776. *Reversible Electrodes in Tri-n-butyl Phosphate Solutions*

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The Pt | H_2, Ag | AgCl, and Pt | Fe(II)–Fe(III) electrodes give reversible, reproducible potentials, stable for a few hours, in tri-n-butyl phosphate (TBP) solutions containing water. The second electrode system follows the Nerst law fairly accurately. The glass electrode also gives a reversible potential, but its reproducibility and stability are limited. Acid-base and redox titrations can be carried out very readily in a wet tributyl phosphate medium with the aid of these electrodes. Measurements on the cell H_2 | HCl and H_2O in TBP | AgCl | Ag give the activity of hydrochloric acid in tributyl phosphate as a function of both the acid and the water concentration.

The electrical conductivities[1] of mineral acids and salts in tri-n-butyl phosphate (TBP) solutions containing some dissolved water are sufficiently high to permit potentiometric work, provided that instruments of sufficiently high input impedance are employed. Familiar electrodes can be used. A preliminary Note[2] has already been published on potentiometric measurements on hydrochloric acid solutions in tributyl phosphate saturated with water.

The present Paper explores some of the types of potentiometric operations that can be carried out in tributyl phosphate. It is worthy of note how extensive these are, despite the low dielectric constant (dry, 7·8; water-saturated, 10·0).[3] Potentiometric methods therefore provide a new and powerful means of investigating a solvent of wide interest.

Electrodes.—The Pt | H_2 electrode. A conventional platinised platinum electrode, with pre-saturated hydrogen bubbling past it, gave steady potentials to within ± 0·3 mv against Ag | AgCl in solutions of hydrochloric acid in tributyl phosphate saturated with water, down to 0·01M-hydrochoric acid. Different electrodes were reproducible to ±0·3 mv. In more dilute solutions, or in solutions deficient in water, deterioration occurred after, a few hours; the potential became sensitive to the rate of flow of gas, and the electrode whitened.

The Ag | AgCl electrode. Ag | AgCl electrodes were prepared by a pyrolytic method,[4] to avoid occlusion of water. They usually reached a stable potential against Pt | H_2 in hydrochloric acid in tributyl phosphate of fixed water content in about an hour. Freshly prepared electrodes tended to come to equilibrium more rapidly than aged electrodes. Reproducibility from electrode to electrode of the final steady potentials was within ±0·3 mv.

The glass electrode. A glass electrode manufactured by the Cambridge Instrument Co. Ltd. to British Standard 2586, with Ag | AgCl in either an aqueous or a tributyl phosphate solution of hydrochloric acid as internal reference electrode, gave sufficiently stable readings for acid-base titrations in tributyl phosphate containing approximately 3M-water; reproducibility was, however, not better than a few millivolts. The electrodes were stored in water when not in use; after a period of use in tributyl phosphate they tended to give erratic readings, but could be restored by immersion in water.

A glass electrode only approximates to a true hydrogen electrode, and in tributyl phosphate the discrepancies can be substantial, as Figure 1 shows. Here, the e.m.f. of the cell Pt | H_2 | HCl(c_1) in TBP | glass | HCl(c_2) in water or TBP | AgCl | Ag is plotted against c_1, the concentration of hydrochloric acid in the external solution.

If the glass behaved like a perfect semipermeable membrane, the e.m.f. at all values of

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[1] T. V. Healy and H. A. C. McKay, *Trans. Faraday Soc.*, 1956, **52**, 633; E. Hesford and H. A. C. McKay, *J. Inorg. Nuclear Chem.*, 1960, **13**, 156, 165; A. S. Kertes, *ibid.*, 1960, **14**, 104.

[2] H. A. C. McKay and J. H. Miles, *Nature*, 1963, **199**, 65.

[3] J. H. Miles, *J. Inorg. Nucl. Chem.*, 1964, **26**, 2308.

[4] A. S. Keston, *J. Amer. Chem. Soc.*, 1935, **57**, 1671.

c_1 would be the same as that of the cell Pt | H_2 | HCl(c_2) in water or TBP | AgCl | Ag, which is indicated by E_{Int}. The very large deviations from E_{Int} at high values of c_1 constitute a very large " acid error," and are worthy of further study. The curves in Figure 1 are, however, sufficiently flat at the lower acidities to warrant the use of the glass electrode in tributyl phosphate.

