JOURNAL OF MATERIALS SCIENCE 24 (1989) 3285–3288

Classification of simple amalgams

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Taking into account the type of phase diagram of metal–mercury, solubility, heat of dissolution process, activity and diffusion coefficient of a metal in mercury as well as the kinetics of electroreduction of metallic aquo-cation on a mercury electrode with an amalgam formation, a general classification of simple amalgams into four groups is proposed. On this basis some experimentally unknown amalgam properties may be predicted which have significant meaning in technical and chemical applications.

1. Introduction

Comparatively much work has been published on the classification of simple amalgams. However, there is no work which simultaneously takes into account several amalgam properties as a basis of the divisions. It is hoped that the classification proposed here will allow experimentally unknown properties of a simple amalgam to be foreseen if a minimum amount of information (for example solubility and ability to form intermetallics with mercury is available.

2. Previous divisions of amalgams into groups

In order to give an idea of previous attempts to generalize amalgam features, a brief collection of papers dealing with this subject is presented in Table I. From a contemporary point of view, the grouping of several elements in particular classes in the past is quite surprising, and is an interesting window on the knowledge on amalgams at those times. Table I also contains a few works [2, 3, 16] which reported valuable observations, but in which no classification, in the strict sense, was done.

3. The proposed classification of simple amalgams

The starting point of this work is the essential experimental data on amalgams which were collected, selected and compared with existing theoretical predictions in the previous paper [17].

The formation of intermetallics by metals with mercury has an influence on their solubility, heat of dissolution, activity and diffusion coefficients. If no intermetallics are formed, the binary systems M–Hg are nearer to ideal ones, but no ideal system is known. It was also found that a straight-line relationship between logarithms of the solubility and reduction kinetics of metallic cations on mercury exists. Let us successively analyse the information on individual elements described in the preceding paper [17] to achieve their systematization.

If, for example, we consider barium amalgam, we observe in the phase diagram Ba–Hg that the melting point (m.p.) of the most stable HaHg (1095 K) is higher than the m.p. of pure barium (1002 K). The barium solubility in mercury of 0.49 mol % at 298 K is lower than it would be expected (11 mol %) for an ideal solution model. Heat of 262 kJ is released during the dissolution of 1 mol Ba in a large amount of mercury. The activity coefficient of barium in its diluted amalgam is 1.7×10^{-41} because the difference ($E^0_{\mathrm{Ba(Hg)/Ba(II)}} - E^0_{\mathrm{Ba/Ba(II)}}$) is 1.203 V. The diffusion coefficient of barium in mercury of $7 \times 10^{-6}\,\mathrm{cm^2\,sec^{-1}}$, instead of $1.1 \times 10^{-5}\,\mathrm{cm^2\,sec^{-1}}$, indicated that in the resulting diluted amalgam, diffuse molecules of approximate composition $BaHg_6$ exist, but not barium atoms. The kinetics of electroreduction of Ba(II) from an aqueous solution on a mercury electrode with the subsequent formation of a barium amalgam is moderate ($2 \times 10^{-3}\,\mathrm{cm\,sec^{-1}}$). If a thorough study is made of alkali, alkaline earth (except beryllium) and rare earth metal amalgams, qualitative, but sufficiently contrasting, similarities of these amalgam features to those described for barium amalgam may be observed. In this way the classification groups are formed.

3.1. Group I: Li, Na, K, Rb, Cs, (Fr), Mg, Ca, Sr, Ba, (Ra), La, Ce, Pr, Nd, (Pm), Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

All these metals (M) form intermetallics (IC) with mercury. The most stable ICs melt congruently at temperatures mostly higher than the m.p. of the pure M (for alkaline earths and Ln at a constraining pressure). The solubilities of these compounds, which are in equilibrium with their saturated amalgams, are about, or higher than, 10^{-3} mol % M. Practical aspects of amalgam applications suggest that the solubility demarcation line should be placed at level of 10^{-3} mol % at 298 K because at this or higher metal concentrations the corresponding amalgam half-cell potential is well defined and the amalgam may be effectively used in a chemical reaction of a technological process.

