INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ELECTROANALYTICAL CHEMISTRY*

DIFFUSION COEFFICIENTS OF METALS IN MERCURY

Prepared for publication by
Z. GALUS

Department of Chemistry, University of Warsaw, 02-093 Warsaw, Poland

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Abstract - Methods used in the determination of diffusion coefficients of metals in mercury are briefly discussed; this discussion is limited to those involving electroanalytical techniques, which are preferentially used in determinations. Advantages of chronoamperometric procedure are presented. Diffusion coefficients of various metals in mercury reported in literature are given together with additional information. Their values refer mostly to $25^{\circ}C$, however, diffusion coefficients measured at other temperatures are also, at least partly, reported. In the case of some metals, where the discrepancy of experimental results is low, "suggested values" are given.

INTRODUCTION

Diffusion coefficients of metals in mercury are necessary for the elucidation of the electrode kinetics of amalgam electrodes. They may also furnish important information about the state and properties of metals dissolved in mercury.

Careful inspection of papers on the determination of diffusion coefficients of metals in mercury shows that frequently electroanalytical methods were used in these studies. Probably this is due to the fact that amalgams as a rule are unstable and in contact with air or with water may easily decompose.

Using electroanalytical techniques, amalgams may be easily prepared in situ, and soon after preparation may be oxidized. If this oxidation is carried out under conditions such that the diffusional transport of a metal in the amalgam limits the measured parameters /such as limiting current or transition time/, then from the value of these parameters one may easily calculate the diffusion coefficient.

If the conditions of the oxidation meet those assumed in the derivation of the equations used in calculations one may believe that diffusion coefficients obtained are correct. Three decades ago amalgam polarography was used and the Ilkovic equation applied to calculate the diffusion coefficient of metal atoms in mercury /refs. 1-3/ /from limiting anodic currents/. Later this method was found /ref. 4/ to give rather unreliable diffusion coefficients depending to some extent on the height of the amalgam reservoir.

CHRONOAMPEROMETRIC DETERMINATION

The technique that has been most widely used in recent years is the chronoamperometric oxidation of the metals from the amalgam of a finite volume. Usually the hanging amalgam drop was used. As a rule the amalgam was prepared by electroreduction of ions of the metal onto the hanging mercury drop electrode. Later the newly formed amalgam was oxidized at positive potentials such that the current was controlled by the rate of the diffusion of the metal to the amalgam-solution interface.

Using the hanging electrode with radius of the order of 5×10^{-2} cm the condition $t \ll r_o^2 / D_M$ may be fulfilled for times not exceeding several tens of seconds, and then the current-time curve corresponding to such oxidation is described by the equation

$$i_l = -nFAD_M C_M^o \left[\frac{1}{(\pi D_M t)^{1/2}} - \frac{1}{r_o} \right] \qquad /1/$$

where i_l is the limiting current, D_M and C_M^o are the diffusion coefficient and the concentration of metal in the amalgam, respectively. A is the electrode surface and r_o its radius, t is the time of electrolysis and the other symbols have their usual significance.

In practice equation /1/ is valid within the error of measurements if the radius of the drop is about 5×10^{-2} cm and time of electrolysis does not exceed approximately 30 s. For smaller electrodes this time is obviously shorter.

Equation /1/ may be used in several ways to get D_M, but the method proposed by Stevens and Shain /ref. 5/ to analyse the chronoamperometric data in the plot $i_l t^{1/2}$ vs $t^{1/2}$ seems to be the most fruitful. In such a case, if equation /1/ is obeyed, a straight line should be observed. The slope of this line - R and the intercept with the $i_l t^{1/2}$ axis - Z are related to D_M. Also the following equation is used in D_M determination

$$D_M = \left[\frac{R r_o}{Z \pi^{1/2}} \right]^2 \qquad /2/$$

The great advantage of this method /equation 2/ is that it does not require the concentration of the amalgam to be exactly known. This is very important in the study of unstable amalgams /ref. 6/. This method gives reliable diffusion coefficient values as has been shown by Stevens and Shain /ref. 5/ and later by Dowgird and Galus /ref. 6/. Another method of analysis of chronoamperometric data was developed by Stromberg and Zakharova /ref. 7/ and also by Kao and Chang /ref. 8/.

DATA FROM LITERATURE

Diffusion coefficients of metals in mercury are compiled in Table 1. Since almost all newer data were obtained utilising anodic oxidation of amalgams by one of several techniques such as chronoamperometry, chronopotentiometry or amalgam polarography, the method used in D_M determination has not been indicated.

