as double molecules.[12] From molecular weight determinations for acetic acid by the cryoscopic method with benzene as solvent[13,14] and the study of the Raman spectra of aqueous acetic acid solutions,[15] it is apparent that acetic acid at concentrations higher than 20% exists as dimers.

Compound formation between solvent and solute is the only cause of negative deviation from ideality and since a positive deviation was observed, this evidence also favors the absence of compound formation.

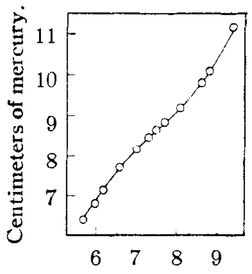

Fig. 2.—Dilatometry with rising temperature.

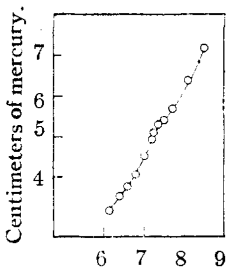

Fig. 3.—Dilatometry with falling temperature.

Recent studies of the polymorphism of stearic acid[16] and palmitic acid[17] show a similarity of the polymorphism of those acids to that revealed here for acetic acid. In fact, a plot of the dilatometric data of Ward and Singleton[17] for palmitic acid gives a curve similar to those of Figs. 2 and 3 for acetic acid, and shows a transition point in the neighborhood of 25.5°.

PHILADELPHIA, PENNA.

---

[12] W. W. Lucasse, R. P. Koob and J. G. Miller, *J. Chem. Education*, **21**, 454 (1944).

[13] J. M. Peterson and W. H. Rodebush, *J. Phys. Chem.*, **32**, 709 (1928).

[14] C. R. Bury and H. O. Jenkins, *J. Chem. Soc.*, 688 (1934).

[15] S. I. Leitman and S. A. Ukholin, *J. Chem. Phys.*, **2**, 825 (1934).

[16] W. S. Singleton, T. L. Ward and F. G. Dollear, *J. Am. Oil Chemists' Soc.*, **27**, 143 (1950).

[17] T. L. Ward and W. S. Singleton, *J. Phys. Chem.*, **56**, 696 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN AND THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Diffusion Coefficients of Certain Metals in Mercury

BY W. CHARLES COOPER AND N. HOWELL FURMAN

RECEIVED AUGUST 4, 1952

A discussion of the electrochemical methods of determining the diffusion coefficients of individual metals through mercury is presented. Diffusion coefficient data for the metals zinc, cadmium, lead, copper, thallium, tin and bismuth are presented. Diffusion coefficients for tin and bismuth, derived from polarographic data, were found to be 1.68×10^{-5} and 0.99×10^{-5} cm.^{2} sec.$^{-1}$, respectively. The nature of dilute amalgams is examined, and evidence of compound formation in dilute mercurial solution between mercury and the metals copper and bismuth is presented.

Introduction

One approach to a study of the diffusion of metals in mercury is through the measurement of diffusion coefficients. According to Smith[1] the diffusion coefficient D can be defined by the formula

$$dS = -Dq\frac{dc}{dx}dt$$

in which dS is the quantity of the diffusing substance which passes a given point in the time dt through a cross-section q of a diffusion cylinder under the influence of the concentration gradient dc/dx.[2]

All experimental methods used to determine diffusion coefficients hinge on the various possibilities for the determination of concentration changes. In the case of amalgams the possibilities are not so numerous as they are with aqueous solutions, since all the optical methods which have been applied successfully to such solutions cannot be used. Although chemical analysis and density determinations can be used for amalgams, the principal methods are electrochemical in nature. The purpose of this paper is to discuss briefly these electrochemical methods with particular emphasis on the polarographic method used by the authors and to examine the nature of dilute amalgams in the light of diffusion coefficient data.

Methods of Measuring Diffusion Coefficients

E.m.f. Methods.—The diffusion coefficients of cadmium, zinc and lead in mercury were determined by Meyer[3] who made the amalgam the anode of a small cylindrical cell. By electrolysis the metal in the amalgam was put into solution from the under base of the amalgam. The rate of diffusion of the metal atoms to the under surface of the amalgam was determined by measuring the potential between the upper region of the amalgam and a constant amalgam reference electrode at various time intervals. A disadvantage of Meyer's method is the fact that an accurate determination of the height of the small amalgam column is very difficult. Here is a serious source of error, since in the equation used for the calculation of D the height of the column appears as h^2.

Meyer's student von Wogau[4] determined the diffusion coefficients of a number of individual metals in mercury employing a method analogous to that of Graham.[5] A cylindrical column of mercury was covered over by the amalgam of the metal being investigated whereupon the diffusion

---

[1] G. McP. Smith, THIS JOURNAL, **36**, 847 (1914).

