Electrode Potentials in Anhydrous Formic Acid

By *V. Pleskov*

Anhydrous formic acid is a solvent which presents undoubted interest from the electrochemical point of view. It combines a high dielectric constant—57.0 at 21° (Drude's [1] measurements)—with strong solvent action towards a large number of salts and organic compounds, as was shown by the work of Zanninowitch-Tessarin [2], Aschan [3], Kendall and Adler [4]. The electrochemical properties of formic acid solutions were the object of a number of investigations by Schlesinger and coworkers[5] who have shown that this solvent possesses high ionizing properties; the coefficient of electrical conductivity of 0.1 *N* solutions attains as a rule, 0.9 and more. Formic acid is moreover a solvent with clearly expressed acid properties; this is borne out, besides its chemical nature, by the fact that it considerably strengthens weak bases and reduces the strength of acids (Hammett and Dietz[6], Schlesinger and Martin[7]). As shown by Funk and Römer[8],

---

[1] P. Drude, Z. physik. Chem., **23**, 267 (1897).
[2] H. Zanninowitch-Tessarin, Z. physik. Chem., **19**, 251 (1896).
[3] O. Aschan, Chem. Ztg., **37**, 1117 (1913).
[4] J. Kendall and H. Adler, J. Am. Chem. Soc., **43**, 1470 (1921).
[5] H. Schlesinger and R. Calvert, J. Am. Chem. Soc., **33**, 1924 (1912). H. Schlesinger and A. Martin, ibid., **36**, 1589 (1914); H. Schlesinger and C. Coleman, ibid., **38**, 271 (1916); H. Schlesinger and R. Mulliniz, ibid., **41**, 72 (1919); H. Schlesinger and F. Reed; ibid., **41**, 1921 (1919); H. Schlesinger and E. Bunting, ibid., **41**, 1934 (1919).
[6] L. Hammett and N. Dietz, J. Am. Chem. Soc., **52**, 4795 (1930).
[7] H. Schlesinger and A. Martin, J. Am. Chem. Soc., **36**, 1589 (1914).
[8] H. Funk u. F. Römer, Z. anorg. Chem., **239**, 288 (1938).

many chlorides, *e. g.* $CaCl_2$ liberate upon treatment with anhydrous formic acid free HCl and form the corresponding formates; this is undoubtedly to be explained by a far-going solvolysis due to the same factor.

We have established in previous papers the existence of considerable shifts of the standard potentials of some elements in liquid ammonia[9] and hydrazine[10] and connected this with the basic character of these solvents and their solvating action towards a number of ions. The aim of the present paper was to measure the electrode potentials in anhydrous HCOOH, a typical acid solvent.

Experimental part

S o l v e n t. Chemically pure formic acid was preliminarily purified by two fractional distillations under reduced pressure and then repeated fractional freezing out under conditions which excluded the access of moisture from the air. The final dehydration was carried out by the method of S c h l e s i n g e r and M a r t i n[7], which consists in treatment with boric anhydride. The latter was obtained by melting preliminarily dehydrated boric acid in a platinum crucible in an electric furnace at 900—1000°; after the evolution of water vapour had ceased the melt was poured out on a nickel plate, cooled in a desiccator and quickly powdered in an Abich mortar. The pre-purified formic acid was dehydrated with boric anhydride during 10—15 days with periodic shaking (to avoid coagulation of the powder). The mixture was then frozen, evacuated with an oil pump, and the anhydrous HCOOH distilled off at room temperature; to avoid carrying along the residue, two glass filters were placed on the way of the vapour. The distillation was repeated twice and the final product stored in sealed ampoules. This treatment yielded a solvent with the following properties: electric conductivity (at 25°)—$(5.8—6.0)\times10^{-5}\Omega^{-1}$, m. p. 8.39—8.40° C, which are in agreement with the best data in the literature.

M e t h o d o f m e a s u r e m e n t. In this investigation we used the method developed for measuring the potentials in hydrazine[10].

---

[9] V. P l e s k o v and A. M o n o s s o n, Acta Phys. Chim., **1**, 871 (1935).
[10] V. P l e s k o v, Acta Phys. Chim., **13**, 662 (1940).