The Pt | Fe(II)–Fe(III) electrode. A bright platinum electrode, immersed in a mixed wet tributyl phosphate solution of iron(II) and iron(III) perchlorates, acidified with perchloric acid, gave potentials reproducible (as between two electrodes in the same solution) to ±0·2 mv. The potentials were measured against Ag | AgCl in standard hydrochloric acid in tributyl phosphate separated by a bridge solution of perchloric acid in tributyl phosphate. The cells had to be painted black to eliminate photochemical reduction of iron(III) in tributyl phosphate, but even so the potentials drifted slightly before reaching a steady value, which probably indicates slow chemical changes in the solution; at iron concentrations down to 5×10^{-4}M the drift never exceeded 1·2 mv, but at 5×10^{-5}M rapid fluctuations in e.m.f. occurred.

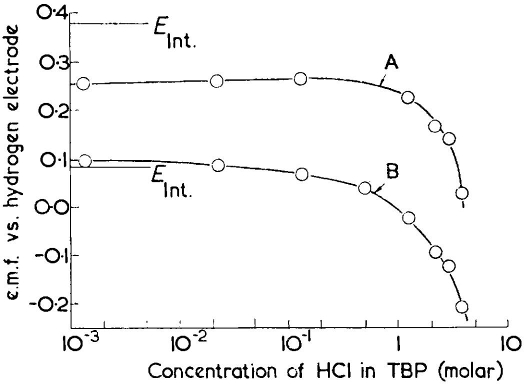

FIGURE 1. Behaviour of glass electrodes in hydrochloric acid in tributyl phosphate. (A) With internal aqueous solution. (B) With internal tributyl phosphate

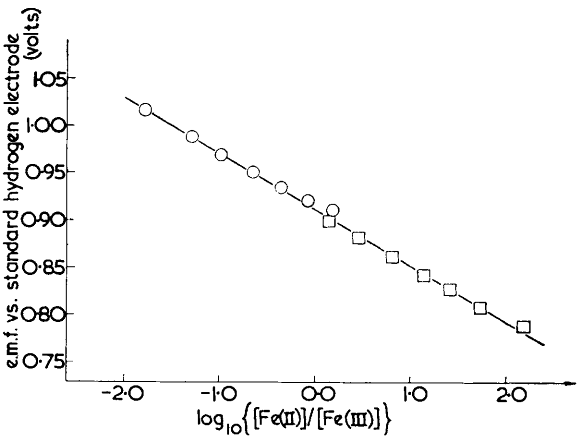

FIGURE 2. Potential of the Pt|Fe(II)–Fe(III) electrode in 1M-perchloric acid in tributyl phosphate as a function of Fe(II) : Fe(III) concentration ratio, for a total iron concentration of *ca.* 7×10^{-3}M. ○, Points obtained by addition of iron(II) to iron(III) solution. □, Points obtained by addition of iron(III) to iron(II) solution

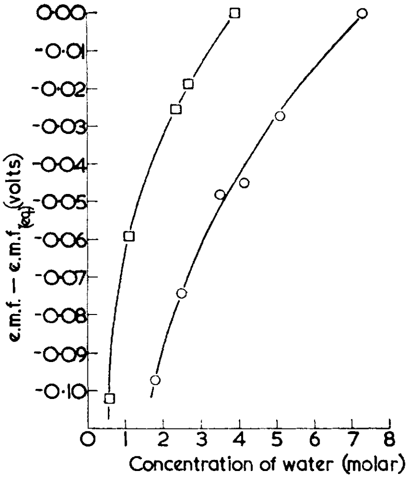

FIGURE 3. Effect of water on e.m.f. of the cell H_2 | HCl and H_2O in TBP | AgCl | Ag. □, 0·0905M-HCl. ○, 1·027M-HCl

The dependence of the potential on the iron(II) : iron(III) concentration ratio is shown in Figure 2 for a total iron concentration of *ca.* 7×10^{-3}M. The line is of slope 59·2 mv per log unit compared with a theoretical value of 59·14 mv per log unit. Similar graphs at *ca.* $5{\cdot}5 \times 10^{-4}$M and 8×10^{-2}M total iron gave 5% steeper slopes; the slight discrepancy may be due to various causes, *e.g.*, variations in the water content of the TBP phase, which however could not have exceeded 3%.