[2] A more critical definition of diffusion coefficient is given by G. S. Hartley and J. Crank, *Trans. Faraday Soc.*, **45**, 801 (1949).

[3] G. Meyer, *Ann. physik. Chem.*, **61**, 225 (1897).

[4] M. von Wogau, *Ann. physik*, **23**, 345 (1907).

[5] T. Graham, *Ann. chem. pharm.*, **121**, 1 (1862).

commenced. After a certain time the column was separated into several layers through the removal of sliding singly perforated glass plates. These plates comprised the column. The amalgam held in the perforation of each plate was analyzed chemically or potentiometrically by measurement against a constant amalgam electrode of the metal under consideration. This method has the disadvantage that the diffusion process is disrupted before the actual measurements are made.

Cohen and Bruins[6] developed a method which gave more accurate, reproducible data than did the methods of Meyer and von Wogau. The principle of their method was first described by des Coudres.[7] A known quantity of the metal was brought into the surface of a large mercury cathode by electrolysis in an electrolytic cell. The rate of diffusion of the metal in mercury was then determined potentiometrically by measuring the potential difference between the mercury surface and a constant amalgam electrode at various intervals of time after the electrolysis. Cohen and Bruins investigated but one metal, *viz.*, cadmium.

Conductance Method.—The diffusion coefficients of cadmium and zinc in mercury were determined by Weischedel[8] who followed the change in concentration occasioned by diffusion directly as a function of time and without disruption of the diffusion process. The amalgam and mercury were stratified in a cylindrical vessel and the electrical resistance between wire probes introduced into the diffusion medium at even intervals was measured. For the calculation of the diffusion coefficient the relative resistance values measured on the probes were plotted against time. A plot of ln ω (where ω = resistance between heights h_1 and h_2 after time t) *vs.* t yielded a straight line, the slope of which gave D, the diffusion coefficient.

Polarographic Methods.—Reboul and Bon[9] used the cathode ray oscilloscope to study dropping amalgam electrodes and applied their technique to determine the rate of diffusion of metals in mercury. They investigated the variations in the instantaneous current measured during the formation of the amalgam drop as a function of time. In the study of diffusion, the mercury of a dropping mercury electrode was connected with one of the ends of a horizontal tube of known length which was filled with pure mercury. At the other end of the tube a little amalgam of the metal being investigated was introduced. Then the time was measured at the end of which the mercury drop showed, by a change in the current–time curve, the presence of the diffused metal. Unfortunately Reboul and Bon present no experimental data so that it is impossible to compare the results of their method with those given by the methods previously discussed.

Furman and Cooper[10] have shown that diffusion coefficients for individual metals through mercury may be derived from polarographic data on dropping amalgam anodes. At 25° the anodic diffusion current $i_d = -607nD^{1/2}Cm^{2/3}t^{1/6}$. If the diffusion current constant $I_D = (i_d/Cm^{2/3}t^{1/6})$ is determined, the diffusion coefficient for the particular metal in mercury can be calculated, since, as the diffusion current equation indicates, $I_D = -607nD^{1/2}$.

The variation in diffusion current constant with supporting electrolyte which has been observed by

TABLE I

DIFFUSION CURRENT CONSTANT DATA FOR TIN AMALGAMS IN VARIOUS SUPPORTING ELECTROLYTES

Concn. amalgam, %	i_d microamp. obsd.	t, sec.	$m^{2/3}t^{1/6}$	$I_D = (i_d/Cm^{2/3}t^{1/6})$
Supporting electrolyte 1 *M* HCl				
0.00041	−3.56	4.53	1.55	−4.88
.00042	−3.49	3.54	1.52	−4.83
.00042	−3.63	4.23	1.56	−4.88
.00402	−32.25	2.68	1.44	−4.88
Supporting electrolyte 4 *M* NH_4Cl–1 *M* HCl				
0.00041	−3.59	4.58	1.53	−4.97
.00042	−3.57	3.71	1.50	−5.00
.00042	−3.64	4.40	1.56	−4.90
.00402	−34.00	3.99	1.55	−4.80
Supporting electrolyte 0.5 *M* H_2SO_4				
0.00041	−3.70	4.71	1.54	−5.11
.00402	−34.97	4.08	1.52	−5.01
Supporting electrolyte 1 *M* HNO_3				
0.00041	−3.55	4.56	1.52	−4.96
.00402	−34.31	3.80	1.49	−5.03
Supporting electrolyte 2 *M* $HClO_4$				
0.00041	−3.68	4.57	1.51	−5.18
.00402	−35.09	3.53	1.29	−5.24

