY OF MERCURY, SODIUM AND POTASSIUM

Substance	Number of bulbs studied	χ_s Observed	χ_s by others			
Mercury	5	-0.169	-0.1675[12]	-0.166[9]	-0.1610[13]	-0.1667[10]
Sodium	4	$+0.599$	$+0.644$[10]	$+0.60$[11]	$+0.60$[9]	$+0.59$[14]
Potassium	4	$+0.462$	$+0.532$[10]	$+0.460$[11]	$+0.52$[9]	$+0.51$[14]

absence of ferromagnetic impurities. For the calculation of χ the value for benzene (0.702×10^{-6}) is taken as standard.

Results

The results obtained for mercury and the two alkali metals are given in Table I. The values of susceptibility given in this report indicate those in 10^{-6} c. g. s. units.

Two mercury bulbs were studied at different temperatures between 30°C and 240°C. The results obtained are given in Table II. The fall in χ-values of mercury is found to be slightly larger than reported by Bates and Baker[12].

TABLE II. χ_s (DIA) OF MERCURY AT DIFFERENT TEMPERATURES

Temp. °C	χ_s Bulb$_1$	χ_s Bulb$_2$
30	0.169	0.169
60	0.169	0.169
90	0.167	0.167
120	0.166	0.166
150	0.166	0.165
180	0.165	0.164
210	0.164	0.164
240	0.163	0.163

In Table III are given the results obtained for sodium and potassium amalgams at room temperature. The last column gives the additive value calculated. Figures 2 and 3 represent the graphical representation of the results

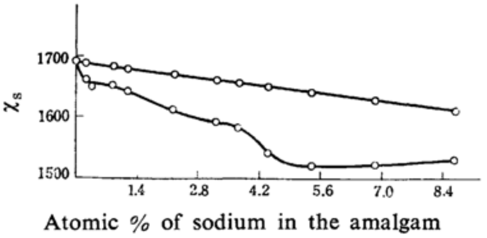

Fig. 2. The magnetic susceptibility of sodium amalgam as a function of atomic per cent of sodium metal in the amalgam.

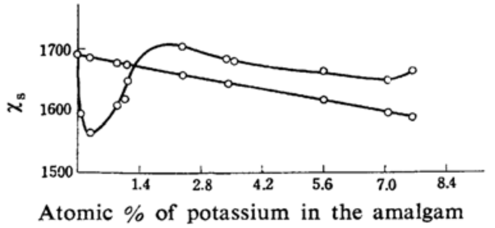

Fig. 3. The magnetic susceptibility of potassium amalgam as a function of atomic per cent of potassium metal in the amalgam.

TABLE III. χ_s (DIA) OF SODIUM AND POTASSIUM AMALGAMS

	Sodium amalgam					Potassium amalgam				
Bulb No.	Weight of amalgam g.	Concentration		χ_s Observed	χ_s Additive	Weight of amalgam g.	Concentration		χ_s Observed	χ_s Additive
		Weight %	At. %				Weight %	At. %		
1	0.4910	0.008	0.070	0.166	0.169	0.4561	0.007	0.037	0.159	0.169
2	0.4132	0.024	0.209	0.166	0.169	0.4904	0.054	0.277	0.156	0.169
3	0.3940	0.043	0.374	0.165	0.169	0.5049	0.174	0.887	0.161	0.168
4	0.3876	0.097	0.839	0.165	0.168	0.3836	0.200	1.017	0.162	0.168
5	0.5298	0.137	1.179	0.164	0.168	0.3762	0.202	1.020	0.162	0.168
6	0.4765	0.263	2.248	0.161	0.167	0.5740	0.232	1.180	0.165	0.168
7	0.4098	0.379	3.211	0.159	0.166	0.4852	0.466	2.316	0.171	0.166
8	0.3841	0.440	3.713	0.158	0.166	0.6683	0.705	3.436	0.168	0.165
9	0.4670	0.530	4.443	0.154	0.165	0.6145	0.717	3.576	0.168	0.165
10	0.4757	0.638	5.316	0.152	0.164	0.3791	1.146	5.613	0.167	0.162
11	0.5012	0.840	6.880	0.152	0.163	0.5206	1.466	7.089	0.165	0.160
12	0.3461	1.080	8.696	0.153	0.161	0.5012	1.583	7.620	0.166	0.159

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12) L. F. Bates and C. J. W. Baker, *Proc. Phys. Soc.*, **50**, 409 (1938).

13) A. Pacualtt, *Ann. Chim.* (*12*), **1**, 527-87 (1946).

14) W. Sucksmith, *Phil. Mag.*, **2**, 21 (1926).

TABLE IV. χ_s (DIA) OF SODIUM AND POTASSIUM AMALGAMS AT DIFFERENT TEMPERATURES

Temperature °C	Sodium amalgam χ_s				Potassium amalgam χ_s						
Bulb No.	1	5	7	10	1	2	5	6	7	8	10
30	0.166	0.164	0.159	0.152	0.159	0.156	0.163	0.165	0.171	0.168	0.167
60	0.166	0.164	0.159	0.152	0.159	0.156	0.162	0.164	0.170	0.169	0.166
90	0.166	0.165	0.158	0.153	0.159	0.156	0.162	0.165	0.170	0.169	0.166
120	0.165	0.165	0.159	0.152	0.160	0.157	0.162	0.163	0.170	0.169	0.165
150	0.166	0.164	0.159	0.151	0.159	0.156	0.161	0.165	0.171	0.168	0.166
180	0.166	0.164	0.160	0.152	0.159	0.156	0.162	0.166	0.170	0.168	0.165
210	0.166	0.164	0.159	0.152	0.159	—	0.163	0.165	0.171	0.168	0.166
240	—	—	—	—	—	—	0.162	—	—	0.169	—

obtained. Four of the above sodium amalgam bulbs and seven of the above potassium amalgam bulbs have been subjected to temperature study in the range 30°C to about 210°C. The results obtained (Table IV) show that, for each specimen, the χ_s values of the two amalgams remain practically constant at all temperatures.