Values reported in Table 1 refer mostly to 25^oC. Values at temperatures other than 25^oC were included only in the cases of elements for which the available data are limited. Values found at other temperatures not much different from 25^oC are also reported. For several elements D_M at several temperatures are given to show the experimental temperature dependence of diffusion coefficients of metals in mercury.

In the compilation, data which significantly deviated from other reported values for similar conditions were not considered.

In a recent paper, Gileadi and coworkers /ref. 9/ investigated the concentration dependence of diffusion coefficients of metals in mercury. Most data reported in Table 1 were obtained for dilute amalgams of the order of 10^{-3} M suitable for electroanalytical measurements. In the case of some amalgams /mostly those of transition metals/,

Table 1. Diffusion Coefficients of Metals in Mercury

Metal	$\dfrac{D_M \times 10^5}{cm^2 s^{-1}}$	Temp. °C	Authors and reference nos.	Metal	$\dfrac{D_M \times 10^5}{cm^2 s^{-1}}$	Temp. °C	Authors and reference nos.
Ag	1.11	25	Schwarz /22/		1.45	25	Stromberg, Zakharova /7/
	0.70	0	Drakin et al. /23/		2.0	25	Schwarz /22/
	1.30	23	" "		1.52	25	Furman, Cooper /1/
	2.67	120	" "		1.66	22	Stackelberg, Toome /3/
	1.05	25	Castleman, Conti /24/		1.51	20	Kao, Chang /8/
					1.68	8.7	von Wogau /17/
Al	1.54	20	Shalaevskaya, Igolinski /25/		3.42	99.1	" "
	1.68	30	" "		1.17	25	Kilina et al. /30/
	2.36	50	" "		1.52	20	Turner, Winkler /31/
	1.23 --1.9[a]	30	Ziegel et al. /9/		1.61	25	Zakharova et al. /32/
					1.53	25	Dowgird, Galus /6/
					1.42	20	Barański et al. /15/
Au	0.73	25	Schwarz /22/		0.92	20	Zakharov /18/
	0.83		Austen /26/		1.57	25	Ma et al. /47/
	0.61	23	Drakin et al. /23/		1.66	25	Lobo, Mills /49/
	0.96	25	Castleman, Conti /24/		1.53	25	Mangelsdorf /54/
	0.85	25	Gumiński, Galus /27/		1.53	25	Shaw, Verhoeven /55/
					1.50	25	Barański, Galus /33/
Ba	0.602	7.8	von Wogau /17/		1.61	25	Stevens, Shain /5/
	1.04	20	Kao, Chang /8/		1.53	25	suggested value
	0.49	20	Barański et al. /15/				
	0.65	20	Bukhman et al. /52/	Ce	0.62	25	Sagadeva et al. /34/
	1.44	60	Bukhman et al. /52/		0.48	25	Sagadeva et al. /35/
Bi	0.99	25	Furman, Cooper /1/	Cs	0.521	7.3	von Wogau /17/
	1.62	25	Stromberg /2/		0.63	25	Schwarz /22/
	1.5	25	Schwarz /22/		0.54	20	Barański et al. /15/
	1.24	25	Stromberg, Zakharova /7/				
	1.35	20	Kao, Chang /8/	Cu	1.06	25	Furman, Cooper /1/
	1.4	20	Nigmatulina, Zebreva /28/		0.93	25	Stromberg, Zakharova /7/
	1.44	20	Barański et al./15/		0.88	20	Kao, Chang /8/
	1.08	25	Mangelsdorf /54/		1.19	20	Barański et al. /15/
					1.08	20	Zakharov /18/
Ca	0.645	10.2	von Wogau /17/		1.00	25	Zakharova et al. /32/
					0.83	25	Kilina et al. /30/
Cd	1.81	15	Meyer /29/		0.88	25	Ma et al. /47/
	1.52	20	Cohen, Bruins /14/		1.00	25	Ignateva, Dubova /48/
	1.53	20	Weischedel /13/		1.01	70	Kilina et al. /30/

