Communication—A Linear Equation Relating Interfacial Tension and Isotension Potentials to Describe Asymmetry in Electrocapillary Curves

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It has been known for more than a century that the interfacial tension of mercury dipped in electrolyte solutions changes with applied potential following a near parabolic course known as the electrocapillary curve. Solution components which are adsorbable on mercury produce asymmetric curves with respect to the potential at the electrocapillary maximum. A simple mathematical description of this asymmetry has, to date, excited and eluded many scientists. Here, a simple new linear relation which describes the electrocapillary curves for the existing data has been shown for the first time.

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Mercury (Hg), also known as quick silver, derives its symbol from its name ‘hydrargyrum’, meaning water-silver. It has a high surface tension in both air (20 °C, 486.5 dyne.cm−1) and water (20 °C, 415 dyne.cm−1).1 Its electrical conductivity as a liquid metal makes it an ideal renewable electrode in polarography.2 The change in the interfacial tension (γ) of mercury in solutions at different applied voltages (E) fascinated pioneers like Lippmann3 and Guoy,4,5 and the electrocapillary curve is therefore an ideal renewable electrode in polarography.2 The change in the surface tension in both air (20 °C, 415 dyne.cm−1) and water (20 °C, 486.5 dyne.cm−1) was obtained from graphs of E vs E′ drawn on a large scale. These are given in are given in Table II along with the following shifts of isotension potentials

$$\Delta E(+) = E_m - E(+)$$; \(\Delta E(-) = E(-) - E_m$$ and

$$\Delta E = \Delta E(+) + \Delta E(-)$$ [2]

and the ratios, \(R(+)\) and \(R(-)\),

$$R(+) = \frac{\Delta E(+) / \Delta E}{\Delta E(-) / \Delta E} = 1 - R(+)$$ [3]

Table I. Interfacial tension (γ) of mercury in aq. KBr solutions at 25°C. a) 0.01 M b) 0.1 M and c) 1 M. Potentials (E) vs 0.1 M calomel electrode. Values at the electrocapillary maximum are in bold. Data from Ref. 9.

| E (V) | γ (dyne/cm) |
|------|-------------|
| 1.592 | 329.8       |
| 1.475 | 349.7       |
| 1.353 | 368.0       |
| 1.227 | 384.3       |
| 1.102 | 398.1       |
| 0.982 | 408.9       |
| 0.868 | 416.9       |
| 0.761 | 422.3       |
| 0.656 | 425.4       |
| 0.572 | 426.3       |
| 0.512 | 425.7       |
| 0.463 | 424.3       |
| 0.417 | 422.0       |
| 0.371 | 418.8       |
| 0.328 | 414.9       |
| 0.286 | 410.3       |
| 0.25  | 405.6       |
| 0.22  | 401.1       |
| 0.191 | 396.3       |
| 0.173 | 392.9       |
| 0.16  | 390.0       |
| 0.144 | 386.7       |

a) 0.01 M b) 0.1 M and c) 1 M. Potentials (E) vs 0.1 M calomel electrode. Values at the electrocapillary maximum are in bold. Data from Ref. 9.

Figure 1 shows the graphs of γ as a function of E. It can be seen that the curves are not symmetrical parabolas and that the electrocapillary maximum (ecm) values of γm and Em shift with the concentration as shown. In this work, the author examined the relationship between the two isotension potentials E(+) and E(−) on either side of the electrocapillary maximum for the same value of γ. The potentials E(+) and E(−) at various values of γ were obtained from graphs of γ vs E drawn on a large scale. These are given in are given in Table II along with the following shifts of isotension potentials

Table II. Isotension potentials (E′) at various values of γ. a) 0.01 M b) 0.1 M and c) 1 M. Potentials (E) vs 0.1 M calomel electrode.

| E (V) | γ (dyne/cm) |
|------|-------------|
| 1.592 | 329.8       |
| 1.475 | 349.7       |
| 1.353 | 368.0       |
| 1.227 | 384.3       |
| 1.102 | 398.1       |
| 0.982 | 408.9       |
| 0.868 | 416.9       |
| 0.761 | 422.3       |
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| 0.463 | 424.3       |
| 0.417 | 422.0       |
| 0.371 | 418.8       |
| 0.328 | 414.9       |
| 0.286 | 410.3       |
| 0.25  | 405.6       |
| 0.22  | 401.1       |
| 0.191 | 396.3       |
| 0.173 | 392.9       |
| 0.16  | 390.0       |
| 0.144 | 386.7       |

a) 0.01 M b) 0.1 M and c) 1 M. Potentials (E) vs 0.1 M calomel electrode.

Results and Discussion

Here, the existing data9 for aqueous solutions of KBr have been used to show a simple linear relation that describes the asymmetry of the curves. For a preliminary report of these results, see Reference 10. The data for γ at various potentials (−E, with reference to 0.1 M KCl calomel electrode, with 0.1 M KBr bridge) for aqueous solutions of KBr at 25°C taken from Reference 9 are assembled in Table I.

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Figure 1. Interfacial tension (γ dyne/cm) vs potential (-E in V) curves for aq. KBr at 25°C, for the γ vs E data in Ref. 9.