As a rule, the solvent used was freshly treated with boric anhydride and had stood not more than one day to avoid possible decomposition of formic acid with formation of water and carbon monoxide. The solutions were stirred and saturated with a current of electrolytic hydrogen, which was purified in the same manner as in the case of hydrazine. All the basic measurements were carried out at $25.00 \pm \pm 0.01°$. The measuring apparatus did not differ from that previously used. As in the case of hydrazine we were compelled to ignore the diffusion potentials arising at the interface between the solutions in both half-cells, since for formic acid no practical means of suppressing them are known. It is probable, however, that the errors involved are not great (according to the data of Schlesinger, the mobilities of a number of cations in HCOOH have close-lying values). The measurements were carried out with dilute solutions (0.01 *N* as a rule) in order to reduce the errors due to the differences in the activity coefficients.

It was not always possible to make up the solutions directly in the apparatus in view of the small weights involved. In such cases we always prepared more concentrated solutions in HCOOH out of the apparatus, under conditions excluding the access of air and moisture. These solutions were then distributed in thin-walled ampoules which were introduced into the apparatus and broken inside it at the right moment by means of an electromagnetic hammer. After this the solutions were diluted with the necessary amount of formic acid which, as in the case of hydrazine, was introduced by distillation from a graduated pipette.

No less than three independent experiments were made with each cell; each experiment consisted of a series of measurements of the e. m. f. lasting 2—3 hours; in some cases the constancy of the e. m. f. was controlled for 24 hours. Work with dilute solutions naturally demanded special precautions against any increase in the amount of metal ions in the solution due to oxides dissolving from the electrodes; special attention was, therefore, devoted to obtaining clean electrode surfaces. In the case of easily oxidized metals (zinc, cadmium, lead) the oxides were removed mechanically in a continuously renewed atmosphere of dry electrolytic hydrogen.

Our choice of salts for the solutions was determined by their sufficient solubility in formic acid and by the possibility of obtaining them in pure anhydrous state. In many cases picrates were the most

suitable objects. Undoubtedly, these compounds undergo far-reaching solvolysis upon solution in HCOOH (this is borne out in particular, by the fact that the resulting solutions are almost colourless) however, the resulting formates, acting as bases in formic acid should be strongly dissociated.

Reference electrode. A number of experiments were carried out in search of a suitable reference electrode; we finally fixed our choice on a silver electrode in a 0.01 *N* solution of silver picrate. The latter was obtained by precipitating twice recrystallized silver nitrate with a slight excess of KOH solution upon heating. The silver oxide deposit was carefully washed and treated with a slightly insufficient amount of picric acid solution (obtained by repeated crystallization from a water—alcohol solution, m. p. 122°); the resulting solution was separated from the excess silver oxide drawn off on a glass filter and dried to constant weight in a vacuum at 130—140°. The silver electrodes were made from silver wire (Kahlbaum) and coated just before the experiment with electrolytic silver from a cyanide bath. After rapid drying in a current of warm air the electrodes were placed in the apparatus which was then immediately evacuated. We always used a pair of electrodes whose potentials did not differ by more than 0.1 mV. The potential of silver under the conditions described was excellently reproducible and accurately followed the changes in concentration of silver picrate in the solution. This was shown by measurements of the e. m. f. of concentration cells of the type

$$\text{Ag/Ag Picr.}/\underset{c_1}{\text{Ag Picr.}}/\underset{c_2}{\text{Ag}},$$

where $c_1 = 0.1$ *N* and c_2 varied from 0.05 to 0.0005 *N*. Some of the results obtained are presented in Table 1.

Table 1

Electromotive force of concentration cells at 25°

c_2	E (V)
0.05	0.0413
0.01	0.0554
0.001	0.1129
0.0005	0.1546

It may be seen from the table that the variation of the e. m. f. with concentration approaches the theoretical prediction (assuming that the mobilities of the cation and anion have close values); this

testifies to the fact that the activity coefficients of the solutions investigated are close to unity. The disadvantage of using a silver electrode for reference is that in many cases the measured e. m. f. becomes exceedingly large (*e. g.* in measurements with the amalgams of alkali metals); however, this is compensated by the simplicity of construction and excellent reproducibility of the electrode.