Table 1 contd. from p. 638

Metal	$D_M \times 10^5$ cm^2 s^{-1}	Temp. °C	Authors and reference nos.	Metal	$D_M \times 10^5$ cm^2 s^{-1}	Temp. °C	Authors and reference nos.
Ga	1.57	25	Stromberg, Zakharova /7/	Mn	1.84	20	Kao, Chang /8/
	1.64	20	Kao, Chang /8/		1.2	20	Lange, Bukhman /40/
	1.72	20	Barański et al. /15/		0.90±0.08	25	Dowgird, Galus /6/
	1.6	25	Zakharova et al. /16/		0.94	20	Barański et al. /15/
	1.74	25	Mangelsdorf /54/		0.81	25	Ma et al. /47/
	1.72	25	Stromberg, Rud /56/				
	1.73	25	suggested value	Na	0.741	9.6	von Wogau /17/
					0.86	25	Schwarz /22/
Ge	1.70	25	Stromberg, Zakharova /36/		0.80	22	Stackelberg, Toome /3/
	1.71	20	Kao, Chang /8/		0.76	20	Kao, Chang /8/
	1.32	25	Karpiński, Kublik /37/		0.84	25	Ma et al. /47/
					0.97	20	Barański et al. /15/
Hg	1.86--1.89	35	Changdar /57/		0.97±0.1	25[b]	Bukhman et al. /41/
	1.5	20	Nachtrieb, Petit /38/		1.78±0.1	60	" "
	1.60	25	Mangelsdorf /54/				
	1.83	25	Hoffman /39/	Ni	0.65±0.03	25	Dowgird, Galus /6/
	1.59	25	Lobo, Mills /49/		0.54	25	Barański, Galus /33/
	1.34	25	Butler, Shuck /53/		0.64	20	Barański et al. /15/
					0.64	25	suggested value
In	1.31	25	Stromberg, Zakharova /7/				
	1.47	22	Stackelberg, Toome /3/	Pb	1.15	25	Kilina et al. /30/
	1.42	20	Kao, Chang /8/		0.97	0	Ravdel, Moshkevich /42/
	1.36	20	Barański et al. /15/		1.16	25	" " "
	1.18	25	Nanda, Shuck /12/		1.33	50	" " "
	1.57	21	Zakharova et al. /16/		1.74	9.4	von Wogau /17/
	1.38	25	Butler, Shuck /53/		2.21	99.2	" "
	1.39	25	Mangelsdorf /54/		1.16	25	Furman, Cooper /1/
	1.38	25	suggested value		1.39	25	Stromberg /2/
					1.17	25	Stromberg, Zakharova /7/
K	0.602	10.5	von Wogau /17/		1.40	22	Stackelberg, Toome /3/
	0.71	25	Schwarz /22/		1.58	15.6	von Wogau /17/
	0.66	20	Kao, Chang /8/		1.39	25	Stromberg /2/
	0.85	20	Barański et al. /15/		1.25	20	Cohen, Bruins /14/
	0.69	25	Ma et al. /47/		1.28	20	Turner, Winkler /31/
	3.5	277	Edwards et al. /50/		1.25	20	Barański et al. /15/
					1.17	25	Dowgird, Galus /6/
La	0.50	25	Sagadeva et al. /35/				
				Pr	0.57	25	Sagadeva et al. /34/
Li	0.763	8.2	von Wogau /17/		0.53	7.3	von Wogau /17/
	0.92	25	Schwarz /22/				
				Rb	0.75	20	Barański et al. /15/
Mg	1.20	25	Mangelsdorf /54/				

Table 1 contd. from p. 639

Metal	$D_M \times 10^5$ $cm^2 s^{-1}$	Temp. °C	Authors and reference nos.	Metal	$D_M \times 10^5$ $cm^2 s^{-1}$	Temp. °C	Authors and reference nos.
Sb	1.40	25	Stromberg, Zakharova /7/		0.39[d]	25	Foley, Liu /11/
	1.47	20	Kao, Chang /8/		1.05	20	Kao, Chang /8/
	1.3	20	Toibaev /45/		1.11	25	Ma et al. /47/
	1.64	25	Ignateva, Dubova /48/		0.91	20	Barański et al. /15/
	1.15	25	Kilina et al. /30/		1.00	11.5	von Wogau /17/
	1.37	70	Kilina et al. /30/		1.06	25	Baticle, Perdu /46/
	2.42	90	Barański et al. /15/		1.00	25	suggested value
Sm	0.52	25	Badavamova et al. /51/	Zn	1.57	25	Stromberg /2/
					1.58	25	Stromberg, Zakharova /7/
Sn	1.68	25	Furman, Cooper /1/		2.42	15	Meyer /29/
	1.30	25	Stromberg, Zakharova /7/		1.67	25	Furman, Cooper /1/
	1.5	25	Schwarz /22/		1.68	20	Kao, Chang /8/
	1.43	20	Kao, Chang /8/		2.4	25	Schwarz /22/
	1.80	9.6	von Wogau /17/		1.67	25	Ma et al. /47/
	1.58	25	Mangelsdorf /54/		2.0	25	Dowgird, Galus /6/
	1.48	20	Barański et al. /15/		1.89	20	Barański et al. /15/
	1.77	10.7	von Wogau /17/		1.46-1.67[e]	20	Weischedel /13/
	1.55	22	Zakharova et al. /16/		1.81	25	Zakharova et al. /32/
					1.51	0	Ravdel, Moskhevich /42/
Sr	0.544	9.4	von Wogau /17/		1.80	30	" " "
	1.08	20	Kao, Chang /8/		2.06	50	" " "
					2.52	11.5	von Wogau /17/
Tl	1.06	21	Zakharova et al. /16/		3.35	99.2	" "
	0.99	25	Furman, Cooper /1/		1.75	21	Zakharova et al./16/
	1.18	25	Schwarz /22/		1.89	25	Lobo, Mills /49/
	1.03	25	Stromberg, Zakharova /7/		1.67	25	Mangelsdorf /54/
	0.98[c]	25	Foley, Liu /11/		1.76	25	Park et al. /59/