TABLE II

DIFFUSION CURRENT CONSTANT DATA FOR BISMUTH AMALGAMS IN VARIOUS SUPPORTING ELECTROLYTES

Concn. amalgam, %	i_d microamp. obsd.	t, sec.	$m^{2/3}t^{1/6}$	$I_D = (i_d/Cm^{2/3}t^{1/6})$
Supporting electrolyte 1 *M* HCl				
0.00384	−20.78	4.06	1.53	−5.47
Supporting electrolyte 1 *M* HNO_3				
0.00384	−21.59	3.32	1.50	−5.81
Supporting electrolyte 0.5 *M* H_2SO_4				
0.00384	−21.02	4.15	1.53	−5.52
.00575	−33.64	3.98	1.56	−5.80
Supporting electrolyte 0.1 *M* tartrate soln. *p*H 3.39[a]				
0.00189	−11.14	4.65	1.59	−5.74
.00189	−10.96	4.48	1.57	−5.72
.00077	−4.57	4.16	1.57	−5.90
Supporting electrolyte 0.1 *M* tartrate soln. *p*H 4.60[a]				
0.00075	−4.09	3.74	1.49	−5.63
.00075	−4.08	3.76	1.49	−5.62
.00077	−4.41	3.72	1.51	−5.89
Supporting electrolyte 0.1 *M* tartrate soln. *p*H 5.09[a]				
0.00075	−4.20	3.74	1.48	−5.82
.00075	−4.18	3.76	1.48	−5.80
.00077	−4.33	3.72	1.50	−5.83

[a] 0.1 *M* in tartaric acid and buffered with acetic acid–sodium acetate mixtures.

---

[6] E. Cohen and H. R. Bruins, *Z. physik. Chem.*, **109**, 397 (1924).

[7] T. des Coudres, *Ann. physik Chem.*, **52**, 191 (1894).

[8] F. Weischedel, *Z. Physik*, **85**, 29 (1933).

[9] G. Reboul and F. Bon, *Compt. rend.*, **224**, 1263 (1947).

[10] N. H. Furman and W. C. Cooper, THIS JOURNAL, **72**, 5667 (1950).

the authors is a disadvantage of the polarographic method as regards the accurate determination of diffusion coefficients. Another limitation of the polarographic method is that it is applicable only to amalgams whose concentration is known accurately and which display anodic behavior. Cooper[11] has found that the metals nickel and cobalt, which are but very slightly soluble in mercury, exhibit no anodic polarographic behavior, although they are quantitatively deposited in mercury. It should be noted that the polarographic method can be applied to the determination of diffusion coefficients in the case of only very dilute amalgams since more concentrated amalgams would fail to drop regularly through the capillary electrode.

Tables I and II present diffusion current constant data for tin and bismuth amalgams determined according to the technique described elsewhere.[10] The average I_D ($= -607nD^{1/2}$) for tin, −4.98, yields a diffusion coefficient of 1.68×10^{-5} cm.^{2} sec.$^{-1}$. The average I_D for bismuth, −5.73, gives a diffusion coefficient of 0.99×10^{-5} cm.^{2} sec.$^{-1}$.

Discussion of Results

Table III presents a comparison of the diffusion coefficients of various individual metals through mercury obtained by the foregoing investigators.

TABLE III

DIFFUSION COEFFICIENTS OF VARIOUS INDIVIDUAL METALS THROUGH MERCURY

Metal	Observer	Temp., °C.	Concn. amalgam, %	Av. $D \times 10^5$, cm.^{2} sec.$^{-1}$
Zinc	Meyer[3]	15.0	0.1	2.42
	von Wogau[4]	8.0–14.3	0.0320–0.167	2.52
	Weischedel[8]	20.0	0.235	1.67
			.475	1.61
			.675	1.56
			.85	1.52
			.90	1.46
Cadmium	Meyer[3]	15.0	0.1	1.81
	von Wogau[4]	8.7	0.116–0.150	1.68
	Cohen and Bruins[5]	20.0	Indeterminable	1.52
	Weischedel[8]	20.0	0.9–1.5	1.53
Lead	Meyer[3]	15.6	0.1	1.58
	von Wogau[4]	9.0–10.0	0.118–0.162	1.74
	Furman and Cooper[10]	25.0 ± 0.5	.00158–0.00304	1.16
Copper	Furman and Cooper[10]	25.0 ± 0.5	.00027–0.00189	1.06
Thallium	von Wogau[4]	11.0–12.0	.137–0.160	1.03
	Furman and Cooper[10]	25.0 ± 0.5	.00216–0.00287	0.99
Tin	von Wogau[4]	9.6–14.0	.124–0.162	1.80
	Cooper (this work)	25.0 ± 0.1	.00041–0.00402	1.68
Bismuth	Cooper and Huber (this work)	25.0 ± 0.1	.00075–0.00575	0.99