Discussion

When very small quantities of a metal goes into solution in mercury one of the three things may hapen; (1) a compound may be formed (2) the metallic atoms may exist in a state of solid solution in mercury and (3) the metal may get dispersed into atoms, each atom, being surrounded by a group of mercury atoms forming a complex molecule.

Bent and Hildebrand[1] suggest the presence of a compound $NaHg_{16}$ as it would explain both vapor pressure and electromotive force data. Inoue[15] and his co-workers claim to identify a compound $NaHg_{14}$ by electrolyzing a saturated sodium chloride solution with mercury cathode. These compounds correspond to about 5.5 and 6.5 atomic per cent of sodium. If such compounds are really formed a pronounced change in the susceptibility will normally be obtained at these concentration. Our results show only a very broad minimum at about 6 atomic per cent as illustrated in Fig. 2. In the case of potassium amalgam the variation of susceptibility at very low concentrations is so rapid (Fig. 3) that compound formation could not account for the change. A study of susceptibility of amalgams at these concentrations and at different temperatures may give us some indications regarding the formation or otherwise of a compound. Our results (Table IV) do not show any such indication. The χ_s values for amalgams of these concentrations are found to be practically constant at all temperatures. It may be observed that for potassium amalgams the minimum is fairly sharp at 0.3 atomic per cent of potassium. The magnetic investigations of alkali amalgams at 18°C by Klemn and Hauschulz[10] have not indicated the formation of compounds at such low concentrations.

According to Rao and Aravamuthachari[9] the alkali atoms do not even exist in a state of solid solution and they have advanced reasons from electrical conductivity data. Inoue and his co-workers[16] have discussed the structure of sodium amalgam with reference to the amalgamation potential, equilibrium potential, electrophoresis, surface tension and viscosity. The structure of the amalgam was considered as a colloidal state.

Rao and Aravamuthachari[9] suggest that when an exceedingly small quantity of an alkali metal is introduced into mercury it is likely that it is dispersed into atoms and each atom is surrounded by a group of mercury atoms forming a complex molecule. It seems quite probable that the initial fall in the diamagnetic susceptibility of mercury is due to this cause. As concentration increases the alkali atoms join in pairs and these pairs of alkali atoms are surrounded by a group of mercury atoms, the decrease of diamagnetism would rapidly disappear and diamagnetism increases. For these to occur, single atoms of the alkali elements should possess a high paramagnetic component and double atoms a strong diamagnetic component. Ample evidence for the former property is borne out by the experiments of Bates and Tai[17], who find that many metals which are diamagnetic in the solid state appear to possess a large paramagnetic component in the amalgam. Also a few metals like manganese which are paramagnetic in the solid state appear to possess nearly 20 times the paramagnetic susceptibility when dissolved in mercury. That two paramagnetic atoms joining together producing a

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[15] Y. Inoue and A. Osugi, *J. Electrochem. Soc. Japan*, **20**, 502-513 (1952).

[16] Y. Inoue, A. Osugi and T. Amawa, ibid., **22**, 121-6 (1954).

[17] L. F. Bates and L. C. Tai, *Proc. Phys. Soc.*, **48**, 795 (1936); ibid., **49**, 230 (1937).

diamagnetic molecule is illustrated by the example of hydrogen. Both the amalgams studied exhibit these effects though in the case of sodium amalgam the initial fall is not as rapid as in potassium amalgam.

The problem could be considered from the point of view of the influence of change in the specific volumes. Maey[18] has shown that the specific gravity of alkali amalgam diminishes rapidly even at low concentrations. The addition of only 0.6% by weight of sodium changes the specific gravity from 13.596 to 12.956. This change corresponds to what would have been obtained, if the mercury had been heated from 0 to 260°C. According to Stoner such an increase in volume would be accompanied by an increase of the paramagnetic susceptibility component of the free electrons. The fall observed in the susceptibility of the mercury at higher temperatures may be due to this cause.

As the amalgam is heated the volume increases. From the above argument this expansion should lead one to expect a further decrease in susceptibility. But the values for the two amalgams for the concentrations studied are not affected by rise of temperature. Is it possible that the lowering of susceptibility due to heating might be compensated by the rise in diamagnetic susceptibility due to the formation of more pairs of alkali atoms in the amalgam? This will mean that such pair formation is induced by temperature.

Summary

The susceptibility of pure mercury was determined at different temperatures. Sodium and potassium amalgams were prepared in a pure state and the susceptibility of the amalgams of different concentrations at different temperatures was studied. The χ-values of amalgams were found to be practically constant in the range of temperature employed.

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Department of Physics
Annamalai University
Annamalainagar
South India

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[18] E. Maey, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", by Mellor, Vol. IV, Longmans Green & Co. (1923), p. 1016.