Typically, the experimental solubility values in this group are lower than those predicted by the theory of an ideal solution. The dissolution process of a metal in mercury is markedly exothermic, therefore it is safer

0022–2461/89 $03.00 + .12

TABLE I Survey of classifications reported for simple amalgams

Author, year	Basis of classification	Classification groups and short characterization
Kettembeil, 1904 [1]	Electrolytic formation of amalgams	I: Li–Cs, Mg–Ba, Zn, Cd, Cu–Au, Tl, Sn, Pb (easy formation). II: B–Ga, C–Ge, Ln (immpossible formation). III: Ti, Zr, Cr, Mn, Fe, Ni–Pt, Bi (separation of a solid from amalgam).
Tammann and Hinnüber, 1922 [2]	Position of a metal in the periodic table	Proximity of places of a metal and Hg causes easier formation of an amalgam and higher solubility of the metal in Hg.
Sen, 1932 [3]	Ratio of atomic radii of a metal and Hg	Metals with radius higher or equal to Hg form amalgams while others do not.
Hohn, 1948 [4]	Type of M–Hg phase diagram	I: Al, Ga, Cr, Mn, Fe, Co, Ni (Ga type). II: Zn, Cd, In, Tl, Sn, Pb, Bi (Zn type). III: Na–Cs, Mg–Ba (Na type of diagram).
Hohn, 1950 [5]	Difference of normal and polarographic half-wave potentials	I: Cr, Fe, Co, Ni, Mg, Ga ($E^{1/2} < E^0$). II: Cu, Zn, Cd, In, Tl, Sn, Pb, Bi ($E^{1/2} \approx E^0$). III: Li–Rb, Ca–Ba ($E^{1/2} > E^0$). IV: Ti–Hf, Nb, Ta, Mo, W, U (no amalgam formation).
Borchers, 1956 [6]	Solubility of a metal, appropriate for metallurgical applications	I: Li–Cs, Mg–Ba, Al, Tl, Sn, Pb, Bi, Cu–Au, Zn, Cd, Te (easily soluble). II: Ce, Ga, Ge, Pd, Pt, Pr (poorly soluble). III: Other elements (practically insoluble).
Jangg and Bach, 1961 [7]	Reactivity of amalgams with water and acids	I: Cr, Fe, Co, Ni, Cu–Au (resistive to nonoxidizing acids). II: Li–K, Zn, Cd, In, Tl, Sn, Pb, Mn (resistant to water). III: Al, Mg, Ti, Ln (reactive with water).
Kozin, 1962 [8]	Practical applications of amalgams and possibility of metallurgical rafination	I: Li–Fr, Be–Ra, Cu–Au, Zn, Cd, Ga–Tl, Sn, Pb, Bi (easily soluble). II: Fe, Co, Ni (poorly soluble but amalgamation possible). III: As, Sb, Ge, Se, Te, B (amalgamation impossible).
Gladyshev, 1963 [9]	Type of phase diagram, degree of filling of d electron level, ionization potentials	I: Li–Fr, Be–Ra (strong interaction of M with Hg). II: B–Tl, C–Pb, N–Bi, Cu–Zu, Zn, Cd (weak interaction of M with Hg). III: all metals with d^1 to d^8 electrons (no interactions of M with Hg).
Jangg, 1965 [10]	Solubility and formation of intermetallics with Hg	I: Li–Cs, Mg–Ba, Mn, In, Tl (easily soluble, intermetallics). II: Cu–Au, Zn, Cd, Sn, Pb, Bi (easily soluble, no or unstable intermetallics). III: Al, Ga, Sb, Cr, Fe, Co (poorly soluble, no intermetallics). IV: Ln, Th, U, Ti, Zr, Ni, Pt (poorly soluble, intermetallics).
Volkov, 1968 [11]	Solubility and formation of intermetallics with Hg	I: Li–Cs, Be–Ba, La, Ce, Sm, Eu, Yb (easily soluble, intermetallics). II: Cu–Au, Pt, U (moderately soluble, intermetallics). III: Zn, Cd, Al, Tl, Sn, Pb, Bi (easily soluble, unstable intermetallics). IV: Cr, Mo, Mn, Ni, Te, Sb, As (poorly soluble, intermetallic possible). V: Ga, Ge, Ti, Zr, V, Ta, W, Fe (immiscible with Hg, no amalgamation).
Smirnov, 1970 [12]	(no basis presented)	I: Li–Cs, Mg–Ba, Ln. II: Cu–Au, Zn, Cd, Al–Tl, Sn, Pb, Bi. III: Ti–Hf, V–Ta, Cr–W, Re, Fe–Os, Co–Ir, Ni, Pt. IV: Be, B, Ge, Sb, Se, Te.
Gladyshev, 1973 [13]; Barański, 1973 [14]	Kind of valency electrons in M	I: elements with s electrons. II: elements with f electrons. III: elements with p electrons. IV: elements with d electrons.
Jangg, 1978 [15]	Solubility and formation of intermetallics with Hg	I: Li–Cs, Mg–Ba, Ln, Mn, In, Tl (easily soluble, intermetallics). II: Cu–Au, Zn, Cd, Sn, Pb, Bi (easily soluble, no or unstable intermetallics). III: Al, Ga, As, Sb, V, Nb, Cr–Mo, Fe–Os, Co, Ir (poorly soluble, no intermetalliccs). IV: Ti–Hf, Ta, Ni–Pt, Rh, Th, U (poorly soluble, intermetallics).
Stromberg and Katyukhina, 1981 [16]	Correlation of solubility with valency electron structure	I: easily soluble metals ($\geqslant 10^{-2}$ mol %) with filled up d electron levels (excluding La, Th). II: poorly soluble metals ($\leqslant 10^{-3}$ mol %) with partly filled d electron levels (excluding Cu, Zn, Pd, Sb, As, Ge, Be, B, Si).

