

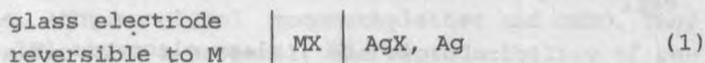
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THE USE OF IONSELECTIVE GLASS ELECTRODES  
IN INVESTIGATION OF THERMODYNAMIC PROPERTIES  
OF ELECTROLYTE SOLUTIONS IN MIXED SOLVENTS

Thermodynamic studies on alkyl halide solutions in mixed solvents with the use of cationselective glass electrodes were reviewed, including conclusions on the usefulness of these electrodes for thermodynamic investigations of solutions.

More and more frequently glass electrodes reversible to monovalent alkaline metal cations are used for thermodynamic studies on electrolyte solutions in water-organic solvent mixtures [1-13] and also, though more rarely, on pure non-aqueous solvents [7, 10, 14].

Most studies are aimed at the determination of free enthalpy of transfer and activity coefficients of electrolyte. Such studies are mostly based on electromotive force (EMF) measurements of cells of the type:



where X is, in principle, a halogen.

Some authors use other electrodes of second kind [10].

Considering the simplified Eisenman's equation [15] describing the potential of glass electrode, the EMF of cell (1) can be expressed:

$$E = E^{\circ} - \frac{RT}{F} \ln (a_M + K_{Mi}a_i + K_{Mj}a_j + \dots) - \frac{RT}{F} \ln a_X^{-} \quad (2)$$

where:

$i, j, \dots$  - remaining ions reversible to the glass electrode,

$K_{Mi}, K_{Mj}$  - selectivity constants.

If  $K_{Mi} a_i \ll a_{M^+}$ ,  $K_{Mj} a_j \ll a_{M^+}$ , which can be obtained always at suitably low activities  $a_i$ ,  $a_j$  etc., equation (2) will assume the simple form:

$$E = E^{\circ} - \frac{RT}{F} \ln a_{M^+} \cdot a_{X^-} \quad (3)$$

Using equation (3) and generally known methods, one can determine the free enthalpy of transfer and electrolyte activity coefficients.

Because of different opinions on the theoretical principles and accuracy of the method, these issues have been verified in several papers [1-5, 8-13, 16-18]. There are two approaches to the verification. First of them comes to verify the theoretical basis of the method, while the second one consists in comparison of the values of free enthalpy and activity coefficients of electrolyte, obtained with the use of glass electrode, with corresponding values obtained by other methods (mainly by measurement of EMF of amalgam electrode cells as well as by measurements of vapour pressure and solubility). The main assumption of the method for measuring the EMF of glass electrode cells is based on the fact that the potential difference between the glass electrode and the metal (or amalgam) electrode, reversible to the same cation, is independent of the solvent. Such an assumption is reasonable due to the fact that the process taking place in the cell



consists of the cation  $M^+$  transfer from the glass electrode to the metal electrode. The EMF of cell (4), equal to the potential difference between metallic electrode and glass electrode, is then described by the free enthalpy of the metal ion transfer from the metal to the glass layer of the glass electrode. Thus the EMF value of cell (4) is affected only by a value formally independent of the kind of solvent. The above assumption implies a statement that the free enthalpy of transfer of electrolytes from water to any solvent can be unequivocally described by the equation:

$$\Delta G_t^{\circ} = -F (E^{\circ S} - E^{\circ W}) \quad (5)$$

where:

$E^{\circ S}$  - standard EMF of cell (1) in any solvent,

$E^{\circ W}$  - standard EMF of cell (1) in water.

The unequivocal nature of the description of the free transfer enthalpy by equation (5) leads, when using an ionselective glass electrode, to a thesis that there is no change in the superficial glass layer when water is replaced by water-organic solvent mixtures (or non-aqueous solvents). Such a statement can be partly verified by measuring the EMF of the same cell of type (1) in saturated MX solutions. Since the saturated solution and solid phase are in equilibrium then, the sum of anion and cation chemical potentials is constant and independent of the solvent. The cell EMF measured in saturated solution should also be constant and independent of the solvent. Differences between the EMF values measured in such a way can be interpreted by changes in the hydration of glass [3] unless other side processes affect the EMF value. Negligible changes in the EMF in saturated solutions, when water was replaced by water-alcohol mixtures, were found in the following systems: KCl-H<sub>2</sub>O-methanol, KCl-H<sub>2</sub>O-ethanol, KCl-H<sub>2</sub>O-glycol, NaCl-H<sub>2</sub>O-t-butanol [2].