Although Meyer's and von Wogau's values for zinc and cadmium agree fairly well, they are considerably higher than those obtained by Weischedel. Weischedel's value for cadmium corresponds closely with that of Cohen and Bruins. The polarographic data of Furman and Cooper[10] for zinc and cadmium amalgams substantiate the results of Weischedel and of Cohen and Bruins. Thus it would appear that Meyer's and von Wogau's diffusion coefficients are of doubtful validity. However, von Wogau's diffusion coefficient for thallium agrees reasonably well with that given by the polarographic method.

Compound Formation in Dilute Amalgams.—Both Meyer and von Wogau assumed that metals in mercurial solution exist as monatomic molecules. Although certain metals (zinc, cadmium, tin, lead, iron) have been found to exist as such when present individually,[1,12] other metals are known to undergo compound formation when dissolved in mercury. This is true particularly of the alkali and alkaline earth metals.[13] Of the heavier metals, copper and thallium are known to form compounds. Russell, Cazalet and Irvin[14] report finding six copper-mercury compounds ranging from Cu_7Hg to $CuHg_4$. Freezing point data presented by Richards and Daniels[15] indicate the existence of the compound Tl_2Hg_5.

In a study of the compounds formed when two metals are dissolved in mercury, Russell, *et al.*,[12,14,16] found that the formula of the compound which is present will depend on the concentration of the metals in the mercury. It is conceivable that the binary compounds formed between a single metal and mercury behave in an analogous manner.

Indications of compound formation in dilute amalgams are to be had from a suitable relationship involving diffusion coefficient data. In his abstract of Meyer's paper Ostwald[17] intimated that in the case of diffusion of metals in mercury the relation, $D \times \sqrt{\text{atomic weight}} = \text{constant}$, should hold. This relation is analogous to the expression, $D \times \sqrt{\text{molecular weight}} = \text{constant}$, which was found by Euler[18] to apply to the diffusion of a number of non-electrolytes in aqueous solution. However, Meyer[19] held Ostwald's proposition as improbable since, according to Riecke[20] the mean free path depends on the quotient $D \times \sqrt{\text{atomic weight}}$. Thus if the relation, $D \times \sqrt{\text{atomic weight}} = \text{constant}$, were true, all metals diffusing in mercury would have the same mean free path. Meyer[19] proposed the relation, $D \times$ specific gravity $=$ constant. Von Wogau used his diffusion coefficient data to dispute both Ostwald's and Meyer's propositions. Smith,[1] in a re-examination of von Wogau's data, claimed that the relation, $D\sqrt{M} = \text{constant}$, did apply to metals diffusing in mercury, and pointed out that von Wogau had erred in assuming that all metals were present in mercury as monatomic molecules.

From the data presented in Table III, it can be seen that certain of von Wogau's data are in considerable disagreement with values obtained by other investigators. Weischedel and Cohen and Bruins have questioned the reliability of the data

---

[11] W. C. Cooper, unpublished work.

[12] A. S. Russell, P. V. F. Cazalet and N. M. Irvin, *J. Chem. Soc.*, 841 (1932).

[13] G. McP. Smith, *Z. anorg. Chem.*, **58**, 381 (1908).

[14] A. S. Russell, P. V. F. Cazalet and N. M. Irvin, *J. Chem. Soc.*, 852 (1932).

[15] T. W. Richards and F. Daniels, THIS JOURNAL, **41**, 1732 (1919).

[16] A. S. Russell and H. A. M. Lyons, *J. Chem. Soc.*, 857 (1932).

[17] W. Ostwald, *Z. physik. Chem.*, **24**, 530 (1897).

[18] H. Euler, *Ann. physik Chem.*, **63**, 273 (1897).

[19] G. Meyer, *ibid.*, **64**, 752 (1898).

[20] E. Riecke, *Z. physik. Chem.*, **6**, 564 (1890).

of both von Wogau and Meyer. Using the data of Weischedel, Cohen and Bruins, and those furnished by the polarographic method, the authors found the relation, $D\sqrt{M}$ = constant, to be invalid for the diffusion of metals in mercury.

