A New Linear Equation Relating Interfacial Tension of Mercury and

Isotension Potentials Describing Asymmetry in Electrocapillary Curves

- Dedicated to the polarographer, Prof. J. Heyrovsky* (Dec. 20, 1890 – Mar. 27, 1967).

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Abstract

It has been known for over a century that the interfacial tension of mercury dipping in electrolyte solutions changes with applied potential following a near parabolic course called the electrocapillary curve. Solution components adsorbable on mercury produce asymmetric curves with respect to the potential at the electrocapillary maximum. A simple mathematical description of this asymmetry has so far exercised and eluded many scientists. Here, the author shows a simple linear relation which describes the electrocapillary curves, using the existing data.

Key words: Electrtocapillay curve; Interfacial tension; Asymmetric curves; Adsorption; Electrtocapillary equation.

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1. Introduction.

Mercury (Hg), also known as quick silver, derives its symbol from its name 'hydrargyrum'meaning water-silver, due its fluidity and silvery appearance. A general introduction to the interesting properties and uses of this metal can be found in [1]. It has a round atomic number of 80, high atomic weight of 200.6, high density of 13.69/g.cm^{-3}, high surface tension in air (20°C) of 486.5 dyne.cm^{-1} and in water (20 ^{o}C) of 415 dyne.cm^{-1} [2]. Its electrical conductivity as a liquid metal makes it an ideal renewable electrode in polarography [3]. The change of interfacial tension (γ) of mercury in solutions at different applied voltages (E) fascinated pioneers like Lippmann [4,5] and Guoy[6,7]. The parabolic γ vs E electrocapillary curves have since been of great value in the study of interfacial phenomena.

   A large body of literature exists on the properties and study of electrocapillary curves. See for detailed introduction, e.g., [8,9]. The parabolic dependence of the interfacial tension, γ on E is usually described by (see e.g., [3]),

$$\gamma_m - \gamma = (1/2)C'(E – E_m)^2 \tag{1}$$

where γ_m is the interfacial tension at the electrocapillary maximum corresponding to the potential, E_m and C' = - d$^2\gamma$/dE^2 is the specific capacity. In the ideal case of a parabola, C' must be a constant. However, this is not the case since the ionic components of the solution interact with the charged mercury surface differently at different potentials. The electrocapillary curve is therefore not a symmetrical parabola. See for many examples, [3,8,9]. This asymmetry has been treated mathematically by many. To cite a recent

example [10], the $\gamma = f(E)$ curves are described by an empirical (complicated) polynomial of the sixth order. Ionic components like halides, which adsorb on the positively charged mercury surface to the left of the electrocapillary maximum, lower the γ_m values and shift the corresponding potential, E_m to negative values. This is shown in Figure 1 for aqueous solutions of KBr, for the data in [11]. In this work, this data has been used to show a simple linear relation that describes the asymmetry of the curves.

2. Present work.

The interfacial tension (γ) data 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 [11] are assembled in Table 1. Figure 1 shows the graphs of γ as a function of E. It can be seen that the curves are not symmetric parabolas and that the ecm (electrocapillary maximum) values of γ_m and E_m shift with concentration as shown. Here the author took a different step from the previous workers, to see the relation between the two isotension potentials E(+) and E(-) on either sides of the electrocapillary maximum for the same value of γ. These are tabulated in Table 2. On calculating the following shifts of isotension potentials (see Table 2),

$$\Delta E(+) = E_m - E; \ \Delta E(-) = E - E_m \text{ and } \Delta E = \Delta E(+) + \Delta E(-) \qquad (2)$$

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

$$R(+) = \Delta E(+)/\Delta E \text{ and } R(-) = \Delta E(-)/\Delta E = 1 - R(-) \qquad (3)$$

it was a pleasant surprise to find, *for the first time,* that R(+) and hence R(-) vs γ are straight lines. These are shown in Figure 2. Therefore the following simple linear relations hold for the dependence of γ on R(+) [= 1 – R(-)]:

a) 0.01M: $\gamma = 1095.3R(+) + 52.01$ (4a)

b) 0.10M: $\gamma = 661.85R(+) + 115.01$ (4b)

c) 1.0M: $\gamma = 792.32R(+) + 31.65$ (4c)

Therefore, in general, the simple linear relation holds for the electrocapillary curve:

$$\gamma - \gamma_m = K_s[R(+) - R(+)_m]$$ (5)

where K_s (dyne.cm^{-1}) is the slope of the γ vs R(+) straight line, which depends on the solute (s) and its concentration, and $R(+)_m$ is the ratio when $\gamma = \gamma_m$.