Z i n c. The choice of a zinc salt suitable for the measurements presented some difficulty since most of the salts of this metal, in particular, the picrate, formate and sulphate are insoluble in formic acid. It was found, however, that $ZnCl_2$ is well soluble and yields solutions whose electrical conductivity differs little from that of the salts of the alkali metals. Zinc chloride (Merck «for analysis») was dehydrated in a current of hydrogen chloride and distributed in molten state in small ampoules. A more concentrated solution (about 0.1 *N*) was first prepared; this was diluted to the required degree in the apparatus. The electrodes were made of Kahlbaum zinc; their surface was cleaned with a piece of glass immediately before the measurements. The potential of zinc was constant to 0.2 mV and highly reproducible. For the cell

$$\overset{-}{Zn} \mid \underset{0.01\ N}{ZnCl_2} \mid \underset{0.01\ N}{AgPicr./}\overset{+}{Ag}$$

$E_{25^\circ} = 1.326_4$ V; $\Delta E/\Delta t = -0.0006$ V/°C (the temperature coefficient was determined in the interval 15—25°). For a similar cell with a 0.001 *N* $ZnCl_2$ solution we found $E_{25^\circ} = 1.354$ V. The difference is thus equal to 0.028 V, which may be taken as proof that the activity coefficients of these solutions are close to unity.

C a d m i u m. As in the case of zinc the chloride was the only salt whose solubility was sufficient for the measurements. Cadmium chloride (Kahlbaum «for analysis») was dehydrated in a current of HCl; the solutions and the electrode (Kahlbaum) were prepared as in the case of zinc. The potential varied within the limits of 0.04 mV. For the cell

$$\overset{-}{Cd} \mid \underset{0.01N}{CdCl_2} \mid \underset{0.01N}{AgPicr.}\mid\overset{+}{Ag}$$

we found as an average

$$E_{-5^\circ} = 0.924_3 \text{ V}; \quad \Delta E/\Delta t = -0.0007 \text{ V/°C}.$$

Lead. Among the lead salts investigated, $PbCl_2$, $PbSO_4$, $Pb(NO_3)_2$ were found to be practically insoluble (the latter reacts with decomposition of HCOOH and evolution of gas). PbI_2 is slightly soluble and separates out upon the addition of water to the solution; its solubility, however, is very small (0.1%). Lead formate is more soluble (about 0.3% at 25°); it was chosen for the measurements. It was prepared according to Schlesinger by mixing aqueous solutions of $Pb(NO_3)_2$ and NaHCOO (Merck c. p.) in the presence of a small amount of HCOOH. The deposit was twice recrystallized, washed by alcohol and dried in a vacuum at 120°. For electrodes we used strips of sheet lead (Kahlbaum) with a freshly cut surface. The e. m. f. of cells with lead electrodes were highly reproducible in individual experiments (to 0.2 mV). For the cell

$$\overset{-}{Pb}/Pb(HCOO)_2/AgPicr./\overset{+}{Ag}$$
$$0.01N \qquad 0.01N$$

we found $E_{25°} = 0.889_5$ V:

$$\Delta E/\Delta t = -0.00054 \text{V}/°\text{C}.$$

Copper. We did not succeed in finding a salt of univalent copper soluble to any degree in anhydrous formic acid so that a measurement of the potential Cu/Cu· was impossible; considerable difficulties were also encountered in the attempt to work with salts of bivalent copper. We tried $CuSO_4$, $CuBr_2$, $CuCl_2$, $Cu(NO_3)_2$ and $Cu(CH_3COO)_2$ but none of these compounds was sufficiently soluble to permit of carrying out measurements. According to the data of Davidson and Holm[11] copper formate is very slightly soluble in formic acid (0.004 mol. % at 35°). In attempting to use copper picrate we discovered a curious phenomenon. The picrate obtained by dissolving CuO in an aqueous solution of picric acid, recrystallizing from a water—alcohol solution and drying in a vacuum at 140°, is highly soluble in anhydrous formic acid and yields completely transparent blue solutions. After a short interval (from 5 min. to half an hour, depending, evidently, on the presence of traces of dust and other mechanical impurities) the solution suddenly begins to grow turbid and a green crystalline deposit rapidly separates out, which upon investigation proved to be copper formate; the picric acid remains in solution. If a small amount of