to prepare such amalgams by electrolysis or cementation. The liquid amalgams deviate strongly from Raoult's law, activity coefficients of the metals are very small because the liquid phase contains exclusively MHg_x molecules, but no naked metal atoms. This is reflected in the magnitude of the diffusion coefficients which are, as a rule, lower than the values predicted by the simple Sutherland–Einstein (SE) equation. The kinetics of the electroreduction of an aquo-ion on mercury is sufficiently fast; the lower the valency of an ion the higher is the rate. Such processes occur at more positive potentials than $E^0_{\mathrm{M/M}^{n+}}$ for several hundreds of millivolts. Due to the significantly ionic character of the bonding of MHg_x solvates in a mercury medium, one may imagine (especially for the alkali metals) that the critical stage of the electrode process is the reaction of re-solvation $M^+(H_2O)_y \rightleftharpoons M^+Hg_x$ and the electron exchange is subsequently possible at other points of the mercury electrode surface.

3.2. Group II: Mn, Cu, Ag, Au, Zn, Cd, Al, Ga, In, Tl, Sn, Pb, Bi

Similar to the preceding group, the ordered metals are easily soluble in the mercury (higher than 10^{-3} mol %) but their interaction with mercury is rather weak. Even if an IC is formed, it is decomposed at temperatures frequently not higher than 400 K. These amalgams are easily prepared by direct dissolution of the metal in mercury, cation electroreduction or cementation. Enthalpies of the dissolution are small, positive as well as negative. Slight deviations from Raoult's law are analogically positive or negative and the activity coefficients oscillate around unity. The electroreduction of cations takes place at potentials of approximately $E^{\circ}_{\mathrm{M/M}^{n+}}$; these are the fastest electrode processes. The diffusion of these metals in mercury almost fulfil the SE equation and only metals forming ICs with mercury (Mn, Cu, Ag, Au, Tl) show lower diffusion coefficients; however, this understatement is much smaller than for the metals of group I.

3.3. Group III: V, Nb, Ta, Cr, Mo, W, (Tc), Re, Fe, Ru, Os, Co, Ir, B, C, Si, Ge, As (?), Sb

Taking into account the experimental difficulties, the amalgam features of this group are insufficiently known. Owing to the very low (below 10^{-3} mol %) or immeasurably low solubility of some metals in mercury, an acquaintance with properties of homogeneous amalgams is frequently impossible. The amalgams prepared by chemical reactions or electroreduction are very easily oversaturated by several orders of magnitude, probably forming colloidal dispersions, which has frequently led inexperienced investigators to incorrect results. Characterization of this group, to a significant degree, is therefore more like a reasonable prediction from the author's point of view. The dissolution of these metals in mercury is always endothermic and the degree of dissolution is distinctly lower than it could be for the ideal solution. The reluctance of these metals to form homogeneous amalgams originates from the increase in activity after their dissolution in mercury. The discharging of these aquo-cations onto the mercury electrode occurs very slowly and with a significant overpotential. Some of these cations are not even reducible from an aqueous solution. One may safely anticipate the diffusion coefficient values directly from the SE equation, because these metals do not undergo a stable solvation by mercury. Deviations from Raoult's law should be rather positive; however, it is not possible to test them experimentally.