Somewhat higher differences (up to 3 mV) were found by L a n i e r [1] in his investigation of NaCl saturated solutions in the mixtures: H<sub>2</sub>O-methanol, H<sub>2</sub>O-ethylene glycol, H<sub>2</sub>O-diethylene glycol monomethyl ether, H<sub>2</sub>O-dioxane, H<sub>2</sub>O-urea, and H<sub>2</sub>O-N,N-dimethylformamide.

Authors of paper [3] have carried out investigations of the EMF in saturated solutions of RbCl in mixtures of water and 1-propanol, acetone, ethyleneglycol monomethylether and DMSO. They have found that except for 1-propanol, the reproducibility of results, obtained with use of glass electrodes, was poor. The same authors have analysed the accuracy of EMF measurements of glass electrode cells and found that the recorded 0.1 mV accuracy did not reflect the precision of the measurement itself. A scatter of results of about 0.1 mV can be obtained at low organic solvent content in water. It is possible that the maximum scatter is lower than 1 mV, even at 85% of organic solvent in the system, but in the case of other solvents the scatter is higher and reaches 2 mV [3]. It seems that apart from the changes in glass hydration some other factors can affect from the measurement accuracy.

P o i n t u d and J u i l l a r d [4], in their examination of the free enthalpy of transfer of alkaline chlorides in water-urea mixtures, have attributed their poor results reproducibility to the hydrolysis of urea and interaction of the hydro-

lysis products with the electrode material. It also follows from the above cited paper that the value of free transfer enthalpy can depend also on the type of glass electrode and its manufacturer, although some other papers, among others of the same authors, do not confirm that conclusion. One could have believed that this phenomenon depends on the type of mixed solvent. Other authors [8] suggest that the measurement accuracy can be limited by such factors as ability of solvent to oxidation (e.g. methanol), difficulties in solvent purification and also increased solubility of silver halides from the silver-silver halogen electrode (e.g. in DMSO). The comparison of values of the free enthalpy of alkaline halides transfer obtained by the EMF measurement of cell type (1) with corresponding values obtained with the amalgam electrode show that the worst conformity is obtained for  $\text{Cs}^+$  ions [2, 5, 8, 16, 19, 20]. The difference  $\Delta G_t^{\circ} \text{ amal.} - \Delta G_t^{\circ} \text{ glass}$  in the case of  $\text{Cs}^+$  ions often shows opposite sign than for other ions [8]. The worst reproducibility of measurements for  $\text{Cs}^+$  ions was also found in paper [4]. It seems that the above conclusions on caesium salt solutions are confirmed by the results reported in paper [12].

Authors of paper [8] have put forward a general conclusion that the conformity of values  $\Delta G_t^{\circ}$  obtained with glass and amalgam electrodes is very good at the organic solvent content (particularly non-reactive) not exceeding 40% b.wt. The authors have drawn their conclusion from the comparison of results obtained in the systems: water-methanol [2, 20], water-DMSO [5, 16, 19], water-t-butanol [2, 8], water-dioxane [3, 21]. Similar comparisons were carried out by S m i t s and coworkers [3, 5] with the systems: water-DMSO [5, 19, 22, 23], water-dioxane [3, 24-26], water-ethanol [3, 27], water-acetone [3, 28], water-tetrahydrofuran [3, 29]. These authors consider the accuracy of the method for determination of free enthalpy of transfer with glass electrodes to be satisfactory. According to S m i t s and coworkers [3, 5] the main advantages of using ionselective glass electrodes are rapidity and simplicity of the free enthalpy determination. The above conclusions seem to be confirmed also by other results of examination with a glass electrode. J u i l l a r d and coworkers [11] have obtained a good conformity of the differences  $\Delta G_t^{\circ} (\text{Cl}^-) - \Delta G_t^{\circ} (\text{Br}^-)$  and  $\Delta G_t^{\circ} (\text{Cl}^-) - \Delta G_t^{\circ} (\text{I}^-)$ , in mixed solvent water-t-butanol, with data of E l s e m o n g y [30]. It has been shown in paper [9] that the average activity coefficients

of NaCl and KCl in water-ethanol mixtures found by the method of EMF measurements with glass electrode and by the method of vapour pressure measurements are in good conformity.