Similar results, which confirm the above equation, were obtained for the existing data on electrocapillary curves for HCl, $HClO_4$ and Na_2SO_4. These will be presented in a different paper.

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Table 1. Interfacial tension (γ) of mercury in aq. KBr solutions at 25°C.
a) 0.01 M b) 0.1 M and c) 1M. Potentials (-E) vs 0.1M calomel electrode.
Values at the elctrocapillary maximum are in bold. Data from [11]

a) 0.01M		b) 0.1M		c) 1M	
E	γ	E	γ	E	γ
(V)	(dyne/cm)				
1.592	329.8	1.543	331.7	1.488	334.0
1.475	349.7	1.428	351.4	1.373	353.4
1.353	368.0	1.307	369.5	1.254	371.2
1.227	384.3	1.182	385.6	1.136	386.7
1.102	398.1	1.059	399.3	1.025	398.9
0.982	408.9	0.94	409.9	0.931	407.4
0.868	416.9	0.833	417.4	0.858	412.5
0.761	422.3	0.745	421.9	0.799	415.5
0.656	425.4	0.678	424.0	0.75	417.0
0.572	**426.3**	**0.624**	**424.5**	**0.705**	**417.4**
0.512	425.7	0.578	424.1	0.663	417.0
0.463	424.3	0.536	422.8	0.621	415.7
0.417	422.0	0.494	420.7	0.581	413.7
0.371	418.8	0.452	417.8	0.54	410.9
0.328	414.9	0.411	414.1	0.499	407.2
0.286	410.3	0.341	405.7	0.46	402.9
0.25	405.6	0.312	401.4	0.425	398.3
0.22	401.1	0.285	396.9	0.394	393.6
0.191	396.3	0.265	392.9	0.367	389.1
0.173	392.9	0.242	388.5	0.343	384.5
0.16	390.0	0.23	385.7	0.323	380.5
0.144	386.7			0.307	376.7

Table 2. 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; $\Delta E(+) = E_m - E(+)$ and $\Delta E(-) = E(-) - E_m$. The ratios, R(+) = $\Delta E(+)/\Delta E$ and R(-)= $\Delta E(-)/\Delta E$.

a) 0.01M. E_m = 0.572; γ_m = 426.3

								ECM
γ	390	395	400	405	410	415	420	426.3
E(+)	0.160	0.182	0.216	0.245	0.285	0.330	0.390	
E(-)	1.180	1.130	1.080	1.030	0.970	0.900	0.810	
ΔE	1.020	0.948	0.864	0.785	0.685	0.570	0.420	
$\Delta E(+)$	0.412	0.390	0.356	0.327	0.287	0.242	0.182	
$\Delta E(-)$	0.608	0.558	0.508	0.458	0.398	0.328	0.238	
$R_\gamma(+)$	0.404	0.411	0.412	0.417	0.419	0.425	0.433	0.437
$R_\gamma(-)$	0.596	0.589	0.588	0.583	0.581	0.575	0.567	0.563
$\Delta E(+)/\Delta E(-)$	0.678	0.699	0.701	0.714	0.721	0.738	0.765	0.774

b) 0.1M E_m = 0.624; γ_m = 424.5

γ	390	395	400	405	410	415	420	424.5
E(+)	0.250	0.275	0.305	0.335	0.375	0.420	0.490	
E(-)	1.145	1.100	1.050	0.995	0.935	0.870	0.780	
ΔE	0.895	0.825	0.745	0.660	0.560	0.450	0.290	
$\Delta E(+)$	0.374	0.349	0.319	0.289	0.249	0.204	0.134	
$\Delta E(-)$	0.521	0.476	0.426	0.371	0.311	0.246	0.156	
$R_\gamma(+)$	0.418	0.423	0.428	0.438	0.445	0.453	0.462	0.468
$R_\gamma(-)$	0.582	0.577	0.572	0.562	0.555	0.547	0.538	0.532
$\Delta E(+)/\Delta E(-)$	0.718	0.733	0.749	0.779	0.801	0.829	0.859	0.880

