

NOTE ON THE PAPER "UEBER PHASENGRENZPOTENTIALLE ZWISCHEN WÄSSRIGEN UND NICHTWÄSSRIGEN ELEKTROLYTLÖSUNGEN", BY K. SCHWABE AND H. GEISLER\*

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THE GENERAL conclusion of the paper<sup>1</sup> is, that the diffusion potential between aqueous and non-aqueous electrolyte solutions of equal concentration will be small. The authors arrive at this result by measuring the emfs of a number of cells, which values, after some algebraic manipulations, are thought to give twice the value of this diffusion potential.

There is much confusion on the subject of diffusion potentials between electrolyte solutions in different solvents, which potentials in principle cannot be measured<sup>2</sup>, and we think that the conclusion of Schwabe and Geisler is based on an incorrect interpretation of the measured emfs.

From the description of their cells we conclude that, according to the IUPAC convention,  $U_a$  is negative and  $U_b$  and  $U_c$  are positive. (We suppose that the + and - signs indicate the polarity of an electrode with respect to its counterpart.) However, from Tables 1 and 2 it follows that a positive value is assigned to  $U_a$  (which gives the result  $U_a \approx U_b - U_c$ ).

Following the IUPAC convention gives  $U_a \approx U_c - U_b$  and further,  $D_1 \approx D_3 - D_2$ . Therefore, instead of Schwabe and Geisler's equation (1) we have

$$\begin{aligned} \varepsilon_D(\text{NaAz, KCl}) + \varepsilon_D^L(\text{CH}_3\text{OH, H}_2\text{O}) \approx \varepsilon_D(\text{NaAz, H}^+\text{A}^-) - \varepsilon_D(\text{KCl, H}^+\text{A}^-) \\ + \varepsilon_D^L(\text{CH}_3\text{OH, } x\text{H}_2\text{O}) - \varepsilon_D^L(\text{H}_2\text{O, } x\text{H}_2\text{O}). \end{aligned}$$

This means that the diffusion potential between electrolyte solutions in methanol and in water is not much altered by interposing an electrolyte solution in a methanol-water mixture. This result is obvious and does not give any information about the diffusion potential between electrolyte solutions in different solvents.

In our view, diffusion potentials between electrolyte solutions in different solvents can only be estimated when an estimate has been obtained of the primary medium effects for the various individual ions,<sup>2,3</sup> which Schwabe and Geisler did not try.

Presumably they have followed another convention, which permits one to define the cell emf alternatively as the potential of the left electrode minus that of the right electrode, ( $U_a$ ), and conversely, ( $U_b$  and  $U_c$ ). In this case the description of the cells (p. 148) and the values of the emfs in Tables 1 and 2 can be brought into agreement. However, the error then lies in the incorrect definitions of  $U_a$ ,  $U_b$ ,  $U_c$ ,  $U_d$  and  $U_e$  on p. 152, which should read

$$\begin{aligned} U_a &= -E_A + D_1 + E_B, \\ U_b &= -E_A - D_2 + E_X + E_{st} + E_C, \\ U_c &= -E_B - D_3 + E_X + E_{st} + E_C, \\ U_d &= -E_A - D_2 + E_F, \\ U_e &= -E_B - D_3 + E_F. \end{aligned}$$

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Consequently

$$-D_1 = D_2 - D_3 \text{ etc}$$

A minor objection to Schwabe and Geisler's paper is as follows. The diffusion potentials  $E_j^*$  given by de Ligny and Rehbach<sup>4</sup> are not based on the *assumption*, but on the *convention*, that the standard potential of the hydrogen electrode is equal to zero in each solvent. So these values do not have the meaning of Galvani potential differences between two solutions, but are purely conventional values, which are useful in pH\*-determinations in methanol-water mixtures.

#### REFERENCES

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### STELLUNGNAHME ZU DER BEMERKUNG VON M. ALFENAAR UND C. L. DE LIGNY\*

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1. IN UNSERER Arbeit<sup>1</sup> haben wir festgestellt, daß für die "Phasengrenzpotentiale"  $D_1$ ,  $D_2$ ,  $D_3$  (i.e.) annähernd gilt  $D_1 \approx D_2 - D_3$  und somit  $D_2$  wie  $D_3$  nicht wesentlich vom Lösungsmittel abhängig sind. An diesem Ergebnis ändert selbstverständlich die Verwendung der IUPAC-Schreibweise nichts. Wenn man zur Abkürzung für die in unserer Arbeit verwendeten 3 Potentiale  $[E_X + E_{St} + E_C] = E^X$  setzt, folgt mit dieser Schreibweise für die Kettenspannungen,

$$U_a = (E_B + D_1) - E_A,$$

$$U_b = (E^X + D_2) - E_A,$$

$$U_c = (E^X + D_3) - E_B.$$

Dabei ist  $E_A$  das Potential der Elektrode  $\text{Hg}/\text{Hg}_2\text{Cl}_2(\text{s}), \text{KCl}(\text{s}), \text{H}_2\text{O}$ ,  $E_B$  das Potential der Elektrode  $\text{Hg}/\text{Hg}_2\text{Az}_2(\text{s}), \text{NaAz}(\text{s}), \text{CH}_3\text{OH}(98\%)$ ,  $E^X$  das Potential der Kombination C: innere Ableitelektrode, Puffer, Glaselektrode/X mit X = Pufferlösung in  $x \text{H}_2\text{O}(1-x) \text{org. LM}$ . Die Kettenspannung  $U_A$  bezieht sich auf die Kette  $-A_{D_1}^{\parallel} B$ , + die Kettenspannung  $U_B$  bezieht sich auf die Kette  $-A_{D_2}^{\parallel} X | C$  + die Kettenspannung  $U_C$  bezieht sich auf die Kette  $-B_{D_3}^{\parallel} X | C$  +

Analoges gilt für die Ketten d und e (i.c.) Unser experimentelles Ergebnis lautet dann:  $(U_b - U_c) - U_a = (D_2 - D_3) - D_1 \approx D$  unabhängig vom Lösungsmittel, wobei natürlich alle Kettenspannungen  $> 0$  sind, daraus folgt die oben nochmals zitierte Beziehung  $D_1 \approx D_2 - D_3$ .

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