The following values were obtained for the standard potential of Fe(II)–Fe(III) couple in *ca.* 1M-perchloric acid in tributyl phosphate containing *ca.* 2·2M-water, against the standard hydrogen electrode at equimolarity:

Total iron concentration	0·2M	8×10^{-2}M	7×10^{-3}M	$5{\cdot}5 \times 10^{-4}$M
Potential	0·922v	0·936v	0·911v	0·932v

Mean 0·926v

Reversibility tests. All the electrodes used were subjected to tests for reversibility, in which the current flowing was measured as a function of the externally applied potential; on both sides of the balance-point. Very good linear plots were obtained in all cases.

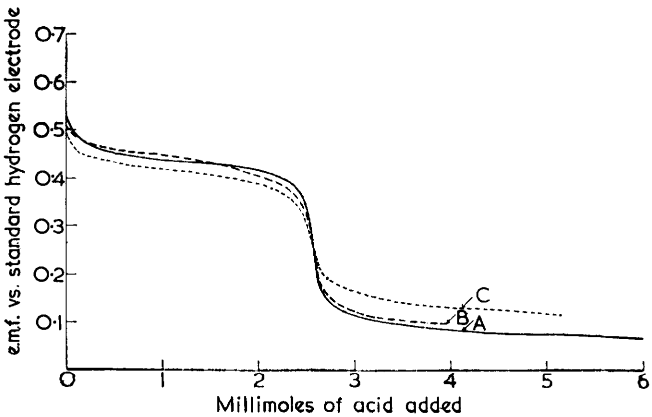

FIGURE 4. Titration of tributylamine with mineral acids in tributyl phosphate. (A) 0·592M-perchloric acid. (B) 0·384M-hydrochloric acid. (C) 0·635M-nitric acid

Effect of Water.—As has been indicated, all our observations have been made on tributyl phosphate solutions containing water; many of the solutions were in fact saturated with water, *i.e.*, obtained by equilibration with an aqueous phase.

In order to assess how closely variations in the water-content should be controlled, the e.m.f. of the cell

$$H_2\,|\,HCl \text{ and } H_2O \text{ in TBP}\,|\,AgCl\,|\,Ag$$

was measured as a function of water concentration, with the results shown in Figure 3. The solutions were prepared by passing hydrogen chloride gas into tributyl phosphate, and adding different amounts of water. Near the point of saturation with water, the e.m.f. changes by *ca.* 12 mv for 1M-change in water concentration, and the effect increases as water is removed. This is important for absolute measurements, and fairly close control of the water is then necessary, but the effect can be ignored in potentiometric titrations.

Potentiometric Titrations.—Acid-base titrations can readily be carried out in wet tributyl phosphate solutions with the aid of a glass electrode and a Ag | AgCl electrode in standard hydrochloric acid, the latter connected to the titration compartment through a bridge filled with TBP saturated with water. Figure 4 gives some typical titration curves; the end-point of 2·56 ± 0·01 mM may be compared with the value of 2·54 mM calculated from the amount of tributylamine taken.

It is even possible to carry out such titrations with the ordinary equipment used for aqueous solutions, *i.e.*, a glass electrode and a saturated calomel electrode, both filled with aqueous solutions, and a pH meter.

A titration of nitric acid against tributylamine in presence of uranyl nitrate is shown in Figure 5; the end-point is still satisfactory, and remains so even with a fourfold increase in the uranyl nitrate concentration, or with 20% v/v tributyl phosphate in kerosene as solvent.

Figure 6 shows the result of a redox titration in wet tributyl phosphate. At the end-point, the potential is unstable, but this does not affect the accuracy of the measurement.