c) 1M E_m = 0.705; γ_m = 417.4

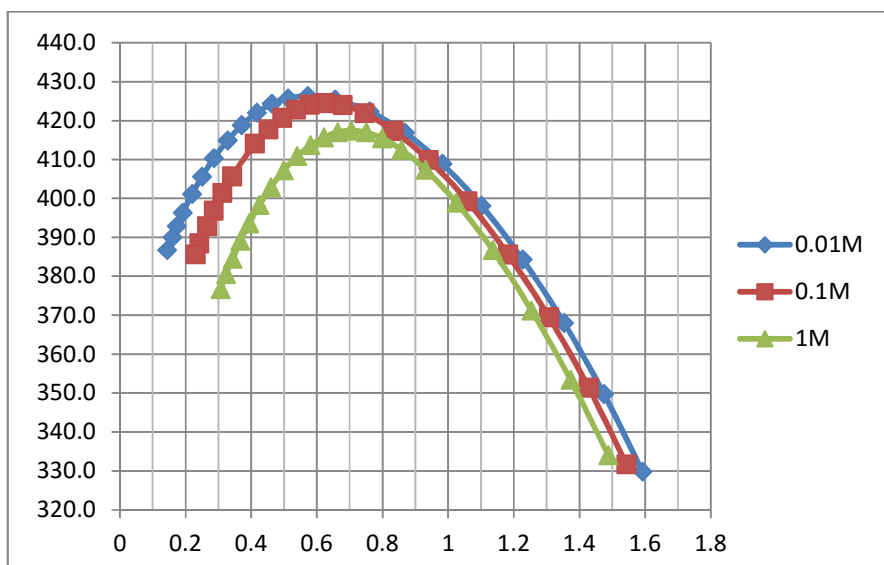|								
γ	380	385	390	395	400	405	410	417.4
E(+)	0.320	0.350	0.370	0.405	0.440	0.480	0.530	
E(-)	1.190	1.150	1.110	1.060	1.010	0.960	0.895	
ΔE	0.870	0.800	0.740	0.655	0.570	0.480	0.365	
$\Delta E(+)$	0.385	0.355	0.335	0.300	0.265	0.225	0.175	
$\Delta E(-)$	0.485	0.445	0.405	0.355	0.305	0.255	0.190	
$R_\gamma(+)$	0.443	0.444	0.453	0.458	0.465	0.469	0.479	0.487
$R_\gamma(-)$	0.557	0.556	0.547	0.542	0.535	0.531	0.521	0.513
$\Delta E(+)/\Delta E(-)$	0.794	0.798	0.827	0.845	0.869	0.882	0.921	0.949

Figure 1. Interfacial tension (γ) vs potential (-E) for aqueous solutions of KBr at 25° C. γ vs E data from [11]. At any value of γ, the potential difference, $\Delta E(+) = E_{ecm} - E(+)$ and it is less than $\Delta E(-) = E(-) - E_{ecm}$. This is the assymmetry of the EC curve.
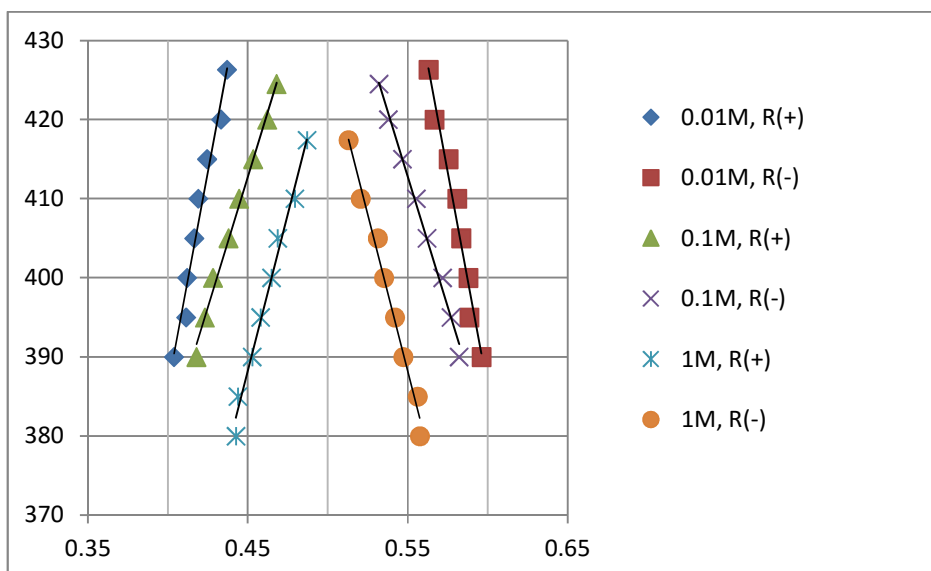

Figure 2. Linear dependence of interfacial tension (γ) on the ratio, R(+) (left) and R(-) (right) for aq. solutions of KBr at 25°C. Equation for the straight lines:

γ - γ$_m$ = K$_s$[R(+) - R(+)$_m$].