It appeared to the authors that if the values of the diffusion coefficients were to give reliable indications of compound formation, a more fundamental approach to the problem was necessary. From kinetic theory it is known that the diffusion coefficient is related to the mean free path of the diffusing particles whether they be atoms or molecules and that mean free path depends on the dimensions and velocity of the particles. In Fig. 1 the diffusion coefficients obtained by Weischedel, Cohen and Bruins and the authors are plotted against the radii of the metal atoms.[21] It would be expected that copper would diffuse at about the same rate as zinc since these metals have approximately the same atomic radius and atomic weight. However, copper diffuses much more slowly than does zinc, a fact which indicates that copper does not exist in dilute mercurial solution in monatomic form but in all probability in molecules of a copper-mercury compound. Since bismuth has about the same atomic weight as lead but a much smaller atomic radius (1.46 *vs.* 1.74 Å.), it would be expected that bismuth would diffuse more rapidly than lead. However, this is not the case and the existence of molecules of a bismuth-mercury compound in dilute mercurial solution is indicated.

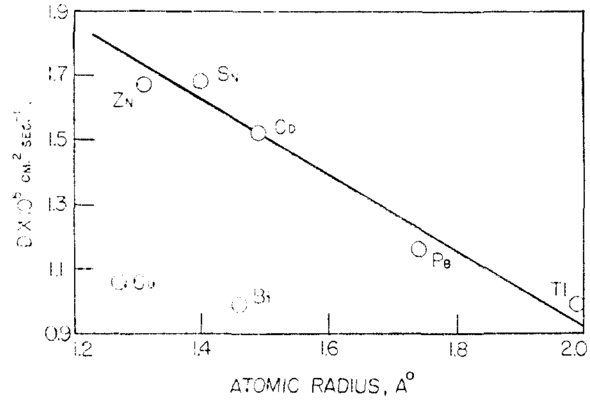

Fig. 1.—Relation between diffusion coefficients of metals in mercury and radius of metal atoms.

ADDED IN PROOF.—After the completion of the present paper, the authors' attention was directed to a paper by Turner and Winkler[22] in which these authors, using the equation of Strehlow and von Stackelberg[23] for the anodic diffusion current of a dropping amalgam electrode, reported the values 1.52×10^{-5} and 1.28×10^{-5} cm.^{2} sec.$^{-1}$ for the diffusion coefficients of cadmium and lead in mercury.

Acknowledgment.—The authors express their thanks to E. I. du Pont de Nemours & Co., Inc., and the Wisconsin Alumni Research Foundation for financial assistance to one of them (W. C. C.). The authors are also grateful to James C. Huber of the University of Wisconsin for his work on bismuth amalgams.

---

(21) Handbook of Chemistry and Physics, 31st ed., 1949, p. 2680–2682.

(22) R. C. Turner and C. A. Winkler, *Can. J. Chem.*, **29**, 469 (1951).

(23) H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

MADISON 6, WISCONSIN
PRINCETON, NEW JERSEY

[CONTRIBUTION NUMBER 111 FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE]

Studies in Low Concentration Chemistry. II. The Radiocolloidal Properties of Silver-111

BY GEORGE K. SCHWEITZER AND JAMES W. NEHLS

RECEIVED JULY 2, 1952

A method has been devised for the separation of carrier-free silver-111 from irradiated palladium foil based on the formation of radiocolloids in basic solution. The effects of coagulation time, *p*H, method of removal and the presence of non-aqueous solvents on the formation of these radiocolloids have been determined, and the ability of the radiocolloids to reform after an initial removal has been studied. The results obtained agree with previous observations on radiocolloids of other elements.

Introduction

It has been known for a number of years that certain radioactive isotopes of the heavy elements form radiocolloids. Radiocolloids may be defined as the agglomerates which form in very low concentration solutions (10^{-8} M and less) and which can be detected by virtue of their radioactivity. Recently, many other elements, including a number of lighter ones, have been shown to exhibit radiocolloidal behavior.[1]

Reasoning from the previous work on other elements, it seemed possible that silver would form radiocolloidal aggregates under suitable conditions. This paper describes the investigations which were carried out to test this possibility.

Experimental

Materials.—All inactive chemicals used were of analytical reagent quality. All water was triply distilled and preserved in carbon dioxide-free air.

Radioactivity Apparatus.—Measurements of the radioactivities of samples were made using a conventional Geiger counting apparatus. All radioactivities were counted for a sufficiently long time to give a maximum standard deviation of 1%.

---

(1) G. K. Schweitzer and W. M. Jackson, U. S. Atomic Energy Commission Document ORO-48, 28 pp. (1951); to be published. A. C. Wahl and B. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 142–148.