[11] A. Davidson and V. Holm, J. Am. Chem. Soc., 53, 1350 (1931).

copper formate is introduced into a fresh transparent solution of picrate, a deposit immediately separates out and the solution is discoloured. It is evident that the copper picrate immediately undergoes solvolysis upon solution, but the resulting formate yields a supersaturated solution and only crystallizes in the presence of dust particles and other crystallization nuclei. This phenomenon made it possible to measure the potential of copper. Table 2 presents the variation of the e. m. f. with the time for the cell

$$\overset{-}{\text{Cu}}|\text{CuPicr.}_2\,|\,\text{AgPicr.}_2|\overset{+}{\text{Ag}}$$
$$0.01\ N \qquad 0.01\ N$$

in an experiment which may be regarded as typical. The measurements were carried out at 25°; zero time corresponds to the dissolution of picrate after the formic acid in the apparatus has melted.

Table 2

Potential of the Cu-electrode

Time (min.) . .	0	2	4	6	8	10	12	14
E (V) . .	0.3145	0.3143	0.3150	0.3148	0.3149	0.3151	0.3194	0.3310
Time (min.) . .	16	20	30	50	—	—	—	—
E (V) . .	0.3384	0.3410	0.3415	0.3418	—	—	—	—

As appears from the table the potential of the copper electrode remained constant for 10 min., then the formate deposit began to separate out and the potential started to increase up to the 20th min. when it once more took on a constant value exceeding the initial value by 27 mV. This evidently corresponded to a steady state concentration of $Cu^{\cdot\cdot}$ ions with a solubility of copper formate of about 0.001 N (at 25°). Table 3 which is a summary of the initial and final e. m. f. of this cell in various experiments, characterizes the reproducibility of the measurements.

Table 3

	E_{in}	E_{fin}
	0.3144	0.3416
	0.3148	0.3425
	0.3145	0.3418
	0.3152	0.3410
Average . .	0.3147	0.3417

We consider that the initial value of the e. m. f. may be taken on good grounds as a characteristic of the standard potential of copper,

even though it does correspond to a strongly supersaturated solution of the formate. The temperature coefficient of the e. m. f. was not determined for this cell.

M e r c u r y. We could not find a single salt of bivalent mercury suitable for the measurements; $HgCl_2$, HgI_2, $Hg(NO_3)_2$ are insoluble in HCOOH (the last-named salt reacts with decomposition). Attempts to make use of the picrate and formate were also unsuccessful; both salts turned out to be very unstable and practically insoluble in formic acid. Among the compounds of univalent mercury, HgCl and HgI are insoluble (the latter dissolves slightly upon heating), while $HgNO_2$ reacts with decomposition. We succeeded in making measurements of the potential with the formate. This salt was prepared by precipitating a $HgNO_3$ solution with a solution of sodium formate. If the washing (with water and alcohol) and drying are carried out quickly, a pure white product is obtained, which is stable on storage and leaves no residue upon solution in formic acid (the solubility is of the order of 1—2% at ordinary temperature). The e. m. f. of the cell

$$\overset{+}{\text{Hg}} \,|\, \text{HgHCOO} \,|\, \text{AgPicr.} \,|\, \overset{-}{\text{Ag}}$$
$$0.01\ N \quad 0.01\ N$$

is equal (mean value) to

$$E_{25^\circ} = 0.0012\text{V}, \quad \Delta E/\Delta t = -0.00046\ \text{V}/^\circ\text{C}.$$

The variations of the potential did not exceed 0.5 mV; however, in the course of time the e. m. f. began to increase systematically (due, perhaps, to partial decomposition of the mercury formate solution).

H y d r o g e n. As already point out, measurements of the potential of hydrogen in formic acid are of particular interest. Such measurements were undertaken by H a m m e t t and D i e t z [6], but these authors failed to obtain a reversible hydrogen electrode. Preliminary experiments carried out by us had shown that this problem can be solved by using platinum electrodes platinized in the usual way, provided the electrode undergoes cathodic polarization immediately before the measurements (in the same solution). This was accomplished by adding to the two platinized platinum electrodes (of surface area about 2 cm^2 each) a third auxiliary electrode, fixed on the same ground joint and serving as anode. The polarization was

carried out with a current of 5—7 mA during one minute (each electrode in turn).