3.4. Group IV: Be(?), (Ac), (Pa), Th, U, (Np), Pu, Sc, Y, Ti, Zr, Hf, Rh, Ni, Pd, Pt, Se, Te, (Po)

The amalgams of these metals could indeed be prepared by a direct contact of the elements because the metals react with mercury; however, such a process is extremely slow. Because MHg_x film, formed on the metal surface, is poorly soluble in mercury (below 10^{-3} mol %), as a consequence a further progress of the reaction between free metal and mercury is inhibited. The experimental solubilities are most frequently higher than expected from the ideal solution theory. Nevertheless, all these metals are not resistant to corrosion in liquid mercury as are the metals of group III. Practically, cementation, electrochemical and chemical methods are used for the preparation of these amalgams, which are comparatively better known than those of group III. Owing to the compensation of the exothermic effect of MHg_x formation and the significant endothermic effect of cohesion forces in these metals, the heat of dissolution of a metal in mercury is moderately endothermic or exothermic (excluding some anomalies for Th, Pt, and Pd). Logarithms of the activity of these metals in mercury are not much different from zero. The electrode processes are slow and occur at temperate overpotentials. Similar to group I, the diffusion coefficients are very much lower than those calculated from the SE equation; bonding between the metal and mercury has a rather covalent character. Although the thermal stability of some MHg_x compounds is significant and peritectic decomposition temperatures reach even 830 K, typically these temperatures are ever lower than the m.p. of pure elements (excluding Se and Te). Rather negative deviations from Raoult's law are expected; however, they are not confirmable experimentally.

The affiliation of beryllium and arsenic to their groups is debatable. On the one hand beryllium is reported not to interact with mercury [18]. On the other [19], the amalgam of composition $BeHg_2$ may be thermally decomposed when mercury is distilled out, but it is not possible to separate mercury from the amalgam by pressing. The formation of $BeHg_2$ has not yet been confirmed by X-ray tests. Beryllium is more resistant to mercury corrosion than nickel, titaniuim or zirconium [20] which are similarly soluble in mercury and form ICs with it. This might be ascribed to the covering of beryllium with a protective BeO film. No oxidation of beryllium from a freshly prepared amalgam in voltammetric conditions has been observed [21] making beryllium similar to iron [22] or cobalt [23] rather than nickel [24] or titanium [25]. Nevertheless, the activity coefficient of beryllium in its diluted amalgam is much smaller than unity, indicating that beryllium interacts with mercury [17]. A similar situation is found in the case of arsenic: some authors [26] have suggested a spontaneous formation of As_2Hg_3 and others [27] simply state that pure arsenic crystallizes out from its oversaturated amalgam; however, the activity coefficient of arsenic in the diluted amalgam is surely much higher than unity, indicating that arsenic does not interact with mercury [17]. Therefore beryllium should belong to group IV and arsenic to group III of the classification.

Later the heavier Lns may be moved from group I to group IV due to their decreasing solubilities (below 10^{-3} mol %), but little is known about the behaviour of these amalgams. The ICs of An are thermally less stable than the ICs of lanthanides but An cations are hardly reducible to the metallic state, therefore Ans belong to group IV. Palladium is significantly soluble and its dissolution in mercury is exothermic, but the stabilities of its ICs with mercury are rather low.

4. Conclusions

The classification proposed is very similar in the main part to that carried out by Jangg [15]; however, much better documentation is presented here. Affiliation of a metal to one of the groups visualizes a class of experimental difficulties: investigation of the amalgams of group II is easiest and of group IV the most difficult.

Aquaintance with other features of amalgams, especially of groups III and IV, will surely make the classification stronger. It is believed that other liquid alloys, based on Ga, In, Sn, Pb, Bi or alkali metals as solvents, might be classified in the same way as the amalgams.

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Received 4 May
and accepted 10 October 1988