Notes to Table 1

[a]For small amalgam conc. increasing from 0.9 to 1.4 mM.   [b]Extrapolated.

[c]Tl mole fraction 0.00713.   [d]Tl mole fraction 0.4158.   [e]0.5 to 1.9 M amalgam.

high concentrations of the amalgam could not be obtained because of the limited solubility of the majority of these metals in mercury /ref.10/. Frequently, the concentration of metal in these studies was not reported by authors.

One of most suitable amalgams for such studies is thallium amalgam, since the solubility of this metal in mercury is very high, about 0.42 mole fraction at 25°C /ref.10/. The study of the dependence of D_{Tl} on the mole fraction thallium in the amalgam was carried out by Foley and Liu /ref.11/, who varied the mole fraction from X_{Tl} = 0.0075 to 0.458. At the lowest concentration they found D_{Tl} to be $0.98 \times 10^{-5} cm^2/s$, which is similar to those found by other workers. With the increase of X_{Tl} in the amalgam, D_{Tl} decreased linearly up to X_{Tl} = 0.2857, which corresponds to the Tl_2Hg_5 which exists in the liquid amalgam. Above X_{Tl} = 0.35 the change of D_{Tl} was small. The change of the relative Walden product with concentration of Tl in the amalgam led to the conclusion that the solutions of thallium in mercury are not regular.

However, Nanda and Shuck /ref.12/ studying the diffusion coefficient of indium in its amalgams of concentrations ranging from 3.5 to 20.0 atomic per cent give for $\underline{D}_{In}$ the empiricial equation

$$\underline{D} = 2.71 \times 10^{-3} /1 + 2.66 \underline{X}/ \exp /{-3260}/\underline{RT}/ \qquad /3/$$

which shows an increase of $\underline{D}_{In}$ with the amalgam concentration. Also in this case it was suggested that the diffusion involves a species more complex than the indium atom or ion.

The informations on the trend in the change of the diffusion coefficient with amalgam concentration in the case of other metals are also diverse.

Gileadi and coworkers /ref.9/ found that $\underline{D}$ of aluminium is dependent on the concentration of the metal in the amalgam, being larger in the case of a more concentrated amalgam. But Weischedel /ref.13/ who determined diffusion coefficient of cadmium in its concentrated amalgams /from 0.9 to 1.5 wt. per cent/ reports one common value for this range of concentration and in addition this value is practically identical with that reported by Cohen and Bruins /ref.14/ for 0.06 wt. per cent Cd amalgam, and also with $\underline{D}_{Cd}$ found when studying amalgams with concentrations of the order of 10^{-3} M /refs. 6,15/.

When studying diffusion coefficient of zinc Weischedel /ref.13/ found some concentration dependence of $\underline{D}_{Zn}$.

The influence of the change of concentration /in the region of $10^{-4} - 5 \times 10^{-3}$ M/ on the diffusion coefficients of metals in several amalgams was studied also by Zakharova, Kilina and Rakhmanina /ref.16/. Small changes of $\underline{D}$ were reported.

No dependence of diffusion coefficient of Cd, Zn, Mn, Cu and Tl on amalgam concentration was reported by Ma, Kao and Chang /ref.47/, but only diluted amalgams /up to 10^{-2} M/ were studied.

It follows from these results that the problem of concentration dependence of diffusion coefficients of metals in mercury calls for greater attention and more work is required in this field in the future.