Some difficulty was occasioned by the choice of the electrolyte. Hammet and Dietz used solutions of benzene-sulphonic acid, but this compound is difficult to obtain in anhydrous state; besides, there are no data on its strength in HCOOH. Our investigations were carried out with HCl solutions, whose electrical conductivity in formic acid was studied by Schlesinger, Martin and Coleman. It has already been observed that the strength of the acids, HCl included, derceases in HCOOH. However, the coefficient of electrical conductivity of a 0.01 N solution is 0.86, so that the error here involved cannot be great.

Hydrogen chloride was prepared from c. p. sulphuric acid and ammonium chloride dried over concentrated sulphuric acid and magnesium perchlorate and stored in a gas buret over mercury. The solution was prepared directly in the apparatus for potential measurements. For this purpose the tube for hydrogen inlet in the half-cell was provided with a special side-tube, through which the formic acid contained in the half-cell was saturated with a measured quantity of hydrogen chloride. In view of the fact that the solubility of the latter in HCOOH is not very great and the passage of hydrogen through the solution might have noticeably affected its concentration, the solution was forced upon completion of the measurements into a weighed bulb containing water, and the HCl content was determined gravimetrically. Prior to the measurements the solution was saturated with a current of hydrogen for 10—15 min. whereafter the electrodes were polarized as described above, and readings of the e. m. f. begun. The experiments have shown that after 5—10 min. the potentials of the two electrodes were equalized and remained constant to 0.5 mV throughout the rest of the measurements.

Table 4 presents the results of the measurements of the e. m. f. for the cell

$$\overline{\text{Pt}}\ \text{H}_2\,|\,\text{HCl}\,|\,\text{AgPicr.}\,|\,\overset{+}{\text{Ag}}$$
$$c \quad 0.1N$$

at 25°, obtained in individual experiments and reduced to $P_{H_2}=760$ mm

Table 4

Potential of the H_2-electrode

c	0.01021	0.01003	0.00989	0.00101	0.00105
E	0.1691	0.1702	0.1714	0.2251	0.2248

Interpolation for $c = 0.01\ N$ gives

$$E_{25°} = 0.170_3 \text{V};\ \Delta E/\Delta t = -0.00034\ \text{V/°C}.$$

Alkaline metals. Measurements of the potentials of the alkaline metals are of special interest as offering a possibility of comparing the potential series in various solvents. Achievement of these measurements by the Lewis method using amalgam electrodes presented some difficulty, in view of the comparatively high degree of dissociation of the solvent itself and its acid character. This difficulty could be overcome by carrying out the measurements in alkaline solutions, *i. e.* in solutions of the formates of the corresponding metals. Nevertheless, experience proved that measurements with stationary amalgams cannot be realized, for 10—20 sec. after the formation of a fresh surface of amalgam the potential begins to fall, due, obviously, to interaction of the alkali metal with the solvent. All the data given below were, therefore, obtained with a dropping electrode (2—3 drops of amalgam per second). In order to decrease the errors caused by accumulation of the formate in the solution, the volume of the half-cell with amalgam electrode was increased to 50 cm^3 the electrode being placed in the upper half of the vessel. All the amalgams were prepared electrolytically by a method already described[12]. Their concentrations were the same as those of the amalgams employed by Lewis and Kraus[13] (Na), Lewis and Keyes[14] (K, Li), Lewis and Argo[15] (Rb) and Bent, Forbes and Forziati[16] (Cs) which made it possible for us to utilize the data of these authors on the potential difference between the amalgam and the pure metal.