The Activity of Hydrochloric Acid in Tributyl Phosphate.—Measurements on the cell $H_2 | HCl$ (c_{HCl}) and H_2O (c_{H_2O}) in TBP | AgCl | Ag make it possible to calculate the activity a_{HCl} of hydrochloric acid in tributyl phosphate. Measurements on solutions saturated with water have been reported previously,[2] and are shown again in Figure 7 for the sake of this discussion, while measurements on solutions deficient in water are given in Figure 3.

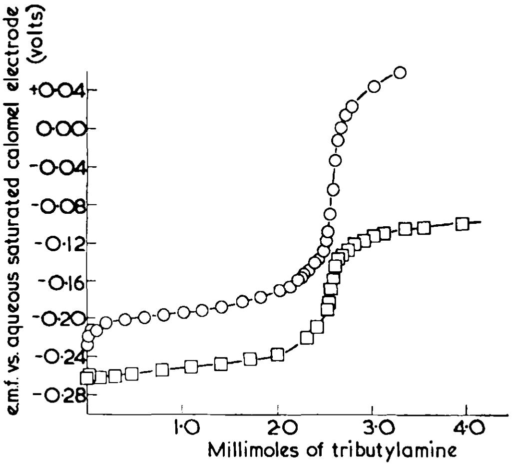

FIGURE 5. Effect of added uranyl nitrate on titration of 0·103M-tributylamine with 25 ml. of 0·105M-nitric acid in tributyl phosphate. ○, No uranyl nitrate. □, 0·103M-uranyl nitrate

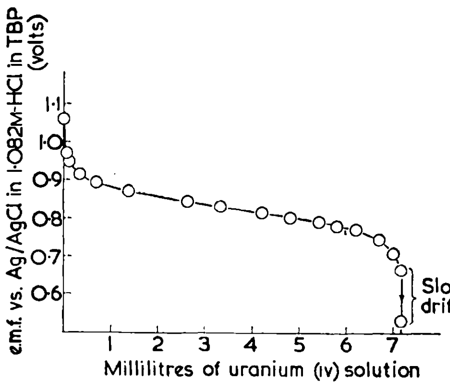

FIGURE 6. Titration of 10 ml. of 0·106M-iron(III) with 0·0742M-uranium(IV) in *ca.* 1M-perchloric acid in tributyl phosphate

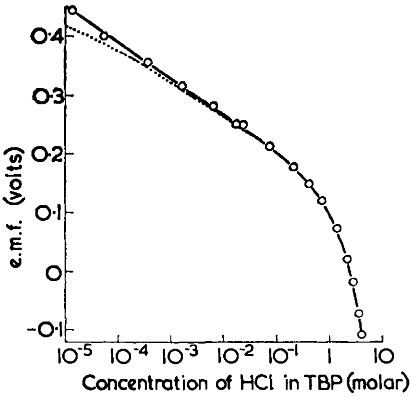

FIGURE 7. E.m.f. of the cell Pt | H_2 | HCl in water-saturated TBP | AgCl | Ag. The dotted curve includes a correction for the ionisation of hydrochloric acid in tributyl phosphate (see text)

The e.m.f. of the cell is given by the expression

$$E = E^\circ - (\boldsymbol{RT}/)\boldsymbol{F} \ln a_{HCl}.$$

The usual procedure is to obtain E° by extrapolation to infinite dilution, when ionisation is complete and $a_{\mathrm{HCl}} = c_{\mathrm{HCl}}^2$, but this cannot be done in the present case because the hydrogen electrode behaves erratically below 10^{-3}M. However, in solutions sufficiently dilute for un-ionised hydrochloric acid to behave ideally, it would be expected that

$$a_{\mathrm{HCl}} = K(1 - \alpha)C_{\mathrm{HCl}},$$

where K is the ionisation constant and α is the degree of ionisation. This gives

$$E = E^\circ - (\boldsymbol{RT}/\boldsymbol{F}) \ln K - (\boldsymbol{RTF}/) \ln [(1 - \alpha)C_{\mathrm{HCl}}].$$

The dotted curve in Figure 7 shows the effect of plotting E against $(1 - \alpha)C_{\mathrm{HCl}}$, the α-values being taken from Hesford and McKay's[1] Figure 2. Over a range from 10^{-3} to 5×10^{-2}M a straight line with the theoretical slope of 59·15 mv per log unit fits the points closely, and $E^\circ - (\boldsymbol{RT}/\boldsymbol{F}) \ln K$ has the value 0·138. The deviations from the linear law above 5×10^{-2}M can be ascribed to an activity coefficient of (un-ionised) hydrochloric acid in tributyl phosphate. The deviations below 10^{-3}M are not at present understood, but are probably due to experimental errors at the low concentrations concerned, either in the present potentiometric work or in the earlier conductivity work.