M a l a h l a s and P o p o v y c h [10] have determined the values of  $\Delta G_t^{\circ}$  (KCl) in water-methanol mixtures by measuring the EMF of cells with glass electrodes and by the solubility method, and they have compared their results with the data of F e a k i n s [20] and A k e r l ö f [31]. According to the authors of paper [11], good conformity of results obtained by the EMF measurements and by the solubility method has proved the usefulness of glass electrodes for thermodynamic investigations. Moreover, Malahlas and Popovych have stated that due to the well known error of amalgam electrodes in water-methanol mixtures [32], their results are probably more reliable. It follows from the paper of F e a k i n s and coworkers [13] that, in some water-organic solvent mixtures (e.g. water-acetone) in comparison with glass electrodes. According to the authors opinion, this results from the electrode chemical process which is an intermediate stage in an extensive cycle of reactions. In such cases, the use of ionselective glass electrodes is a more reliable approach. On the other hand, D a s, B o s e and K u n d u [17, 18] have considered more critically the EMF measurements of cells with glass electrodes. They have compared the values of  $\Delta G_t^{\circ}$  obtained in water-acetonitrile [3, 12] and water-DMF [3] systems by means of glass electrodes, with those obtained with amalgam electrodes. D a s and coworkers [18], using additionally arguments from papers [8, 33-35], have drawn a general conclusion that the use of glass electrodes for thermodynamic studies in water-organic solvent systems is based on doubtful assumptions and can lead to errors which increase with decreasing water content. This concerns mainly mixtures of water and polar aprotic solvents. According to the mentioned authors, glass electrodes can be used for thermodynamic studies only in mixtures of high water content.

#### CONCLUSIONS

The above review allows to draw several general conclusions which are resultants of opinions from the cited papers.

1. In water-organic solvent mixtures at low non-aqueous solvent content (up to 40-60%), the discrepancy between results obtained

with glass electrodes and amalgam electrodes can be accepted as negligible.

2. In some cases the differences mentioned above are increased with the increase of the organic solvent content to the extent dependent on the type of solvent.

3. It seems that conclusions 1 and 2 concern particularly mixtures of water and polar aprotic solvents.

4. The accuracy of the EMF measurements with the use of glass electrodes is:

a) definitively the worst one in the case of caesium ions,

b) better than that of the amalgam electrode measurements, particularly in the case the amalgam reacts with the given solvent.

5. The comparison of literature data (e.g. values of  $\Delta G_{\text{t}}^{\circ}$ ) leads to the statements that:

a) it is impossible to establish an unequivocal relation between the composition and type of solvent and the value of the difference (and even its sign)  $\Delta G_{\text{t}}^{\circ}$  (amalgam el.) -  $\Delta G_{\text{t}}^{\circ}$  (glass el.),

b) the discrepancy between the values of  $\Delta G_{\text{t}}^{\circ}$  obtained by other methods (e.g. EMF measurements of cells with amalgam electrodes, vapour pressure, solubility) is often higher than the differences given in a).

Statements a) and b) support the method with use of glass electrodes. It seems that in order to be able to draw more definite conclusions, some additional precise comparative investigations are required, using various glass electrodes, various solvents and measurement methods.

6. The determination of the free transfer enthalpy with use of glass electrodes is a rapid and simple method and it seems reliable that, despite some confusions, its accuracy is acceptable under definite conditions.

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ZASTOSOWANIE SZKLANYCH ELEKTROD JONOSELEKTYWNYCH  
DO BADAŃ TERMODYNOMICZNYCH  
WŁAŚNOŚCI ROZTWORÓW ELEKTROLITÓW W MIESZANYCH ROZPUSZCZALNIKACH

Przeanalizowano w oparciu o dane literaturowe możliwości zastosowania jonoselektywnych elektrod szklanych do wyznaczania  $\Delta G^{\circ}$  przeniesienia elektrolitu z wody do mieszanin woda-rozpuszczalnik organiczny metodą pomiaru SEM odpowiednich ogniw. Porównano wartości wielkości termodynamicznych (głównie  $\Delta G^{\circ}_T$ ) uzyskane przy użyciu elektrod szklanych z analogicznymi wartościami otrzymanymi na innej drodze. Na tej podstawie wyciągnięto wnioski dotyczące przydatności elektrod jonoselektywnych zamiast kłopotliwych w użyciu elektrod amalgamatowych.