Table II. Interfacial tension (γ) (dyne/cm) of mercury in aq. KBr at 25°C. Isotension potentials, E(+) and E(−) (in V) from Fig. 1 and their difference, ΔE; ΔE(+) = E(+ ) - E(−) and ΔE(−) = E(−) - E(−). The ratios, R(+) = ΔE(+)/ΔE and R(−) = ΔE(−)/ΔE.

|       | E(+)  | E(−)  | ΔE   | ΔE(+) | ΔE(−) | R(+) | R(−) | ΔE(+)ΔE(−) | ECM  |
|-------|-------|-------|------|--------|--------|------|------|-----------|------|
|       |       |       |      |        |        |      |      |           |      |
| γ     |       |       |      |        |        |      |      |           |      |
| 0.01 M| 0.160 | 0.182 | 0.216| 0.245  | 0.285  | 0.330| 0.390| 0.405     | 0.410| 0.415| 0.420| 0.426.3 |
| 0.1 M | 0.180 | 0.200 | 0.230| 0.260  | 0.300  | 0.350| 0.400| 0.410     | 0.415| 0.420| 0.424 | 0.424.5 |
| 1 M   | 0.250 | 0.275 | 0.305| 0.335  | 0.375  | 0.420| 0.470| 0.480     | 0.490| 0.500| 0.515| 0.473.8 |

Figure 2. Interfacial tension (γ dyne/cm) vs the ratio, R(+) (left) and R(−) (right).

From the data in Table II, it can be seen that R(+) increases with increasing γ for any given concentration, and also that it increases with concentration for any given value of γ. A pleasant surprise was to find for the first time that graphs of R(+) vs γ and the symmetrical R(−) [ = 1 − R(+)] vs γ are straight lines, as shown in Fig. 2. These lines follow the simple relations (slopes and intercepts are regressed values), for all three concentrations, a) 0.01 M, b) 0.10 M and c) 1.0 M.

\[ γ = 1095.30 R(+) − 52.01 = −1095.30 R(−) + 1043.29 \]  

\[ γ = 661.85 R(+) + 115.01 = −661.85 R(−) + 776.86 \]  

\[ γ = 792.32 R(+) + 31.65 = −792.32 R(−) + 823.97 \]

Table II. Interfacial tension (γ) (dyne/cm) of mercury in aq. KBr at 25°C. Isotension potentials, E(+) and E(−) (in V) from Fig. 1 and their difference, ΔE; ΔE(+) = E(+ ) - E(−) and ΔE(−) = E(−) - E(−). The ratios, R(+) = ΔE(+)/ΔE and R(−) = ΔE(−)/ΔE.

a) 0.01 M, E(+m) = 0.572; γm = 426.3

| γ     | E(+)  | E(−)  | ΔE   | ΔE(+) | ΔE(−) | R(+) | R(−) | ΔE(+)ΔE(−) | ECM  |
|-------|-------|-------|------|--------|--------|------|------|-----------|------|
|       |       |       |      |        |        |      |      |           |      |
| 0.01 M| 0.160 | 0.182 | 0.216| 0.245  | 0.285  | 0.330| 0.390| 0.405     | 0.410| 0.415| 0.420| 0.426.3 |
| 0.1 M | 0.180 | 0.200 | 0.230| 0.260  | 0.300  | 0.350| 0.400| 0.410     | 0.415| 0.420| 0.424 | 0.424.5 |
| 1 M   | 0.250 | 0.275 | 0.305| 0.335  | 0.375  | 0.420| 0.470| 0.480     | 0.490| 0.500| 0.515| 0.473.8 |

b) 0.1 M, E(+m) = 0.624; γm = 424.5

c) 1 M, E(+m) = 0.705; γm = 417.4

On eliminating the constants by using the values γm and R(+)m for the ecm, one gets the simple linear relation,

\[ γm − γ = K_e [R(+)m − R(+) \]  

where \( K_e = \frac{dy/dR(+) = \text{constant (dyne.cm}^{-1})} {\text{is the slope of the γ vs R(+) straight lines. A proper interpretation of the slopes can be made after analyzing the electrocapillary curves for other adsorbable halides.}}\)

The last rows in a-c in Table II show the ratios ΔE(+)/ΔE(−) = R(+)/R(−). It can be seen that with increasing concentration, these ratios increase. Graphs of γ vs these ratios and of γ vs ΔE are also
nearly linear, but Eq. 7 seems to be the good choice for the data used here.

Summary

A new solution for the long-unsolved problem of the asymmetry of $\gamma$ vs $E$ electrocapillary curves has been provided in terms of the isotension potentials, $E(+) and E(-)$ (see Eq. 2). Using the existing data for aqueous KBr solutions, it is shown here for the first time that $\gamma$ vs the potential ratio $R(+) (see Eq. 3)$ follows the simple linear Eq. 7, where, $K_s$ is a constant independent of $\gamma and E$, but dependent on the solute (s) and its concentration. Similar results, which confirm Eq. 7, were obtained for HCl, HClO₄, and Na₂SO₄. These will be presented in a future longer paper.

References

1. A. W. Adamson and A. P. Gast.; Physical chemistry of surfaces; 6th edition, Wiley, 1997.
2. J. Heyrovsky and J. Kuta. Principles of Polarography. Publishing House of the Czechoslovak Academy of Sciences, Prague, 1965.
3. G. Lippmann, Ann. Chim. Phys., 5, 494 (1875).
4. G. Gouy, Ann. Phys., 6, 3 (1916).
5. G. Gouy, Ann. Phys., Constitution of the electric charge at the surface of an electrolyte, 7, 129 (1917).
6. D. C. Grahame, Chem. Revs., 41, 141 (1947).
7. P. Delahay, Double Layer and Electrode Kinetics, Interscience, NY (1965).
8. A. Lewandowski, T. Majkowski, M. Galinski, and Z. Naturforsch., 64a, 263 (2009).
9. J. Lawrence, R. Parsons, and R. Payne, J. Electroanal. Chem. & Interfacial Electrochem., 162, 193 (1988).
10. R. Heyrovksa, http://vixra.org/abs/1603.0359; http://vixra.org/pdf/1603.0359v1.pdf.