When water is removed from tributyl phosphate solutions of hydrochloric acid, a_{HCl} rises. Indeed, if the process is carried far enough at concentrations >1M, the solutions give off acid fumes. In Figure 3, the change in E on removal of water can be interpreted as a change in $(\boldsymbol{RT}/\boldsymbol{F}) \ln a_{\mathrm{HCl}}$; over the range plotted, a_{HCl} changes by a factor of about 50. This is a large effect, indicating that changes in the water-content of the tributyl phosphate phase may have considerable influence on partition coefficients, *e.g.*, in the presence of a salting-out agent, which lowers the water activity.

The magnitude of the effect is in general agreement with the results of measurements of the water-content of the tributyl phosphate phase. Kertes's results[1] for the water-content fit very closely to the equation

$$c_{\mathrm{H_2O}} = f(a_{\mathrm{H_2O}}) + 4{\cdot}8\ c_{\mathrm{HCl}},$$

where $c_{\mathrm{H_2O}} = f(a_{\mathrm{H_2O}})$ is the relationship determined by Hardy *et al.*[5] for tributyl phosphate–water mixtures. If we assume that this relationship holds for slightly water-deficient, as well as for water-saturated, solutions of hydrochloric acid in tributyl phosphate, then we obtain by differentiation

$$(\partial \ln a_{\mathrm{H_2O}}/\partial c_{\mathrm{HCl}})_{c_{\mathrm{H_2O}}} = -4{\cdot}8/f'(a_{\mathrm{H_2O}}) \,.\, a_{\mathrm{H_2O}}$$

This quantity can be calculated in the vicinity of water-saturation, where $a_{\mathrm{H_2O}}$ is known. It should be equal[6] to $(\partial \ln a_{\mathrm{HCl}}/\partial c_{\mathrm{H_2O}})_{c_{\mathrm{HCl}}}$ obtained directly from the curves in Figure 4. For 0·0905M-hydrochloric acid, the two expressions were found to be 0·64 and 0·63, respectively, *i.e.*, they agree very well.

EXPERIMENTAL

Materials.—Tributyl phosphate was purified as described by Alcock *et al.*[7] Iron(II) and iron(III) perchlorates were prepared by dissolving pure iron powder in perchloric acid, and evaporating the solution under reduced pressure to induce crystallisation; hydrogen peroxide was used as oxidant for the preparation of the iron(III) salt. Solutions in tributyl phosphate were standardised by titration against aqueous cerium(IV) sulphate; the iron(III) was first reduced with zinc amalgam. Uranium(IV) perchlorate solution was prepared by dissolving

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[5] C. J. Hardy, D. Fairhurst, H. A. C. McKay, and (Miss) A. M. Willson, *Trans. Faraday Soc.*, 1964, **60**, 1626.

[6] H. A. C. McKay, *Trans. Faraday Soc.*, 1953, **49**, 237.

[7] K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy, and H. A. C. McKay, *Trans. Faraday Soc.*, 1956, **52**, 39.

dicæsium hexanitratouranate(IV) [8] in perchloric acid, removing the cæsium perchlorate precipitated, precipitating uranium(IV) hydroxide, and redissolving it in ~1M-perchloric acid in tributyl phosphate at 60° under nitrogen.

E.m.f. Measurements.—A Croydon P4 potentiometer was used in conjunction with a very sensitive (1800 mm./μA) galvanometer for balance detection, or in some cases a Vibron electrometer.

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[8] H. A. C. McKay and J. L. Woodhead, *J.*, 1964, 717.