Lithium. The amalgam contained 0.035% Li. Lithium formate, which served as electrolyte was obtained from the carbonate (Merck) and formic acid and was dehydrated in a vacuum at 150°. The average e. m. f. of the cell

$$\overline{\text{Li, Hg}} \,|\, \underset{0.01\,N}{\text{LiHCOO}} \,|\, \underset{0.01\,N}{\text{AgPicr.}} \,|\, \overset{+}{\text{Ag}}$$

was equal to

$$E_{25°} = 2.684\text{V};\ \Delta E/\Delta t = 0.00085\text{V/°}C.$$

[12] V. Pleskov, Acta Phys. Chim., **6**, 1 (1937).
[13] G. Lewis and C. Kraus, J. Am. Chem. Soc., **32**, 1459 (1910).
[14] G. Lewis and F. Keyes, J. Chem. Soc., **34**, 119 (1912); **35**, 340 (1913).
[15] G. Lewis and K. Argol, J. Am. Chem. Soc., **37**, 1983 (1915).
[16] H. Bent, G. Forbes and A. Forziati, J. Am. Chem. Soc., **61**, 709 (1939).

Despite all precautions, the variation of the potential in individual experiments was as much as 1—2 mV.

Sodium. An amalgam containing 0.205% Na was used. The sodium formate was a Merck product, twice recrystallized from anhydrous formic acid and then subjected to prolonged drying in a vacuum at 140°. The potential was more constant than in the case of the lithium, variations of the e. m. f. lying within 0.5 mV. On the average for the cell

$$\overline{\text{Na,Hg}}/\text{NaHCOO}/\text{AgPicr.}/\overset{+}{\text{Ag}}$$
$$0.01N \quad 0.01N$$

we found

$$E_{25°} = 2.747\text{V}; \quad \Delta E/\Delta t = 0.0010\text{V}/°\text{C}.$$

Potassium. The amalgam contained 0.2216% K. The electrolyte was potassium formate (prepared from the carbonate Merck) twice recrystallized from HCOOH and dried in a vacuum at 140—150°. The variations of the potential did not exceed 1 mV. On the average for the cell

$$\overline{\text{K,Hg}}/\text{KHCOO}/\text{AgPicr}/\overset{+}{\text{Ag}}$$
$$0.01N \quad 0.0N$$

we obtained

$$E_{25°} = 2.486\text{V}; \quad \Delta E/\Delta t = 0.0012\text{V}/°\text{C}.$$

Rubidium. The amalgam used contained 2.695×10^{-5} gram-equivalents Rb per gram Hg. The formate was obtained from the carbonate and recrystallized first from HCOOH, then from a mixture of alcohol and ether. It was dried in a vacuum first at 100° then at 150°. The e. m. f. was comparatively steady (the variations not exceeding 0.8 mV). On the average for the cell

$$\overline{\text{Rb,Hg}}/\text{RbHCOO}/\text{AgPicr.}/\overset{+}{\text{Ag}}$$
$$0.01N \quad 0.01N$$

we get

$$E_{25°} = 2.547\text{V}; \quad \Delta E/\Delta t = 0.0007\text{V}/°\text{C}.$$

Calcium. The standard potential of calcium in water was determined by Drucker and Luft[17], who used an amalgam containing 0.0253% Ca. Our measurements were carried out with an amalgam of the same composition prepared by the electrolysis of a solution of $CaCl_2$ (Kahlbaum). The electrolyte was a solution of calcium formate obtained from the carbonate and

[17] C. Drucker u. R. Luft, Z. physik. Chem., **121**, 307 (1925).

dried in a vacuum at 140°. The measurements presented some difficulty since the variations of the potential were quite considerable, attaining 10 mV. Only after the rate of flow of the amalgam was greatly increased, reproducible results were obtained. For the cell

$$\overline{Ca,Hg} \,/\, Ca(HCOO)_2 \,/\, AgPicr. \,/\, \overset{+}{Ag}$$
$$0.01N \qquad 0.01N$$

the average value found was

$$E_{25°} = 2.527\,V; \quad \Delta E/\Delta t = 0.0003\,V/°C.$$

Caesium. The amalgam used contained 0.2327 atom % Cs, as in the work of Bent, Forbes and Forziati. The variations of the e. m. f. did not exceed 0.8 mV. On the average for the cell

$$\overline{Cs,Hg} \,/\, CsHCOO \,/\, AgPicr. \,/\, \overset{+}{Ag}$$
$$0.01N \qquad 0.01N$$

we found

$$E_{25°} = 2.492\,V; \quad \Delta E/\Delta t = 0.0005\,V/°C.$$

Discussion of the results

As pointed out above, in computing the standard potentials in formic acid we were obliged to neglect the differences in the activity coefficients of the various solutions (these cannot be very great for 0.01 N solutions) and also the diffusion potentials. Table 5 gives the data obtained; as in our preceding paper[10], the potential of rubidium was taken as zero. For comparison, the potentials in water and liquid ammonia are also given.