Inspection of the Table 1 shows that further work is also needed with amaglams of alkali and alkali earth metals and also with the metals of lanthanum group. Some new methods and new electrodes should be developed. We have used /ref.15/ a film electrode in the study of alkali earth metal diffusion coefficients but is seems that results are still not very satisfactory. The measurements of these diffusion coefficients should be carried out in non-aqueous solvents.

It is the author's opinion that the results obtained by using hanging amalgam drop electrodes with amalgam oxidation under well controlled potentiostatic conditions should give reliable results.

A suggested $\underline{D}_M$ value is presented in cases where diffusion coefficients determined by several workers led to similar results and these results agree with author's own experience.

The inspection of Table 1 shows that the diffusion coefficients of metals in mercury may differ significantly. The lowest values are those of alkali and alkali earth metals which have large atoms.

The dependence between $\underline{D}_M$ and radii of corresponding atoms /$\underline{r}$/ was analysed by a number of workers based on the Stokes-Einstein equation . Such analysis was reported by von Wogau /ref.17/ and later carried out by Furman and Cooper /ref.1/ Using the equation

$$\underline{D}_M = \frac{kT}{6\pi\eta\,\underline{r}} \qquad /4/$$

where $\underline{k}$ is the Boltzmann constant, η viscosity of mercury and the other symbols have their usual significance, several authors have calculated diffusion coefficients of metals in mercury /refs.18,19/. However calculated values were considerably lower than experimental ones. To explain this difference Gladyshev /ref.19/ assumed that dissolved metals exist in mercury as cations having smaller radii than the radii of free metals. However it is not necessary to make such assumption, if ne considers the fact that in the case of diffusing substance and solvent molecules of similar dimensions the numerical coefficient in equation /4/ should be equal to 4 rather than to 6 /ref.20/. With this lower coefficient one obtains a good agreement between calculated and experimentally determined diffusion coefficients for a number of metals /refs.8, 15, 47, 58/. Such extensive analysis is shown in Fig.1, where $\underline{D}_M^{-1}$ was plotted versus
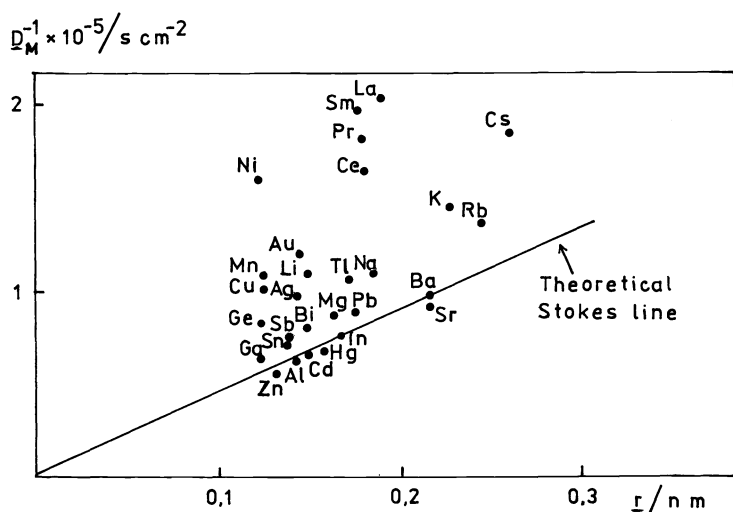

Fig.1. Dependence of $\underline{D}_M^{-1}$ on the atomic radius

radius of the corresponding atom. In the construction of this dependence for some metals the suggested $\underline{D}_M$ was used. The value used in the case of other metals for which we do not give suggested $\underline{D}_M$ values, is underlined.
Analysis of Fig.1 shows that the experimental $\underline{D}_M$ when deviating from the theoretical dependence give lower values only. No one result is placed below the theoretical straight line with exception of small deviations easily explained by experimental error. Significant deviations of $\underline{D}_M$ to lower values observed mostly in the cases of alkali and alkali earth metals as well as for lanthanum group metals show that diffusing specia have larger dimensions than those represented by a radius of a simple atom and as a consequence demonstrate solvation of these metals by mercury atoms. Such a conclusion is well founded for these groups of metals which form in crystalline state the

intermetallic compounds with mercury. When dissolving these metals in mercury a significant heat is evolved. As a result of these interactions the standard potentials of M^{n+}/M /Hg/ are significantly less negative when compared with the corresponding M^{n+}/M standard potentials /ref.21/.

Consequently in the case of other metals which deviate from the line in Fig.1 one may suggest that also such interactions exist in liquid amalgams.

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