Table 5

Standard potentials ($E_{Rb} = 0$)

Element	E_{HCOOH}	E_{H_2O}	E_{NH_3}
Rb	0	0	0
Cs	0.01	0.00	—0.02
K	0.09	0.01	—0.05
Na	0.03	0.22	0.08
Li	—0.03	—0.09	—0.31
Ca	0.25	0.16	0.29
Zn	2.40	2.17	1.40
Cd	2.70	2.53	1.73
H_2	3.45	2.93	1.93
Pb	2.73	2.80	2.25
Cu/Cu^{++}	3.31	3.28	2.35
Hg/Hg^{+}	3.63	3.73	—
Ag	3.62	3.74	2.76

A consideration of the data in the table brings out that for most of the elements there is no great difference between the potential in HCOOH and in water. This is particularly true for all the alkali metals. Their potentials have close-lying values in a whole group of unrelated solvents (water, HCOOH, NH_3, N_2H_4); this fact supports our hypothesis that the energy of solvation of the ions of these metals undergoes but slight changes from one solvent to another. It should also be observed that it is practically immaterial which metal Rb or Cs, is chosen as the «standard» in comparing the potential series in different solvents, inasmuch as, even in two such widely different media as liquid ammonia and formic acid, the potentials of the two elements practically coincide. The potentials of silver, lead and copper are almost the same in water and in HCOOH. As for the first two metals this should be ascribed to the absence of any specific solvation of their ions in either solvent. On the contrary, in the case of copper there is no doubt that considerable hydration takes place. This appears in particular from the existence of numerous stable crystal hydrates of copper salts. However, D a v i d s o n and H o l m [11] have shown that HCOOH also has a stable crystal solvate, $2Cu(HCOO)_2 . 3HCOOH$, and it may be that the energy of solvation of $Cu^{\cdot\cdot}$ is about the same in both solvents. But in general, as far as can be judged from the data in the literature, formic acid is one of the solvents which only rarely form stable crystal solvates. This explains the not very large, but distinct displacements (of the order of 0.2 V) of the zinc and cadmium potentials towards positive values. The considerable tendency towards hydration manifested by the ions of these metals, and the existence of extremely stable crystal-hydrates of their salts are common knowledge.

Most noteworthy of all is the considerable shift of the hydrogen potential, which exceeds 0.5 V. As was pointed out in the introduction, HCOOH is a typically «acid» solvent. The energy of solvation of a proton in it should be greatly reduced so that the shift of the hydrogen potential in the positive direction is quite regular. It should also be remarked that the change in the hydrogen potential in passing from formic acid to liquid ammonia is 1.5 V, a value which demonstratively testifies to the far-reaching difference in the behaviour of the proton in the two solvents. Although our assumption of the constancy of the rubidium potential in different solvents is evidently not quite strict, and hence the comparison of the potential series carried out on

the basis of this assumption can only be aproximate, nevertheless, we esteem that the values of the hydrogen potential found can serve as a characteristic of the acid—basic properties of a number of solvents. An accumulation of such data would make it possible to draw up a quantitative scale of acidity. Work is being continued in this direction.

Summary

1. Measurements were made of the reversible electrode potentials of Rb, Cs, Na, K, Li, Ca, Zn, Cd, H_2, Pb, Cu, Ag and Hg in anhydrous formic acid at 25°.

2. The potential series in HCOOH differs little, in general, from the series in water. A shift of the standard potential in the positive direction is observed in those elements (Zn, Cd) whose ions, though strongly hydrated in aqueous solution, display no marked tendency towards solvation in formic acid. In general, the latter should evidently be considered as an example of a solvent with small solvating power.

3. The considerable positive shift of the hydrogen potential testifies to the small energy of solvation of the proton in HCOOH and fully bears out the «acid» nature of this solvent which is also displayed in a number of other chemical properties.

Karpov Institute of Physical Chemistry,
Laboratory of Non-Aqueous Solutions,
Moscow.

Received April 21, 1945.